

CRYSTAL INVESTIGATIONS OF FORENSICALLY IMPORTANT DRUGS

By

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## ABSTRACT OF THESIS

Crystal Investigations of Forensically Important Drugs

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Microcrystal tests have been used in chemical identification for over 150 years. The tests involve the addition of a crystallizing reagent to a test sample followed by the microscopic observation of characteristic crystals. While this technique predates modern instrumental techniques of chemical analysis, it still has several distinct advantages. Microcrystal tests are rapid, inexpensive, and fairly simple to perform. However, this technique suffers from several criticisms due to the lack of atomic-level structural data from the resulting crystals.

The crystallizing reagent, 5% chloroauric acid prepared from gold(III) chloride in water or dilute hydrochloric acid, is one of the most common reagents used in forensic laboratories in the analysis of suspected drug substances. The crystals precipitating from the reaction of this reagent and illicit substances from three categories of drugs were examined by single crystal X-ray diffraction.

Cocaine is one of the most widely abused drugs, worldwide. Cocaine produces well characterized microcrystals upon mixing with the gold (III) chloride reagent. Ecgonine, the final stable metabolite of cocaine, is structurally similar to the parent drug and also forms crystals when reacted with gold (III) chloride. The

gold (III) chloride salts of cocaine and ecgonine (hydrated and anhydrous) and the hydrochloride salt of ecgonine were determined and compared by single crystal X-ray diffraction.

Single crystals precipitated from the addition of gold chloride test reagent to several structurally similar phenethylamines: amphetamine, methamphetamine, and ephedrine. While all of the other drugs of this category formed salts with the gold chloride anion, amphetamine was the only compound to bind covalently to the gold atom, displacing two chlorides.

In recent years, various cathinone-derived drug products have entered the illicit drug market. Ethylone, α-PVP, pentylylone, dibutylone, ephylone, and 3,4-methylenedioxypyrovalerone (MDPV) were analyzed by single crystal X-ray diffraction in various salt forms, including the product of the gold chloride crystal test with MDPV.

While the use of gold (III) chloride as a crystal precipitating agent is well-established, it is expensive and does not always form crystals with certain drug compounds. The novel application of Erdmann's salt as a crystal precipitating reagent was successfully tested with a representative candidate from each of the previously described classes and the resulting crystals were structurally characterized.

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## INTRODUCTION

Microcrystal tests have been used to quickly identify various compounds since the mid-to-late 19th century. There are several advantages to this analytical technique. The polarized light microscope, the preferred instrument of chemical microscopists, is relatively inexpensive compared to the cost of more advanced instrumentation such as Fourier Transform infrared (FTIR) spectrophotometers, gas chromatograph/mass spectrometers (GCMS), and nuclear magnetic resonance instruments (NMR). Additionally, crystal tests require very small quantities of reagents, saving costs and creating less waste. Recrystallization is itself a technique used to extract or purify compounds from a mixture, eliminating the need for a chromatography or separation of the compound of interest before analysis. In the field of forensic drug analysis, the determination of the chirality of a drug may have legal implications; oftentimes chirality can be determined using the polarized light microscope (PLM) as opposed to more expensive chiral separation techniques. Finally, microcrystal tests generally precipitate crystals as complex salts. When faced with trace quantities of an unknown drug substance, it is best to begin the analysis with non-destructive techniques, such as microcrystal tests. This approach preserves the unknown sample for further analyses. Likewise, there is growing interest in analyzing the resulting precipitate with other techniques including Raman or Infrared microspectrophotometry, FTIR, or powder X-ray diffraction.

Microcrystal tests are not without their limitations or criticisms. Crystals may form in different habits or polymorphs based on environmental conditions in

the lab. Interferents present in the sample may also cause morphological changes in the crystal. The utilization of crystal tests in the scheme of forensic analysis relies heavily on the skill, training, and experience of the scientist. There is some subjectivity to the characterization of the shape and color of the microcrystals. Finally, there is great practical knowledge of the use of microcrystal tests, but there is little understanding of the internal atomic arrangement of the crystal precipitates.

Microcrystals tend to grow in large quantities and very quickly. The rapid growth begins by nucleation as the solution evaporates and the solutes become increasingly concentrated until the first crystals precipitate out of solution. The subsequent crystal growth continues as the molecules or ions in the solution interact with each other in positions and orientations that favor the extension of the crystal lattice or repeating, highly ordered network of atoms. Intra- and intermolecular hydrogen bonds and close contacts promote crystal growth by stabilizing the positions of the atoms and lowering the energy required for continued crystal growth. These interactions are expressed in the morphology of the microcrystals as the crystals grow more quickly in directions that are more energetically favorable.

Single crystal X-ray diffraction provides a means of locating the atomic positions within the crystal lattice and, based upon the van der Waal's radii and the proximity of atoms to each other, determine any existing interactions. The diffraction pattern is a direct result of the unique crystal structure of a material. Therefore, if a microcrystal is truly unique, it will also have a unique diffraction

pattern. Unfortunately, due to their small size of 50 to 100  $\mu\text{m}$ , microcrystals are generally not well suited to this analytical technique. Single crystal X-ray diffraction using the Bruker Apex II diffractometer with the 0.5mm beam collimator requires a crystal approximately 0.1-0.3mm in all dimensions in order to generate sufficient diffraction points and to be contained completely within the X-ray beam. In order to overcome this limitation, the crystals of interest must be grown more slowly which reduces the amount of nucleation in the solution and promotes the growth of smaller quantities of larger crystals. Ideally, the larger crystals maintain the internal arrangement of atoms and bonds, which can be verified by comparison of the powder X-ray diffraction patterns of the single crystal experiments with to the microcrystal experiments.

The research described in Chapters 1, 2, and a portion of Chapter 3 is intended to contribute to the understanding of forensic microcrystal tests by providing the absolute 3D atomic arrangement within the precipitates of the most widely used crystal reagent, 5% aqueous gold(III) chloride and with select illicit drug compounds from three different drug classifications. These chapters include an in-depth description of the geometric and bonding parameters of the crystal precipitates including the hydrogen bonding and close contacts within the crystal lattice that contribute to the morphology of the microcrystal products. Some of the results of the single crystal work suggest that the arrangement of atoms provides the shape and morphology of the macroscopic crystals seen in the microscopic crystal tests. An example would be the herringbone pattern of the  $\text{AuCl}_4^-$  anions seen in the single crystal structure of the cocaine complex with

gold(III) anion as compared to the “herringbone fronds” seen from the microcrystals under the microscope

Powder X-ray diffraction is an under-utilized analytical technique in forensic drug analysis. Most forensic laboratories performing seized drug analyses rely on basic wet chemistry, followed by GCMS or FTIR. If powder diffraction is used, it is typically reserved for the trace evidence section of the lab, testing polymers, minerals, paints, etc. This is despite the recognition by the Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) that X ray diffraction is a “Class A” technique, an analytical method with high discriminating power and structural elucidation capabilities. Powder X-ray diffraction is a powerful technique. Complete analysis requires minor sample preparation, is non-destructive, and can be completed in approximately 30 minutes. Perhaps most importantly, the resulting powder diffraction patterns can be searched against a database or library for spectral matching. Combining microcrystal tests with powder X-ray diffraction satisfies the SWGDrug requirement for two independent analytical tests while taking advantage of the distinct morphology of the microcrystals and the reproducible and searchable diffraction pattern. Single crystal X-ray diffraction of microcrystal precipitates is critical for contributing to the available powder diffraction patterns. First, the absolute structure confirms that both the compound of interest and the crystallizing reagent are present in the crystal. The cell parameters, which can be obtained in less than 30 minutes, can help establish if the crystal product is a polymorph or different crystal habit. Finally, the powder X-ray diffraction pattern

can be calculated from the results of single crystal experiments to produce high quality spectra. Throughout this thesis, the powder diffraction patterns of newly elucidated structures have been provided and are available through the crystallographic information files (CIF) deposited in the Cambridge Structural Database.

While this research was being conducted, an epidemic of novel psychoactive substances emerged. Designer synthetic cathinones, which are amphetamine-type stimulants, found their way into the recreational drug market. The ease of modification and the speed at which new drugs were, and are, being introduced presented and continue to present difficult challenges for forensic and clinical drug laboratories. Single crystal X-ray diffraction proved to be an invaluable technique for the complete structural identification of these emerging compounds when faced with a lack of known reference compounds for comparison or verified Raman, FTIR, or mass spectra or chromatography. Chapter 3, “Bath Salts”, details the analyses of several synthetic cathinones that were identified by single crystal X-ray diffraction as they were encountered in law enforcement seizures. The resulting structural information can now be used to predict some of the physiological effects of these compounds through the analysis of their structure-activity relationships. As the structures of these new compounds are elucidated, and the compound demonstrates similar features with other known drugs, the researchers and clinicians can begin to understand or attribute possible drug effects. As an example, several anecdotal reports of 3,4-methylenedioxypyrovalerone have described effects comparable to 3,4-

methylene dioxy methamphetamine. These effects are likely due to common structural features that result in shared receptor interactions. Interestingly, when these drugs were submitted for testing, both the individuals using these compounds and the law enforcement officers believed the compounds to be some form of 3,4-methylenedioxymethamphetamine (also known as MDMA, ecstasy, or Molly) rather than the actual drug compound found later.

At the suggestion of one of the coauthors on several of the papers that resulted from this work, Chapter 4 explores the use of a lower-cost alternative crystallizing reagent, a 10% aqueous solution of potassium Erdmann's salt. This reagent, readily produced microcrystals suitable for single X-ray crystal experiments, and as with the other crystal structures determined herein, enabled the calculation of powder X-ray diffraction patterns for rapid confirmation of the drug precipitates.

It is the hope of the author that this body of work contributes to the foundation of microcrystal tests, provides an invaluable tool for powder X-ray diffraction confirmation of drugs of abuse, and introduces an effective and low-cost alternative reagent for use in forensic laboratories.

## CHAPTER 1. COCAINE AND ECGONINE<sup>1</sup>

### INTRODUCTION

Cocaine is a naturally occurring alkaloid obtained from the Erythroxylaceae family of plants, and most abundantly from *Erythroxylum coca*.<sup>1</sup> The leaves of the coca plant were chewed by native South Americans for its ability to boost energy, relieve fatigue, and lessen hunger as far back as 3000 B.C.<sup>2</sup> By 1885, cocaine hydrochloride was widely found in pharmacies in the United States and daily use had become commonplace. Demand for cocaine was high and pharmacists required a fast and simple test to verify the identity of the compound when received from distributors. Microcrystal tests were described as a reliable means of drug identification. Beyond the general characteristics of “a crystalline white powder producing numbness on the tongue”, cocaine hydrochloride was described as producing characteristic crystalline precipitates resembling those of fern fronds with auric chloride reagent.<sup>3</sup>

Today in the United States, cocaine is one of the most widely abused illicit drugs, third only to marijuana and psychotherapeutics.<sup>4</sup> The United States Drug Enforcement Administration (DEA) lists cocaine as a schedule II controlled dangerous substance, due to its high tendency for abuse, limited medical use, and potential for physical or psychological dependence.<sup>5</sup> Cocaine is accepted for medical use as a local anesthetic in surgical procedures of the eyes, nose, mouth, and throat. Cocaine is used illegally for its central nervous system stimulant effects.

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<sup>1</sup> Adapted from previous work<sup>9, 17, 18</sup>

Commonly prepared as the hydrochloride salt, cocaine consists of a tropane ring, substituted at the 2 and 3 carbon positions with a methyl ester and benzyl ester, respectively (Figure 1-1). The structure of cocaine was originally determined by Willstätter & Müller<sup>6</sup> in 1898 by chemical means and was verified by a crystal structure analysis of L-cocaine hydrochloride by Gabe & Barnes<sup>7</sup> in 1963; Zhu *et al.*<sup>8</sup> redetermined this structure in 1999. Due to the presence of three chiral centers, cocaine is just one of seven stereoisomers having various degrees of efficacy and potency.

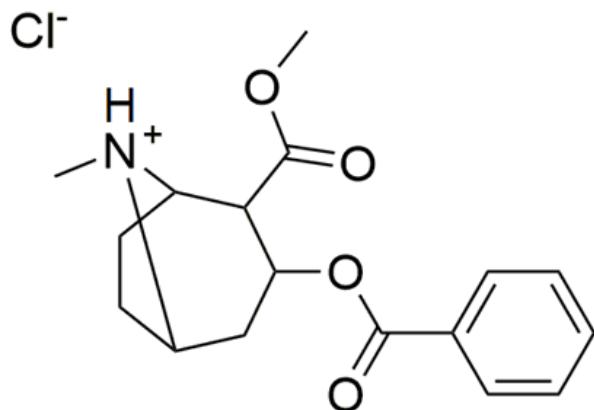


Figure 1-1. Diagram of Cocaine hydrochloride, methyl-3-benzyloxy-8-methyl-8-azabicyclo[3.2.1]octane-4-carboxylate chloride,  $C_{17}H_{22}NO_4^+ \cdot Cl^-$

L-Ecgonine is also among the 22 naturally occurring alkaloids found in the leaves of the coca plant, i.e. *Erythroxylum coca*.<sup>1</sup> A tropane ring structure similar to cocaine, L-ecgonine ( $C_9H_{15}NO_3$ ), a nitrogen-bridged bicyclo[3.2.1]octane, is both a precursor and a human metabolite of L-cocaine (Figure 1-2). The structural difference between ecgonine and cocaine is the replacement of the methyl ester at the 2-carbon position of cocaine with a carboxylic acid and the substitution of cocaine's benzyl ester at the 3-carbon position with a hydroxyl

group. The conversion is obtained by complete acidic, alkaline, or enzymatic hydrolysis of both ester functions in L-cocaine, and can crystallize as the hydrochloride salt.<sup>9</sup>

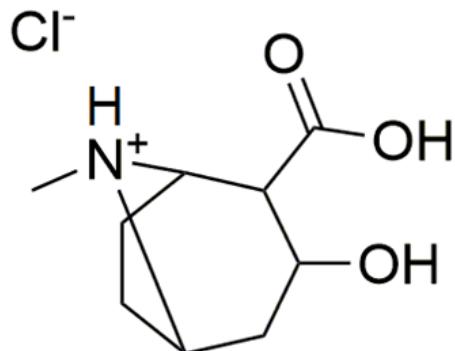


Figure 1-2. Ecgonine hydrochloride, 3-hydroxy-8-methyl-8-azoniabicyclo[3.2.1]octane-2-carboxylic acid chloride,  $C_9H_{19}NO_3^+\cdot Cl^-$

Ecgonine is an important toxicological marker for previous and chronic cocaine use. Cocaine can be broken down by two mechanisms, alkaline hydrolysis to benzoyl ecgonine or catalyzed by pseudocholinesterases to ecgonine methyl ester.<sup>10</sup> Blood or urine sample storage conditions, drug concentration, and time can lead to further hydrolysis to L-ecgonine, the final breakdown product of L-cocaine.<sup>11,12</sup> L-Ecgonine is consistently observed in post mortem blood specimens and whole-blood specimens of cocaine addicts, demonstrating its utility as a stable marker for past cocaine use<sup>13</sup> and is a much better indicator than either of the primary metabolites, benzoyl ecgonine or ecgonine methyl ester.

Microcrystal tests are one of the fastest and simplest techniques for identifying and differentiating L-cocaine from its seven stereoisomers<sup>14</sup> and

similarly related structures, including L-ecgonine, the structurally similar precursor and metabolite of cocaine.<sup>15</sup> This test involves the addition of a 5% w/v solution of chloroauric acid in water ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) to a dilute aqueous acidified (HCl) solution of suspected cocaine, followed by observation of the resulting crystals microscopically.<sup>16</sup> While this test has been employed in the analytical scheme of the identification of cocaine since prior to 1886<sup>3</sup> and ecgonine since 1938<sup>15</sup>, there has been little done to support the understanding of the crystal structure or mechanism of growth.

Single crystal X-ray diffraction (SCD) is the ideal technique for examining the internal arrangement of atoms and bonds within the crystal precipitates. The only limitation of this technique is the need for high quality, single crystals large enough for the single crystal experiment. Typical microcrystal tests produce small crystals on the order of 50 to 100 $\mu\text{m}$  in size. Single crystal X-ray diffraction requires well-formed crystals with dimensions of approximately 0.3mm x 0.1mm x 0.1mm using a 0.5mm beam width. Suitable crystals of ecgonine hydrochloride, cocaine gold (III) chloride, and anhydrous and hydrated ecgonine gold (III) chloride were grown by evaporative condensation and analyzed by SCD.

The three-dimensional structures of the gold(III) tetrachloride salt of L-cocaine<sup>17</sup>, the hydrated and anhydrous gold (III) tetrachloride salts of L-ecgonine<sup>18</sup> and the hydrochloride salt of L-ecgonine<sup>9</sup> have been solved and reported as part of the research contributing to this thesis.

## SUMMARY OF CRYSTAL STRUCTURES DETERMINED

- I. The gold(III) tetrachloride salt of L-cocaine  
*(1R,2R,3S,5S,8S)-3-benzoyloxy-8-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate tetrachlorogold(III)*
- II. The hydrochloride salt of L-ecgonine  
*(1R,2R,3S,5S,8S)-3-hydroxy-8-methyl-8-azoniabicyclo[3.2.1]octane-2-carboxylic acid chloride*
- III. The hydrated gold(III) tetrachloride salt of L-ecgonine  
*Hydronium tetrakis[(1R,2R,3S,5S,8S)-3-hydroxy-8-methyl-8-azoniabicyclo[3.2.1]octane-2-carboxylate] pentakis[tetrachloridoaurate(III)] hexahydrate*
- IV. The anhydrous gold(III) tetrachloride salts of L-ecgonine  
*(1R,2R,3S,5S,8S)-3-hydroxy-8-methyl-8-azoniabicyclo[3.2.1]octane-2-carboxylate tetrachloridoaurate(III)*

## EXPERIMENTAL

### Synthesis and crystallization

For the preparation of the gold(III) tetrachloride salt of (-)-cocaine, (I), I-cocaine hydrochloride (Sigma, lot No. 48 F0208) was dissolved in water to yield a 50  $\mu\text{g mL}^{-1}$  solution. This solution (200  $\mu\text{L}$ ) was combined with 0.5% acidified (HCl) gold(III) chloride ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) (200  $\mu\text{L}$ ) and allowed to crystallize. Extremely long (~1mm x 0.1mm x 0.1mm) gold parallelepiped crystals formed (m.p. 452 K). A crystal suitable for X-ray analysis was cut from one of these long rods<sup>17</sup> to obtain a crystal that would be completely encompassed within the X-ray beam.

For the preparation of I-ecgonine hydrochloride, (II), the salt was dissolved in water to yield a 500  $\mu\text{g mL}^{-1}$  solution, 200  $\mu\text{L}$  of which was combined with 200  $\mu\text{L}$  of 0.5% gold(III) chloride ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) solution acidified with HCl and allowed to crystallize by slow evaporation. Thin, flat, colorless plates of (II), containing no gold, formed, m.p. 519 K.<sup>9</sup>

For the hydrated gold(III) tetrachloride salt of I-ecgonine, (III), an aqueous solution (200  $\mu\text{L}$ ) containing I-ecgonine hydrochloride (100  $\mu\text{g}$ ) was combined with a 0.24% gold(III) chloride ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) solution in 0.24 M HCl (200  $\mu\text{L}$ ). Slow evaporation of this mixture to dryness produced very light-yellow parallelepipeds of (III), which were used directly for X-ray analysis. For the anhydrous gold(III) tetrachloride salt of I-ecgonine, (IV), the same preparation was repeated at a later date and the resulting crystals were used for X-ray analysis. These proved to be anhydrous, most probably because of the lack of

humidity in the laboratory where the crystals were allowed to grow.<sup>18</sup> The crystals were mounted on a Cryoloop using Paratone-N. The Cryoloop is a small nylon filament that has a minimal diffraction profile and secures the single crystal in the X-ray beam. Paratone-N is a viscous oil that secures the single crystal to the Cryoloop and does not diffract. All of the crystal structures were obtained at 100 K with the exception of (I), which was collected at 295K.

**Table 1-1**

Experimental details.

<b>Crystal data</b>	I Cocaine Gold (III) Chloride	II Ecgonine Hydrochloride	III Hydrated Ecgonine Gold (III) Chloride	IV Anhydrous Ecgonine Gold (III) Chloride
Chemical Formula	[C <sub>17</sub> H <sub>22</sub> NO <sub>4</sub> ][AuCl <sub>4</sub> ]	[C <sub>9</sub> H <sub>16</sub> NO <sub>3</sub> ][C] I]	[C <sub>9</sub> H <sub>16</sub> NO <sub>3</sub> ] <sub>4</sub> [H <sub>3</sub> O][AuCl <sub>4</sub> ] <sub>5</sub> ·6H <sub>2</sub> O	[C <sub>9</sub> H <sub>16</sub> NO <sub>3</sub> ][AuCl <sub>4</sub> ]
M <sub>r</sub>	643.12	221.68	2565.86	524.99
Crystal system, space group	Orthorhombic , P <sub>2</sub> <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Orthorhombic , P <sub>2</sub> <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Orthorhombic, P <sub>2</sub> <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	Orthorhombic , P <sub>2</sub> <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a, b, c (Å)	7.7358 (3), 9.4543 (5), 29.9093 (13)	6.6962 (4), 12.0519 (8), 13.0632 (8)	9.2153 (16), 15.299 (3), 51.544 (8)	10.0276 (1), 15.7339 (2), 18.6416 (2)
α, β, γ (°)	90, 90, 90	90, 90, 90	90, 90, 90	90, 90, 90
V (Å <sup>3</sup> )	2187.46 (17)	1054.23 (11)	7267 (2)	2941.15 (6)
Z	4	4	4	8
Density Mg m <sup>-3</sup>	1.953	1.397	2.345	2.371
Radiation type			Cu K $\alpha$	
μ mm <sup>-1</sup>	17.33	3.09	25.82	25.5
Tempera- ture (K)	295 (2)	100 (2)	100 (2)	100 (2)
Shape, color	Parallelepiped, yellow			
Crystal size (mm)	0.45 × 0.21 × 0.08	0.48 × 0.32 × 0.09	0.35 × 0.11 × 0.10	0.23 × 0.17 × 0.10
<b>Data collection</b>				
Diffracto- meter	Bruker SMART CCD APEXII area-detector diffractometer			
Absorp- tion correction	Numerical: Sheldrick, G. M. (2001). SADABS. Version 2. University of Göttingen, Germany.			
T <sub>min</sub> - T <sub>max</sub>	0.042, 0.338	0.319, 0.768	0.040, 0.182	0.067, 0.185
Θ <sub>min</sub> - Θ <sub>max</sub>	3.0, 68.5°			
No. of measured	14526	7772	43458	22091

reflections				
No. of independent reflections	3906	1891	12355	5121
No of observed reflections	3804	1869	12097	5053
[I > 2 $\sigma$ (I)]				
R <sub>int</sub>	0.052	0.037	0.057	0.035
<b>Refinement</b>				
R[F <sup>2</sup> > 2 $\sigma$ (F <sup>2</sup> )], S	0.028, 0.07, 1.05	0.026, 0.064, 1.09	0.04, 0.099, 1.08	0.018, 0.047, 1.08
No. of reflections	3906	1891	12355	5121
No. of parameters	246	140	761	332
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.59, -0.96	0.28, -0.16	3.15, -1.94	0.93, -0.69
Absolute structure	Flack, H. D. (1983). Acta Cryst. A39, 876-881.			
Friedel Pairs	1468	766	5212	2199
Flack parameter	0.025 (14)	0.038 (12)	0.03 (1)	-0.004 (7)

The crystals were mounted on a 360° goniometer head on a Bruker Smart Apex using an Apex2 detector with a Copper X-ray source.

Refinement:

For all structures (I, II, III, and IV), the methyl H atoms were put in ideally staggered positions with C—H distances of 0.98 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . The methylene and methine Hs were placed in geometrically idealized positions and constrained to ride on their parent C atoms with C—H distances of 0.99 and 1.00 Å, respectively, and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

For (I) and (II), all H atoms were found in electron-density difference maps. For (I), the ammonium H atom was similarly placed in an idealized position, with N-H = 0.91 Å, and refined with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ . All H atoms for (II), the amine, acid, and the hydroxyl Hs were all allowed to refine fully.

All N- and C-bound H atoms, and two of the four hydroxy H atoms for (III) and both of the hydroxy H atoms for (IV), were found in electron-density difference maps. For (III), three of the four carboxylic acid H atoms were found, but the remaining acid H atom was disordered and not found. For (IV), both of the acid H atoms were located. The hydroxy and acid H atoms were constrained to idealized positions, with distances fixed at O-H = 0.84 Å and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . In (III), because of the small contribution of their total electron density in the cell, no water H atoms were found in difference maps.

Software used: data collection - SMART APEX2 Bruker,<sup>19</sup>, cell refinement - SMART APEX2, data reduction - SAINT Bruker<sup>20</sup>, program(s) used to refine structure – SHELXTL, molecular graphics – SHELXTL, software used to prepare material for publication - SHELXTL<sup>21</sup>.

For (I), the program(s) used to solve and refine structure: SHELXTL Sheldrick<sup>21</sup>, SHELXTL Bruker<sup>19</sup>.

For (II), (III), and (IV) the program(s) used to solve and refine the structures: SHELXTL <sup>22</sup>.

X-ray data have been deposited in CCDC <sup>23</sup>: cocaine gold(III) tetrachloride(Refcode = "SETLOT") = 638296; l-ecgonine hydrochloride (Refcode = "HITYUF") = 677653; ecgonine gold(III) tetrachloride, hydrate (refcode = "DULFAS")= 765456; ecgonine gold(III) tetrachloride, anhydrous (refcode = "DULFEW")= 765457.

## RESULTS

Single-crystal X-ray diffraction was used to determine the absolute configuration of the gold(III) tetrachloride salt of l-cocaine, (I). The product of the cocaine and gold(III) chloride microcrystal test precipitates from the aqueous solution as a complex salt consisting of a protonated cocaine cation and a gold(III) tetrachloride anion with a melting point of 452 K. Based upon a comparison of the powder diffraction powder (Figure 1-3) and the calculated powder pattern from the single crystal of (I), as well as a comparison of the infrared spectrum of each (Figure 1-4), it is clearly demonstrated that the single crystal accurately represents the microcrystal precipitate.

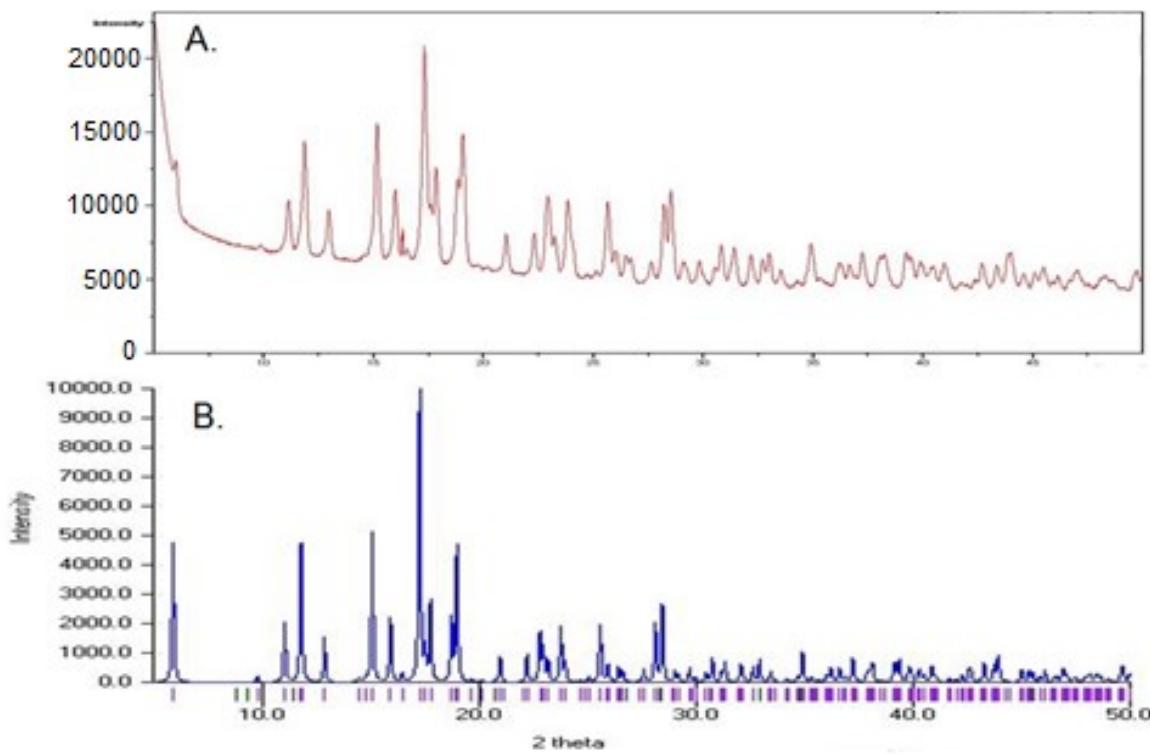


Figure 1-3. Comparison of the X-ray powder diffraction pattern obtained from the cocaine-HAuCl<sub>4</sub> microcrystals with the calculated powder diffraction pattern from the single crystal diffraction experiment.

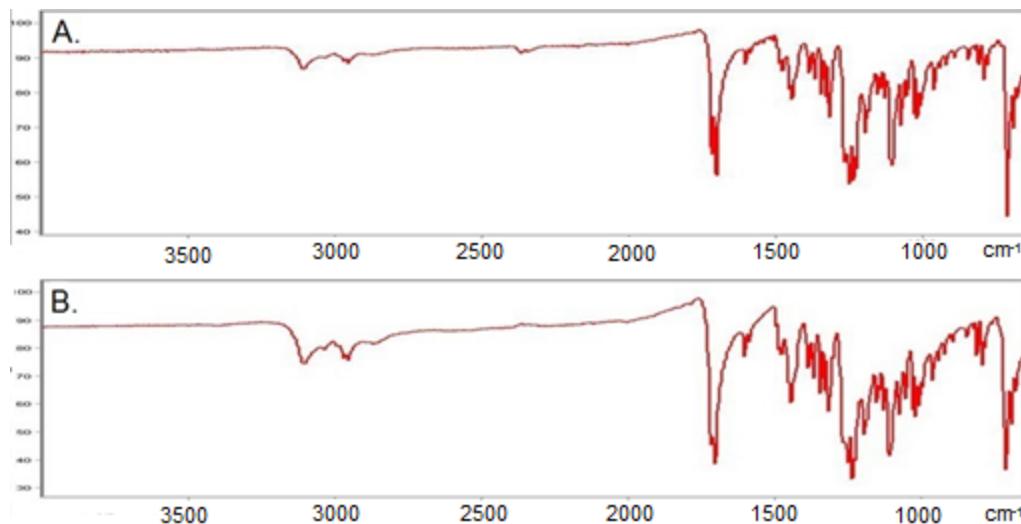


Figure 1-4. Comparison of the FT-IR pattern of (A) the cocaine-HAuCl<sub>4</sub> microcrystals (B) a finely ground portion of a single crystal.

Figure 1-5 shows the asymmetric unit of (I). Charles Fulton, on page 342 of his comprehensive review of microcrystal tests for all products of the gold chloride reagent, proposed that the precipitate was more than a simple salt.

"The reagent compounds have often been misinterpreted in the past as being merely simple salts of those metals that can form 'double salts' with the alkaloids, such as "AuCl<sub>3</sub>" instead of HAuCl<sub>4</sub>. The actual situation is much more complex. The metals concerned, central to long periods of the Periodic Table, dispose of 'auxillary valences' in forming the reagents; that is they form coordination compounds. The simple anions concerned, halides and pseudohalides, are not indifferent partners for two bases or cations at once, but are those and only those that join with the metal in an effective complex such as AuCl<sub>4</sub><sup>-</sup>."<sup>23</sup>

Double salts are salts that dissociate into two or more simple cations or simple anions, such as potassium sodium tartrate, which dissociates into K<sup>+</sup>, Na<sup>+</sup>, and C<sub>4</sub>H<sub>4</sub>O<sub>6</sub><sup>2-</sup>. When dissolved in water, a double salt completely dissociates into simple ions while complex salts do not; the complex ion remains unchanged. In a complex salt, the metal remains strongly bound in a complex ion, such as in

potassium permanganate, where, upon dissociation, the manganese stays bound to the four oxygen atoms forming a single  $\text{MnO}_4^-$  anion. In a coordination complex, the metal becomes the central atom, and non-metal ligands are chemically bound around it.

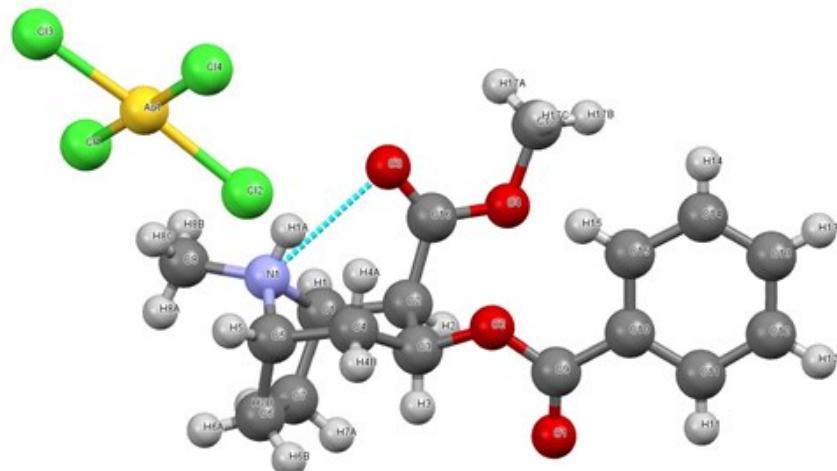


Figure 1-5. The asymmetric unit of (I), the gold(III) tetrachloride salt of cocaine.

In the case of the microcrystalline precipitate of cocaine and the gold(III) chloride reagent, the product is best described as a “complex salt”. The Au atom remains tightly bound to four Cl atoms in a distorted square planar coordination,  $[\text{AuCl}_4]^-$ . The distortion of the  $[\text{AuCl}_4]^-$  anion square planar coordination of (I) was found to be unusual. The Au atom was 0.0056(8) Å above the best least-squares plane of the five-atom moiety. Two opposing Cl atoms (Cl1 and Cl3) are above the best plane by 0.0784(14) Å and the other two (Cl2 and Cl4) are below the plane by 0.0812(14) Å. Table 1-2 describes the selected geometric parameters for the  $[\text{AuCl}_4]^-$  anion in (I). In a search of the Cambridge Structural Database (CSD, Version 5.27, update of May 2006<sup>24</sup>), 89 structures containing

the gold tetrachloride anion are found. However, only 24 show the ‘bowing’ of the square-planar arrangement of the Au atom and the four Cl<sup>-</sup> anions. Of these, only one shows flexing of the Cl<sup>-</sup> anions slightly larger than that seen here. Two opposing Cl<sup>-</sup> (Cl1 & Cl1F) anions in the structure of tetra(methylthio)tetrathiafulvalene bis(tetrachlorogold) (<sup>25</sup>) are above the best plane by 0.087 Å and the other two (Cl2 & Cl3) are below the plane by 0.078 Å. All the other gold tetrachloride anions are more planar than that in (I), mostly forming a nearly perfect square-planar arrangement about the Au atom.<sup>17</sup>

**Table 1-2**

Selected Geometric Parameters (Å, °) for (I)

Au1—Cl2	2.2669 (15)	Au1—Cl4	2.2766 (17)
Au1—Cl3	2.2732 (15)	Au1—Cl1	2.2843 (16)
Cl2—Au1—Cl3	175.52 (8)	Cl2—Au1—Cl1	90.66 (7)
Cl2—Au1—Cl4	89.17 (7)	Cl3—Au1—Cl1	90.37 (7)
Cl3—Au1—Cl4	90.08 (7)	Cl4—Au1—Cl1	176.33 (7)

Figure 1-6 illustrates the hydrogen bonding and close contacts of (I). The intermolecular distance between the protonated nitrogen, N1, and the nearest chlorine, Cl4, is 4.253(5) Å. Within the cocaine cation exists an intramolecular hydrogen bond between the protonated N atom to the carbonyl O atom [N1—O3 = 2.755(6) Å and N1—H1A...O3 = 136°] of the methoxy carbonyl functional group.

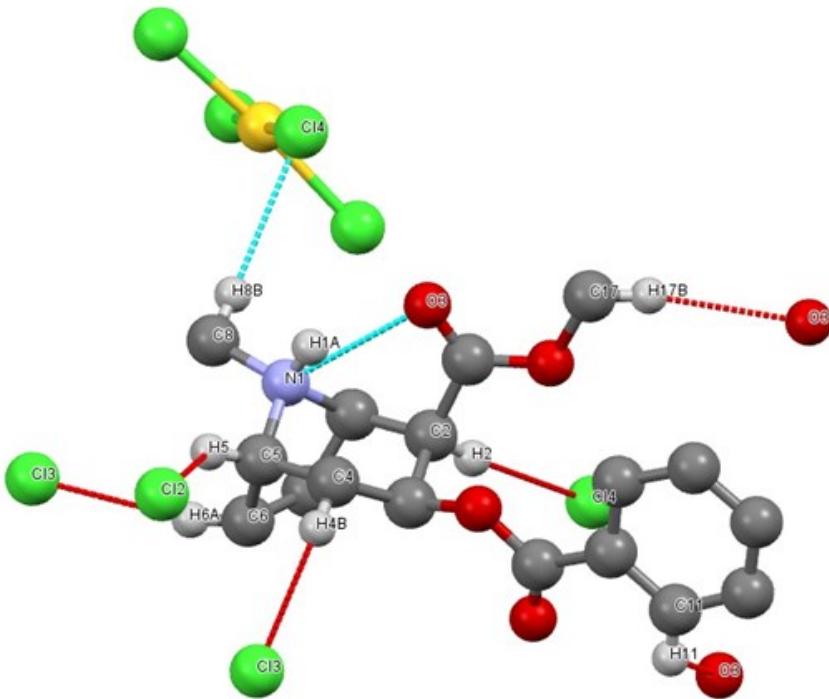


Figure 1-6. A diagram showing hydrogen bonding (cyan dashed lines) and close contacts (red dashed lines) for (I). Extraneous H atoms have been removed for clarity. Only the atoms involved in H bonds are labeled.

The structure of I-cocaine hydrochloride was reported by Zhu *et al.*<sup>8</sup> This structure also contains an intramolecular hydrogen bond [N1-O4 = 2.894(9) Å and N1-H1A...O4 = 155.3(9) $^{\circ}$ ]; however, it involves the methoxy O atom with the N atom, rather than the carbonyl O. This is due to rotation of the C2-C15 bond where the methoxy carbonyl group has a torsion angle of -138.4(8) $^{\circ}$ , presenting the methoxy O4 atom to the nitrogen for H bonding. The intramolecular hydrogen bonding seen in (I) more closely resembles the conformation seen in (-)-norcocaine [N1-O3 = 3.006(2) Å and N1-H1A...O3 = 128.9 $^{\circ}$ ].<sup>26</sup> See Figure 1-7 for an illustrative comparison. According to potential energy calculations

(Figure 1-8) performed by Zhu *et al.*<sup>8</sup>, the energy minimum for the rotation of methoxycarbonyl group occurs at a torsion angle of approximately 95-110°.

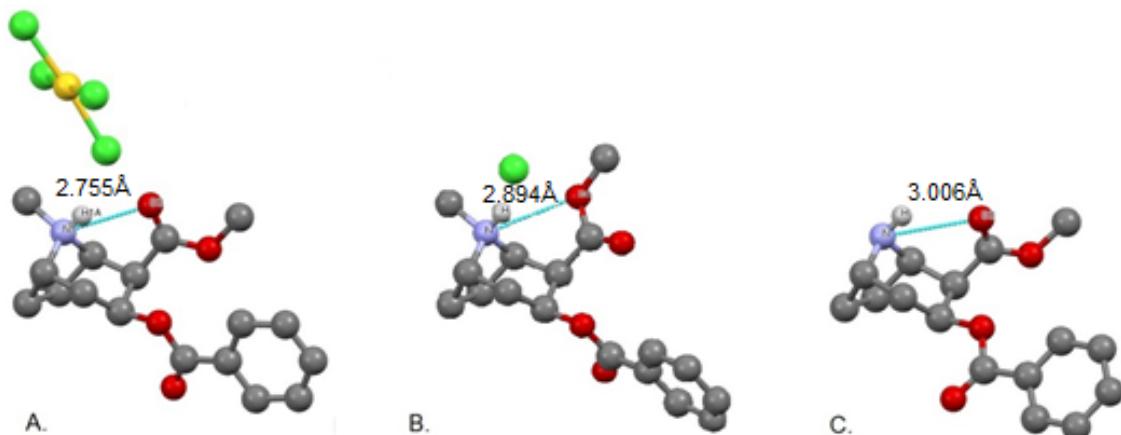


Figure 1-7. An illustration comparing the intramolecular bond distance bewteen N1-H1A and the carbonyl or methoxy O atom of (A) cocaine gold(III) tetrachloride, (B) cocaine hydrochloride, and (C) norcocaine free-base (the desmethyl metabolite of cocaine). Extraneous H atoms have been removed for clarity. Only atoms involved in H bonds are labeled.

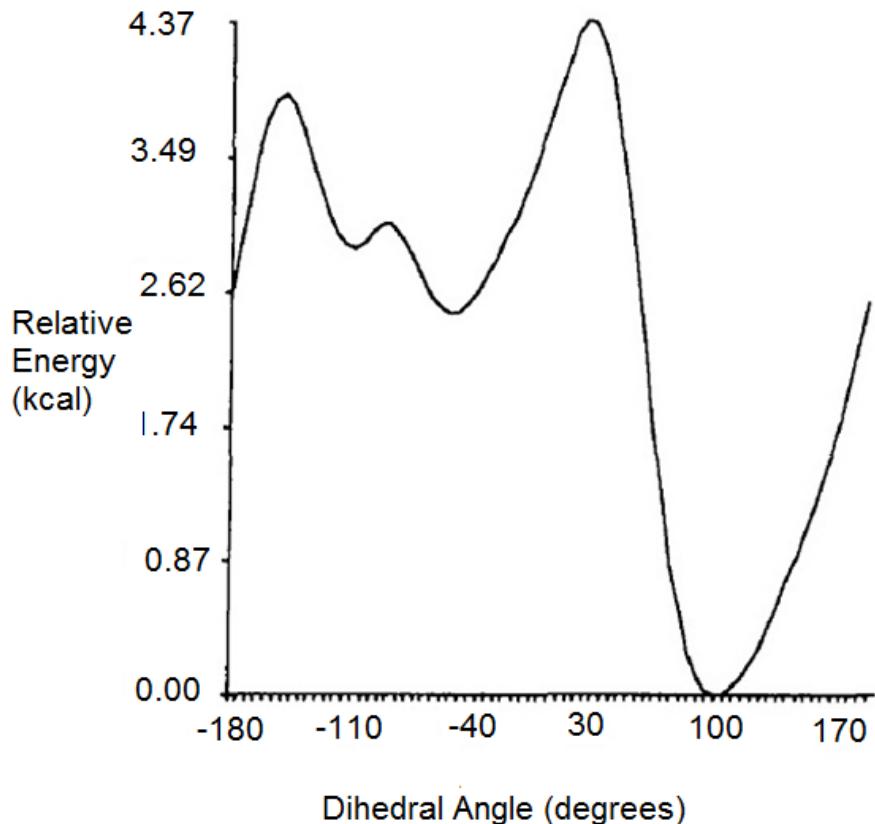


Figure 1-8. Relative potential energy as a function of rotation about the methoxycarbonyl group, C<sub>2</sub>-C<sub>3</sub>-C<sub>15</sub>-O<sub>4</sub>, of cocaine hydrochloride.<sup>8</sup>

In (I), this torsion angle [C<sub>3</sub>-C<sub>2</sub>-C<sub>16</sub>-O<sub>4</sub> = 89.9(6)<sup>o</sup>] lies within the most energetically favorable conformation, see Table 1-3. (Norcocaine 114.6(2)<sup>o</sup><sup>26</sup>; Cocaine HCl -138.4(8)<sup>o</sup><sup>8</sup>; Cocaine (freebase) 179.4<sup>o</sup><sup>27</sup>.

**Table 1-3**

Dihedral angle of the methoxycarbonyl group and length of H bond to protonated N.

	Dihedral Angle (°) C3-C2-C16-O4	H Bond Length (Å) N1-O3	H Bond Angle (°) N1-H1A...O3
Cocaine AuCl <sub>4</sub>	89.9(6)	2.755(6)	136.4
Norcocaine (Freebase)	114.6(2)	3.006	128.9
Cocaine HCl	-138.4(8)	2.894(9) *	155.3
Cocaine (Freebase)	179.4	-	-
Egonine HCl	99.6 (1)	2.761(2)	140
Egonine AuCl <sub>4</sub>	-72.6(5)	2.768	140.4
Egonine AuCl <sub>4</sub> (Hydrate)	-84(1)	2.79(1)	137.3
Egonine AuCl <sub>4</sub> (Hydrate)	-	-	-
Egonine AuCl <sub>4</sub> (Hydrate)	-	-	-
Egonine AuCl <sub>4</sub> (Hydrate)	-	-	-

\* Note the ester O4 participates in the H Bond, not the carbonyl in cocaine HCl

In (I), the carbonyl O3 is involved in two intermolecular close contacts [C11-O3 = 3.24(1) Å and C11-H11...O3 = 125°] and [C17-O3 = 3.542(9) Å and C17-H17B...O3 = 168°], both having a non-bonded C-H...O distance within the standard 2.7 Å range<sup>28</sup>. The cocaine cation makes five close contacts with three of the four Cl atoms of symmetry-related [AuCl<sub>4</sub>]<sup>-</sup> anions. There is a single Cl (Cl1) that is not involved in any close contacts. This chlorine is pointed directly at the closest Au (Au1). The distance between Cl1 and the symmetry (1-x, -1/2+y, 3/2-z) related Au1 is 4.3742(16) Å. The angle formed by the planes of each anion are nearly perpendicular to each other, the least-squares planes of two

$[\text{AuCl}_4]^-$  anions =  $82.81(4)^\circ$ , the linearity from gold-to-gold [Au1-Cl1...Au1( $1-x, -1/2+y, 3/2-z$ )] is  $172.38(6)^\circ$ . The resulting 'herringbone' pattern of  $[\text{AuCl}_4]^-$  anions is shown in Figure 1-9.

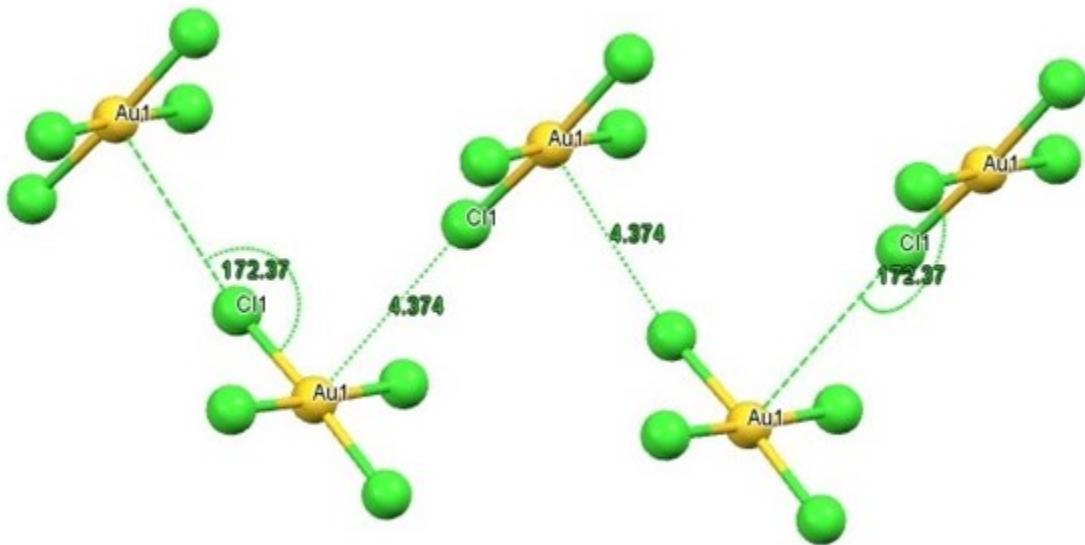


Figure 1-9. Diagram demonstrates the "herringbone" configuration of symmetry related  $\text{AuCl}_4^-$  anions.

In the packing diagram of (I), the cations and anions are evenly spaced with no distinct pockets or areas of clustering of hydrophobic or hydrophilic regions as seen in other examples (Figure 1-10). The benzyl rings lie nearly parallel to the ac plane. As expected, the  $[\text{AuCl}_4]^-$  anion is proximal to the quaternary nitrogen and the staggered arrangement of the anion is observable.

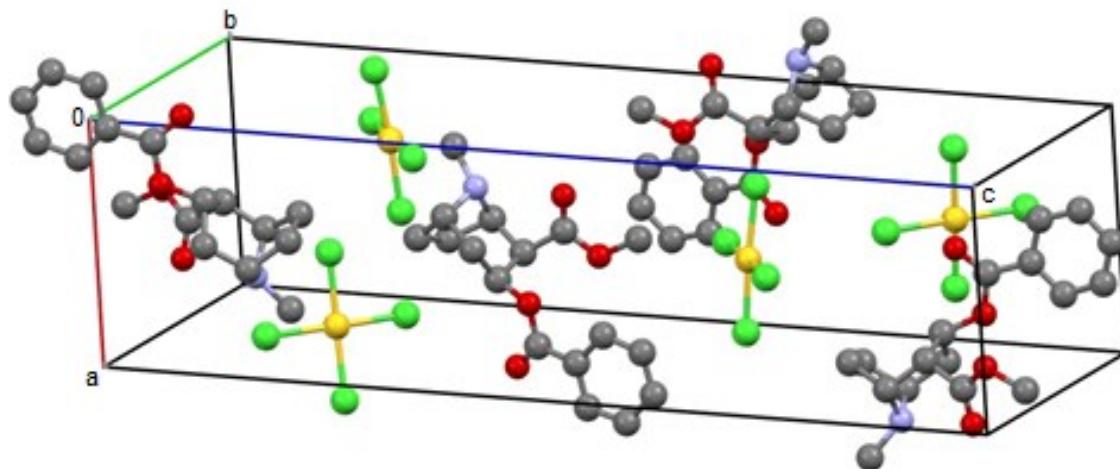


Figure 1-10. The packing diagram of (I).  $\text{AuCl}_4^-$  anions are located in a staggered arrangement near protonated N atoms. All H atoms have been removed for clarity.

Single crystals of ecgonine hydrochloride salt, suitable for X-ray diffraction, precipitated serendipitously from early unsuccessful attempts to crystallize ecgonine with the gold(III) chloride crystallizing reagent. The precipitate crystallizes as a salt with the protonated ecgonine cation and the  $\text{Cl}^-$  anion. Figure 1-11 shows the asymmetric unit of (II) with its numbering.

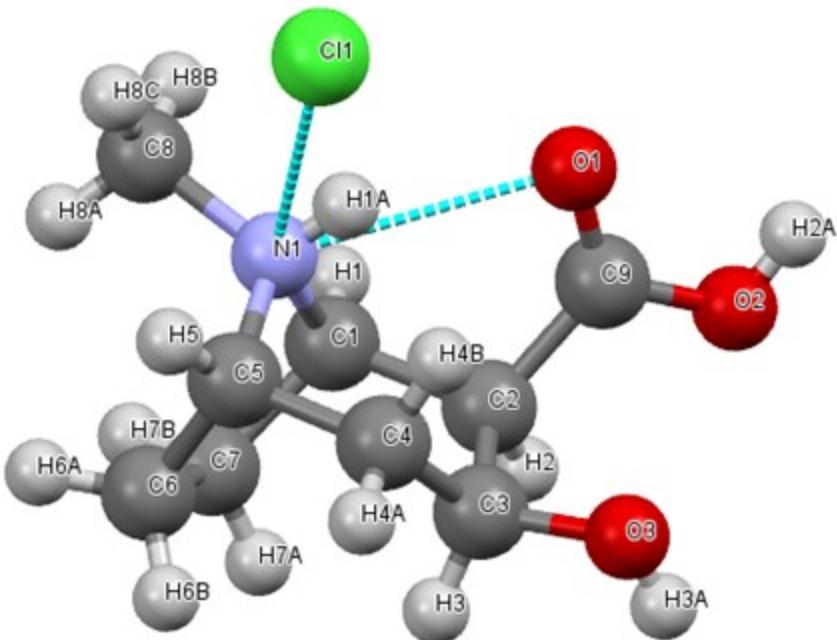


Figure 1-11. The asymmetric unit of (II), ecgonine hydrochloride. The intramolecular H bond and the H bond from the protonated N atom to the chloride anion are indicated by the dashed teal colored lines.

The crystal structure of (II) contains three intermolecular close contacts. The chloride anion is located  $3.282(1)$  Å from the protonated N atom, representing the furthest distance of the three contacts present in the structure [ $\text{N}1\cdots\text{Cl}1 = 3.282(1)$  Å,  $\text{N}1-\text{H}1\text{A}\cdots\text{Cl}1 = 122(1)^\circ$ ]. Additionally, the chloride anion participates in a contact with the hydroxyl O3, [ $\text{O}3\cdots\text{Cl}1 = 3.133(1)$  Å,  $\text{O}3-\text{H}3\text{A}\cdots\text{Cl}1 = 169(2)^\circ$ ] and a contact with the carboxyl O2, [ $\text{O}2\cdots\text{Cl}1 = 2.958(1)$  Å,  $\text{O}2-\text{H}2\text{A}\cdots\text{Cl}1 = 165(2)^\circ$ ]. The latter carboxyl moiety also forms an intramolecular H bond from the O atom of the acid's C=O group to the protonated N atom [ $\text{N}1\cdots\text{O}1 = 2.761(2)$  Å,  $\text{N}1-\text{H}1\text{A}\cdots\text{O}1 = 140(2)^\circ$ ]. This conformation is identical to the intramolecular bonds found in (-)-norcocaine, the

tetrachloroaurate(III) salts of ecgonine and the tetrachloroaurate(III) salt of I-cocaine previously described and shown in Table 1-4. However, this configuration is in contrast to the only other tropane hydrochloride salt, I-cocaine·HCl, studied by Zhu *et al.*<sup>8</sup>, where the protonated N atom is H bonded to the methoxy O atom as opposed to the carbonyl O atom [N···O = 2.894 (9) Å, N—H···O = 110.5 (9)°]. The torsion angle C3—C2—C9—O2 in (II) [99.61 (14)°] is similar to those found in the gold(III) tetrachloride salt of I-cocaine [89.9 (6)°] and in (-)-norcocaine (114.6°), but again is very different from that found in I-cocaine·HCl [-138.4 (8)°]. According to the previously referenced potential energy calculations performed by Zhu *et al.*<sup>8</sup>, the energy minimum for the H bond to the carbonyl group in (I) occurs at a torsion angle C3—C2—C9—O2 of 95–110° within which the ecgonine-HCl is well aligned.

**Table 1-4**

Ecgonine AuCl<sub>4</sub> compared with (-)-norcocaine, L-cocaine AuCl<sub>4</sub>, and L-ecgonine HCl.

Intramolecular hydrogen-bond geometry (Å, °)

	D-H...A	D-H	H...A	D...A	D-H...A
(-)Norcocaine	N-H...O3	0.96	2.31	3.006	129
Cocaine AuCl <sub>4</sub>	N1-H1A...O3	0.91	2.02	2.756(6)	136
Ecgonine HCl	N1-H1A...O1	0.84	2.07	2.761(2)	140
Ecgonine AuCl <sub>4</sub>	N1A-H1NA...O1A	0.93	2.04	2.792(11)	137
Ecgonine AuCl <sub>4</sub>	N1B-H1NB...O1B	0.93	1.99	2.757(11)	138
Ecgonine AuCl <sub>4</sub>	N1C-H1NC...O1C	0.93	2.00	2.734(12)	134
Ecgonine AuCl <sub>4</sub>	N1D-H1ND...O1D	0.93	2.07	2.814(11)	136
	O3D-H3D1...O1C	0.86(3)	1.90	2.743(10)	179
	O3B-H3B1...O1A <sup>i</sup>	0.78(2)	2.02	2.852(10)	172
	O2D-H2D1...O3A <sup>i</sup>	0.98	1.81	2.645(10)	180

Symmetry codes: (i) -x+1, y-1/2, -z-3/2

Figure 1-12 shows the packing of the cell, with extra molecules to illustrate the trigonal H bonding to the Cl<sup>-</sup> counterion from three different L-ecgonine cation units. The chloride anion lies 0.1975(8) Å below the plane formed by its three contact atoms (N1, O2A & O3B). One close intermolecular C—H···O contact exists within the 2.7 Å range surveyed for non-bonded C—H···O packing interactions [C8···O3 = 3.228(2) Å, H8B···O3 = 2.451 Å, C8—H8B···O3 = 135.9°].<sup>28</sup>

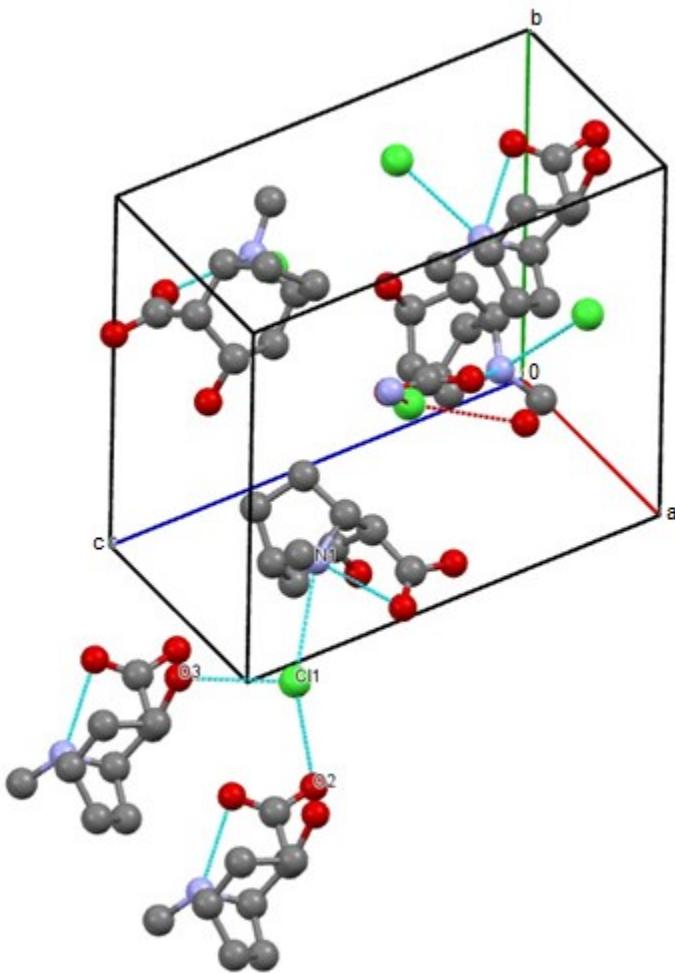


Figure 1-12. The packing diagram of (II). The diagram highlights the trigonal contact to the chloride anion.

The powder diffraction pattern of ecgonine HCl was calculated from the single crystal experiment (Figure 1-13). The powder pattern allows suitably equipped forensic laboratories the ability to identify crystalline samples of ecgonine hydrochloride in less than 30 minutes, another benefit of the X-ray diffraction characterization of illicit drug compounds.

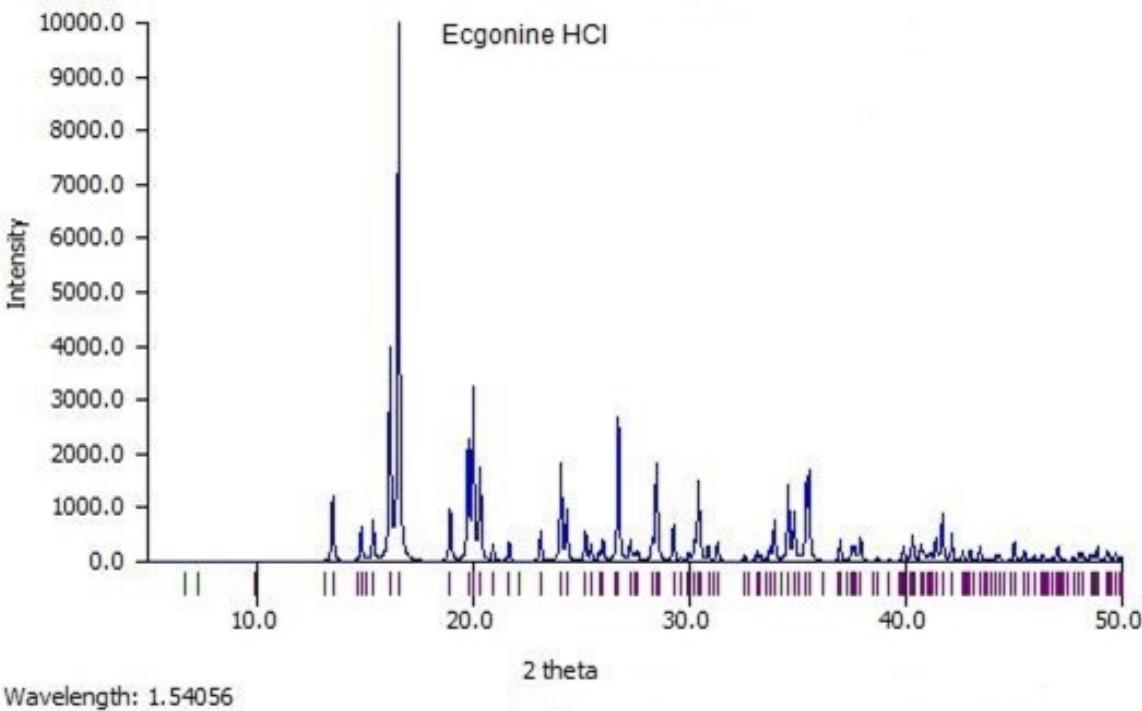


Figure 1-13. The calculated powder X-ray diffraction pattern of (II), ecgonine hydrochloride.

Ecgonine gold(III) chloride crystallizes in two forms, hydrated and anhydrous. The first described (III) is the hydrated form. The asymmetric unit of (III) (Figure 1-14) shows the unusual ratio of four cations to five anions. In the figure of the asymmetric unit, the four ecgonine cations are labelled A through D. The asymmetric unit also contains seven waters of hydration. It is imperative that one of the seven water molecules is a hydronium ion  $[H_3O^+]$  for charge balance. Unfortunately, the extra proton could not be located in the electron density difference mapping.

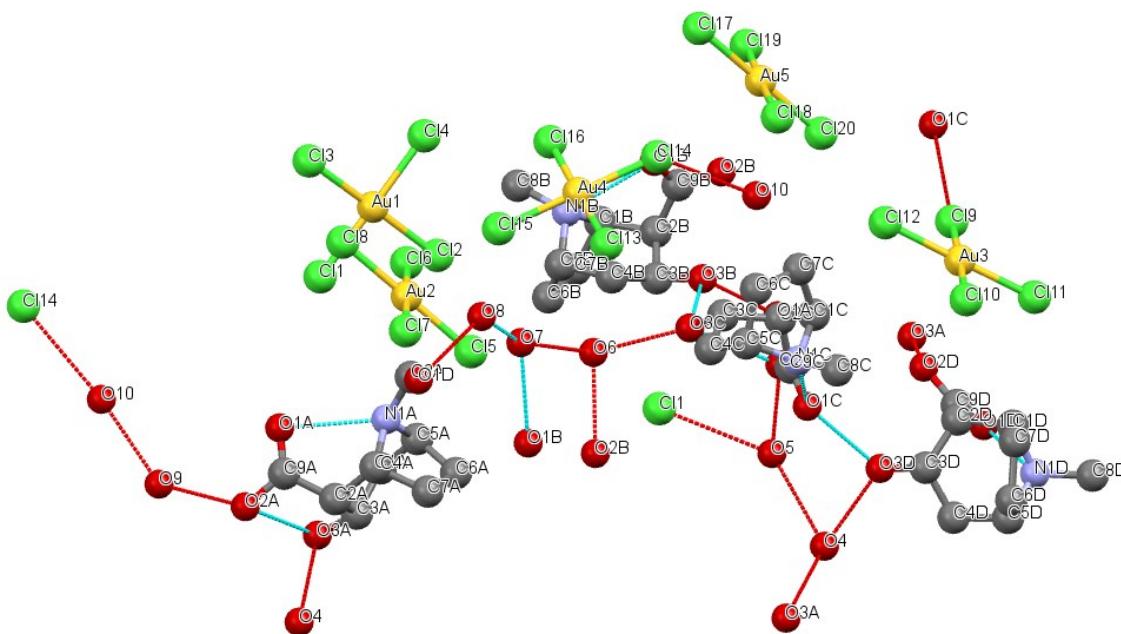


Figure 1-14. The asymmetric unit of (III), the hydrated ecgonine gold(III) tetrachloride salt , showing the numbering scheme and including nine-symmetry related atoms to show the H bonding or contacts.

The positive charge on the cations comes from the protonation of the N atom. As seen with the previous nitrogen bases, each of the four l-ecgonine cations has its quaternary N-bound H atom intramolecularly hydrogen bonded to its carboxyl C=O group. The H bond distances of (III) range from 2.734 Å to 2.814 Å lower than the value observed for (-)-norcocaine [N-O = 3.006 Å]<sup>26</sup>, but comparable to the value for the tetrachloroaurate(III) salt of l-cocaine [N-O = 2.755(6) Å]<sup>17</sup>, and the hydrochloride salt of l-ecgonine [N-O = 2.761(2) Å].<sup>9</sup> The intramolecular bond angles were remarkably more consistent, varying from 136° by only +/- 2°.

In the ecgonine cation designated “B”, the methoxy carbonyl is disordered (C9B-O1B = 1.261(13) Å and C9B-O2B = 1.280(15) Å) which prevents the

determination of the acid H atom. The remaining cations all have clear differences in C – O distances of the acid group ranging from 0.07 to 0.12Å, distinguishing the double bond from the single bond.

The arrangement of cations, anions, and water molecules within the unit cell displays distinct stratification. Four of the five anions (Au1, Au2, Au3, and Au5) form distinct bands starting at the origin of the unit cell and proceeding along the c-axis every quarter length of the cell (Figure 1-15) with the ecgonine cations closely associated and regularly spaced between the anions. These four anions lie in close proximity to the protonated N atom of each cation. The lone exception is the Au4 anion that is embedded within the network of water molecules. The Cl15 atom of this anion is involved in the only Au-Cl...Au close contact [3.361Å], which is slightly longer than the shortest reported Au-Cl...Au contact of 3.281Å found in the CSD<sup>29</sup>.

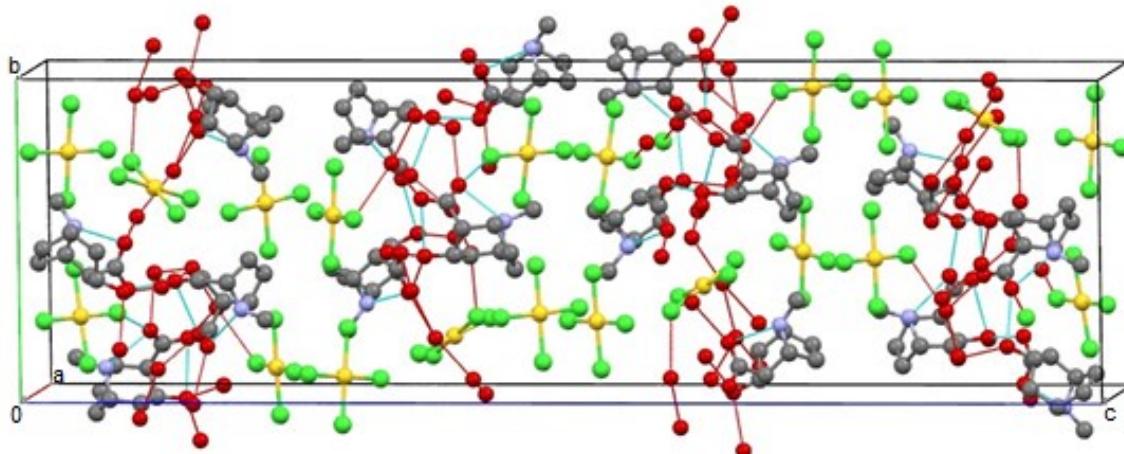


Figure 1-15. A packing diagram for (III), showing four asymmetric units.

The  $[\text{AuCl}_4]^-$  anions of (III) exhibit typical square-planar geometry. Four of the anions are essentially flat with mean deviations from the five-atom plane ranging from 0.006(3) (for the Au3 anion) to 0.013(2) Å (for the Au4 anion). The fifth anion, containing Au1, is slightly distorted having a mean deviation from the plane of 0.048(3) Å, with the Au(III) center 0.0069(11) Å above the best plane and one pair of opposing Cl atoms above the plane by 0.051(2) Å. The other pair of Cl atoms are below the plane by 0.054(2) Å<sup>18</sup>. The Cambridge Structural Database (CSD, Version 5.29, update of 2008<sup>24</sup>) was searched in order to compare and contrast the coordination of the gold(III) tetrachloride anion. The CSD database contains 106 structures with the gold(III) tetrachloride anion, several containing multiple  $[\text{AuCl}_4]^-$  species, for a total of 136 different anions. More than half of these, 71 are essentially flat, and the rest have varying degrees of bowing of the square-planar arrangement of the  $[\text{AuCl}_4]^-$  moiety. Only three show flexing greater than that found in (III), specifically tetra(methylthio)tetrathiafulvalene bis(tetrachloroaurate)<sup>25</sup>, the gold(III) tetrachloride salt of l-cocaine<sup>17</sup> and N-benzyl-N,N-bis(pyridinium-2-ylmethyl)amine chloride tetrachloroaurate(III)<sup>30</sup>.

One of the most fascinating features of (III) is the network of water molecules and, presumably, a single hydronium ion found between the layers of cations and anions. All of the O atoms of the structure fall within a narrow layer of 3.674 Å measured along the c axis of the cell. The cations are all joined into the network by either hydrogen bonds or close contacts, through either their hydroxy or their acid functional groups, to adjacent solvent water molecules.

While only some of the hydrogens on the water molecules could be found reliably on electron density difference maps, the proximity of the O atoms to each other and O atoms of the cations indicates extensive H bonding. The strata of H bonded O atoms (Table 1-5) contains water-to-water (or hydronium) bonds (entries 5, 6, and 7), acid-to-water (entries 8 and 9), hydroxy-to-water (entries 10 and 11), hydroxy-to-hydroxy (entry 12), water-to-acid (entry 13), water-to-carboxyl (entries 14 and 15) and water-to-hydroxy (entry 16). Intermolecular hydroxy-to-carbonyl hydrogen bonds (entries 1 and 2) and the one acid-to-hydroxy hydrogen bond (entry 3) are the only interactions involving H atoms that could be reliably located.

**Table 1-5**

Ecgonine AuCl<sub>4</sub> hydrogen bond network  
Intermolecular hydrogen-bond geometry (Å, °)

	D-H...A	D-H	H..A	D...A	D-H...A
Hydroxy to carbonyl	O3D-H3D1...O1C	0.84	1.9	2.743(10)	179 (Entry 1)
	O3B-H3B1...O1A <sup>ii</sup>	0.84	2.02	2.852(10)	172 (Entry 2)
Acid to hydroxy	O2D-H2D1...O3A <sup>ii</sup>	0.84	1.81	2.645(10)	180 (Entry 3)
	D...A			D...A	
Water to water	O4...O5			2.893(12)	(Entry 4)
	O6...O7			3.012(12)	(Entry 5)
	O7...O8			2.820(11)	(Entry 6)
	O9...O10			2.707(15)	(Entry 7)
Acid to water	O2A...O9			2.538(12)	(Entry 8)
	O2C...O5			2.600(12)	(Entry 9)
Hydroxy to water	O3D...O4			2.773(11)	(Entry 10)
	O3A...O4 <sup>iv</sup>			2.676(11)	(Entry 11)
Hydroxy to hydroxy	O3C...O3B			2.739(11)	(Entry 12)
	O6...O2B <sup>v</sup>			2.646(14)	(Entry 13)
Water to acid	O8...O1D <sup>vi</sup>			2.967(11)	(Entry 14)
	O7...O1B <sup>v</sup>			2.883(11)	(Entry 15)
	O6...O3C			2.713(12)	(Entry 16)
Symmetry codes: (ii) -x+1, y-1/2, -z+3/2; (iv) -x, y+1/2, (v) -z+3/2; x-1, y, z; (vi) x-1, y+1, z.					

Within the asymmetric unit of (III) there are three short Cl...O distances, two of which involve water molecules: O10...Cl14<sup>i</sup> interatomic distance = 3.217(11) Å {symmetry code: (i) -x+1, y+1/2, -z+3/2} and O5...Cl1<sup>ii</sup> interatomic

distance = 3.214(8) Å {symmetry code: (ii)  $-x+1$ ,  $y-1/2$ ,  $-z+3/2$ }. Both are 0.05-0.06Å shorter than the relevant van der Waals' sum of 3.27Å<sup>31</sup>, while the third, Cl9...O1C<sup>iii</sup> interatomic distance = 3.150(8) Å {symmetry code: (iii)  $x+1$ ,  $y$ ,  $z$ } is proximal to the acid carbonyl of an L-ecgonine cation and is shorter than the van der Waals' sum by 0.12Å.

The anhydrous salt, (IV), of ecgonine tetrachloroaurate (Figure 1-16) shows that the cation and anion are again in close proximity to each other, as was found in (I), the gold(III) tetrachloride salt of L-cocaine<sup>17</sup>, and in (III), the hydrate of the ecgonine gold(III) tetrachloride salt<sup>18</sup>. In this structure (IV), each of the two unique L-ecgonine cations also has its quaternary N-bound H atom intramolecularly hydrogen bonded to its carboxyl C=O group as seen in the other salts studied by this group and in contrast to the cocaine hydrochloride salt studied by Zhu *et al.*<sup>8</sup>.

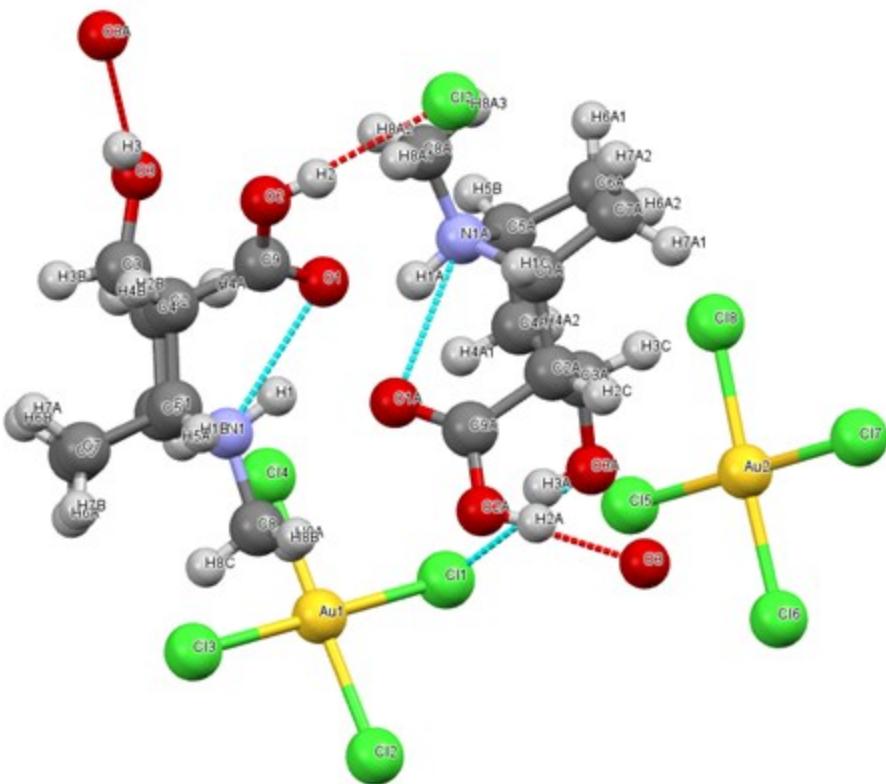


Figure 1-16. The asymmetric unit of (IV) ecgonine gold(III) tetrachloride anhydrous.

Table 1-4 compares the distances and angles of the intramolecular H bonds of the related structures (I, II, and III), (-)-norcocaine, cocaine HCl, cocaine freebase, and both ecgonine HAuCl<sub>4</sub> hydrate (IV) and anyhydrous (V). All of the structures containing an intramolecular H bond to the carbonyl O atom have an average bond distance of less than 2.77 Å. The H-bond in cocaine hydrochloride is to the alkoxy O and is slightly longer at 2.89 Å. It is clear that the H bond is more energetically favorable when the conformation of the dihedral angle exposes the carbonyl O, rather than the alkoxy O, to the protonated N atom.

There are two close hydrogen-bonded contacts involving Cl atoms, one between hydroxy atom O3A and atom Cl1, and the other between acid atom O2

and atom Cl2<sup>i</sup> [Table 1-3; symmetry code: (i) -x+1, y+1/2, -z +1/2]. There are also two hydrogen bonds involving the hydroxy O atoms, between atoms O3 and O3A<sup>i</sup>, and between atoms O2A and O3<sup>ii</sup> [symmetry code: (ii) -x+1, y-1/2, -z+1/2]. The latter involves the acid H atom in the rare *anti* configuration with the H atom pointed away from the carbonyl.

The two independent [AuCl<sub>4</sub>]<sup>-</sup> anions of (IV) show a bowing of the square-planar arrangement. The Au1 anion has a mean deviation from the plane of 0.0132(11) Å, with the Au(III) center 0.0082(4) Å below the best plane. One *trans* pair of Cl atoms is above the best plane by 0.160(5) Å and the other below the plane by 0.120(5) Å. The Au2 anion has a mean deviation from the plane of 0.0174(13) Å, with the Au(III) center 0.0117(5) Å below this plane. One *trans* pair of Cl atoms is above the plane by 0.212(6) Å and the other below the plane by 0.152(6) Å. The distortion of the square planar coordination of the AuCl<sub>4</sub><sup>-</sup> anion is a phenomenon consistently observed in these salts, but to varying degrees of flexing.

The packing diagram of (IV) shows a plane of gold chloride anions bisecting the unit cell parallel to the c-axis, half way along the b cell dimension (Figure 1-17). The remaining anions are located straddling unit cells in the ac plane. The cations are similarly aligned between the planes of anions at 1/3 and 2/3 the cell in b.

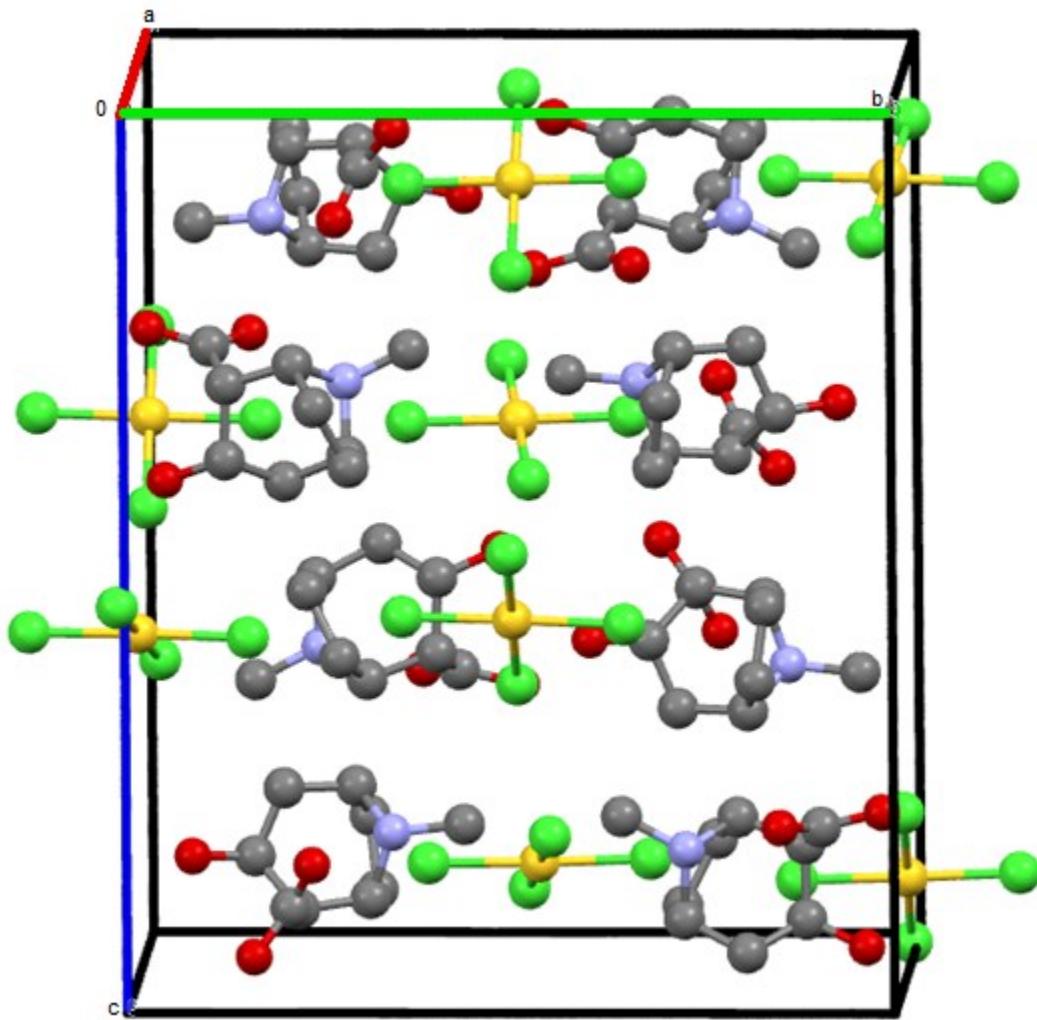


Figure 1-17. The packing diagram of (IV), the anhydrous salt of ecgonine gold(III) chloride.

The powder diffraction pattern of the microcrystals [formed as described by Wood *et al.*<sup>17</sup>] does not uniquely match either the hydrated structure, (III), nor the anhydrous structure, (IV), of the ecgonine Au(III) chloride complex, but has peaks associated with both of them. There are more peaks that are similar to the pure single-crystal generated powder pattern of the anhydrous material, (IV), than to that of the hydrate, (III). However, we cannot conclusively say that the

microcrystal test material is one or the other, or a combination of the two (possibly because of the humidity or lack thereof in the laboratory preparations), or the single crystals grown are of a completely different polymorph from the microcrystals. Forensic science laboratories performing (or those considering performing) powder X-ray diffraction will find the calculated powder diffractions (Figure 1-18) useful for the rapid analysis of the drugs described here or used in conjunction with the gold(III) chloride microcrystal tests.

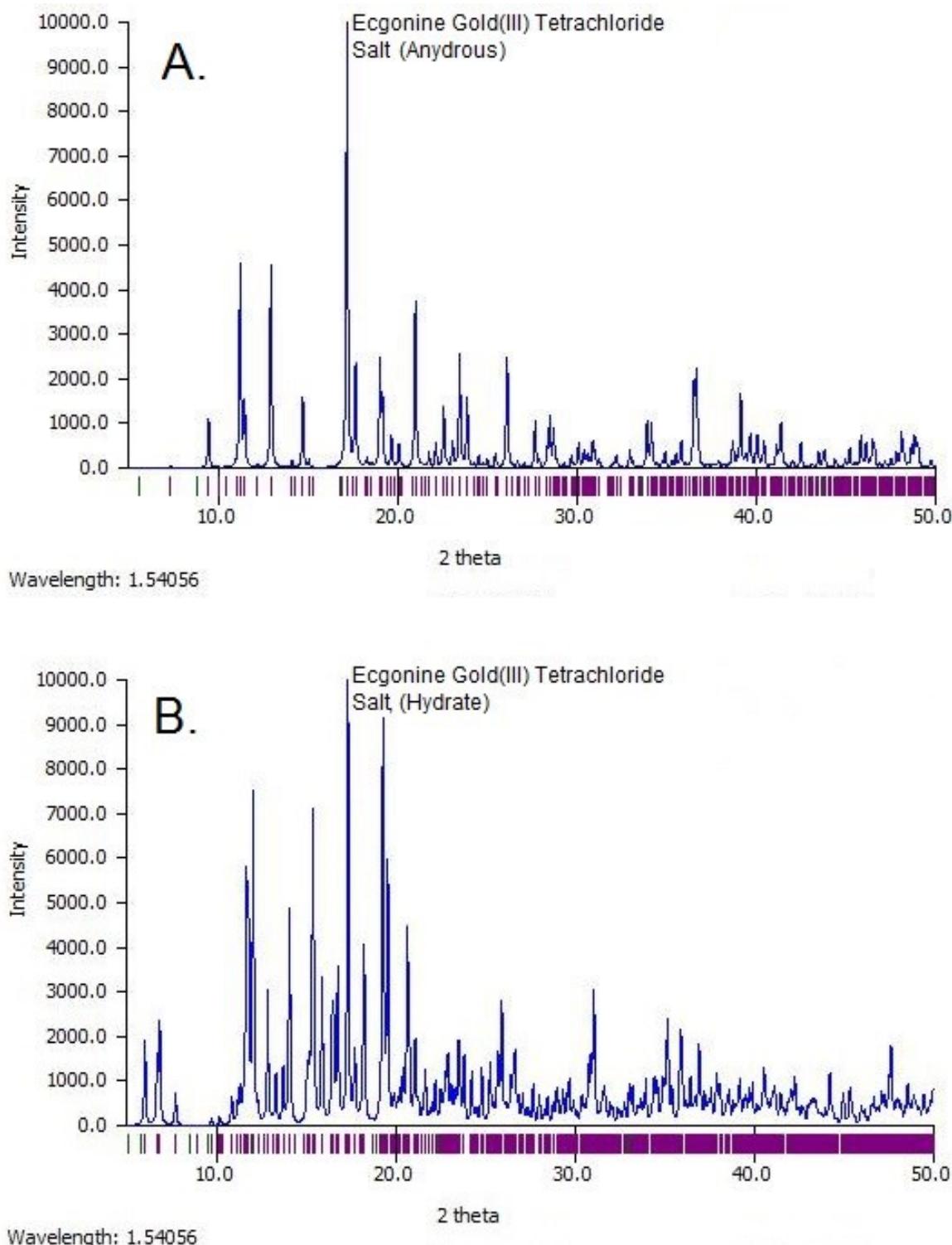


Figure 1-18. The powder X-ray diffraction patterns of (A) the anhydrous ecgonine gold(III) tetrachloride and (B) the hydrated ecgonine gold(III) tetrachloride salts.

## CONCLUSION

The gold chloride microcrystal test has been utilized in the scheme of analysis for cocaine testing for over 150 years<sup>3</sup> with little understanding of the precipitating crystals or the precipitates of structurally related compounds such as ecgonine.<sup>15</sup>

When tested with a 5% solution of acidified aqueous gold chloride, cocaine forms characteristic microcrystals often described as combs or fern fronds (Figure 1-19). The resulting precipitate crystals can best be described as a “complex salt” consisting of a protonated cocaine cation and an  $\text{AuCl}_4^-$  anion as opposed to a coordination complex as was previously postulated.<sup>23</sup>



Figure 1-19. The precipitation product of the cocaine gold(III) chloride microcrystal test (mag. 40x).

The gold(III) tetrachloride salt of I-cocaine (I) has an intramolecular H bond from the protonated N atom to the carbonyl O of the neighboring methyl ester functional group. This contrasts the H bond seen in cocaine hydrochloride that extends from the N atom to the alkoxy O of the same methyl ester.

The  $\text{AuCl}_4^-$  counterion resides proximally to the protonated N atom, 4.253(5) Å from the N atom to the nearest Cl atom. Interestingly, the anion undergoes an unusual distortion of the expected square planar coordination. This feature has been seen in a small number of structures found in the CCDC database, but several of the structures studied as part of this research. It is unclear if the “bowing” is related to the packing of the anions or the proximity of the positively charged N atom. The relationship of the anions to each other also creates an alternating “herringbone” pattern when the cell is packed. This arrangement within the crystal may account for the twinning that gives the microcrystals their characteristic morphology.

Ecgonine is the final product of cocaine metabolism often seen in the toxicology samples of cocaine abusers. It shares the tropane ring structure of cocaine; however, both methoxy ester and benzoyl ester functional groups of cocaine have been hydrolyzed to a carboxylate and hydroxyl functional group, respectively. Ecgonine hydrochloride (II) consists of a chloride anion located 3.282(1) Å from the protonated N atom of the ecgonine cation. The Cl anion participates in two additional H bonds with the carbonyl of one neighboring cation and the hydroxyl of another, resulting in a single chloride bound to three independent ecgonine cations through three different functional moieties. Ecgonine HCl also contains an internal H bond in the energetically preferred conformation from the protonated N atom to the double bonded O atom of the carboxylate.

While both cocaine and ecgonine share a common structural backbone, the product of the gold chloride microcrystal test with each drug is significantly different. Applying the same 5% acidified aqueous gold chloride reagent to ecgonine results in crystals with a thin plate morphology easily distinguished from cocaine-gold(III) chloride microcrystal (Figure 1-20).

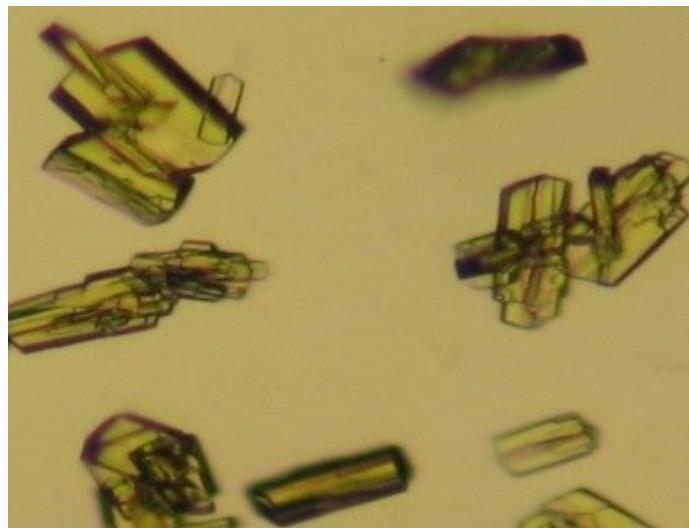


Figure 1-20. The precipitation product of the ecgonine gold(III) chloride microcrystal test (mag. 40x).

Precipitates from this crystal test resulted in two unique single crystals: one, an anhydrous salt containing two cation-anion pairs in the asymmetric unit; the other, a unique hydrate consisting of four ecgonine cations, five gold(III) chloride anions, six waters, and presumably a single hydronium. The microcrystals could not be uniquely attributed to either single crystal through comparison of the powder diffraction patterns and may be a combination of both.

The hydrated ecgonine-gold chloride crystal structure contained an extensive network of hydrogen bonds through the water molecules and the

hydroxyl, carbonyl, and acid O atoms of the cations. This arrangement created a repeating pattern of anions, water molecule, and cations propagating along the c-axis in the cell. Of the five anions, only one was located near the network of water molecules, presumably close to the hydronium ion, although the additional H atom could not be reliably associated to any specific water molecule.

The anhydrous ecgonine gold(III) chloride salt contained two cations and anions in the typical 1:1 ratio in the asymmetric unit. The anions were located near the protonated N atoms and had close contacts with either the hydroxy or acid functional groups of the cations.

Both the hydrate and the anhydrous ecgonine gold(III) chloride salts demonstrated the intramolecular H bond from the N atom to the carbonyl characteristic of this group of tropane alkaloids.

The single crystal structures of the cocaine and ecgonine complexes with gold(III) chloride have demonstrated many unique features due to their H-bonding, close contacts, and three dimensional atomic geometries. This knowledge will contribute to the understanding of the microcrystal precipitates and their formation.

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## CHAPTER 2. PHENETHYLAMINES<sup>1</sup>

### INTRODUCTION

Ephedrine, (2-methylamino-1-phenylpropan-1-ol), along with other naturally occurring ephedrine alkaloids, is obtained by extraction from *Ephedra sinica*, the Chinese medicinal plant *má huáng*, and several other species of the Ephedra genus of plant.<sup>1</sup> Ephedrine, once available in various pharmaceutical and herbal preparations for the treatment of asthma, upper respiratory congestion, and appetite suppression, has been banned from supplement market in the US since 2004.<sup>2</sup>

Amphetamine (1-phenylpropan-2-amine) and methamphetamine (N-methyl-1-phenylpropan-2-amine) are phenethylamines belonging to the same broad class of central nervous system (CNS) stimulant drugs structurally similar to ephedrine<sup>3</sup> and norephedrine<sup>1</sup>. The phenethylamine structural class consists of compounds with a phenyl ring joined to an amine by a 2-carbon bridge. All three compounds examined here have a methyl group attached to the α-carbon. Methamphetamine and ephedrine have an additional methyl group attached to the N atom. In the case of ephedrine, a hydroxyl group is attached to the β-carbon adjacent to the phenyl moiety. Both amphetamine and methamphetamine may be synthesized by either halogenation of the β-hydroxy group of norephedrine and ephedrine, respectively, to the chloro-analog, followed by reduction of the halogen group, or by direct reduction of the β-hydroxy group using hydroiodic acid and red phosphorus.<sup>5, 6</sup>

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<sup>1</sup> Adapted from previous work<sup>27</sup>

Amphetamine, methamphetamine, and ephedrine are well known for their stimulant effects and have been referred to as "amphetamine-type stimulants" (ATS) in literature. The three phenethylamines in this study have established 'sympathomimetic effects'<sup>7</sup>, such as increased blood pressure, alertness, heightened awareness, and appetite suppression, among others.<sup>8</sup> Amphetamine-type stimulants affect the release of the catecholamine neurotransmitters norepinephrine and dopamine in the peripheral and central nervous system, respectively. The release of norepinephrine stimulates the physiological 'fight or flight' response, while the CNS response to increased dopamine is attributed to the mood, excitation, and euphoria sought by illicit drug users.<sup>9</sup> In the United States, both amphetamine and methamphetamine are considered Schedule II Controlled Dangerous Substances (regulated since October 27, 1970), having a high potential for abuse which may lead to severe psychological or physical dependence;<sup>10</sup> ephedrine, while legally prescribed, is a regulated substance in both the USA and the UK. In the US, amphetamine may be prescribed for narcolepsy and attention deficit hyperactivity disorder (ADHD). For a comprehensive review of amphetamine pharmacology, the reader is directed to the 2013 review by Heal *et al.*<sup>11</sup>

In some countries or legal jurisdictions, legislation requires that the chirality of the enantiomer present in the sample be identified for legal purposes. Ephedrine has two chiral centers, resulting in four isomers (d- and l-ephedrine, and d- and l-pseudoephedrine). In this work, the racemate dl-ephedrine was studied. Both amphetamine and methamphetamine have one chiral center, with

the d- enantiomers having a greater reported pharmacological efficacy.<sup>9, 12</sup> As an example, the manufacture and use of d-methamphetamine is strictly controlled; however, l-methamphetamine may be obtained over-the-counter as the nasal decongestant product Vicks™ Vapor Inhaler. Distinction of the optical isomers of d- and l-amphetamine and the optical isomers of d- and l-methamphetamine can be achieved through time-consuming chiral derivatization or with expensive chiral liquid chromatography columns; however, they can easily be resolved using fast and inexpensive microcrystal tests.<sup>13</sup> The United Nations Office on Drugs and Crime published the 'Recommended Methods for the Analysis of Amphetamine, Methamphetamine and Their Ring-Substituted Analogues in Seized Material'<sup>14</sup>, recognizing the benefit of using microchemical or microcrystal tests in the forensic analytical scheme for the testing of suspected amphetamine-type stimulants. Forensically, microcrystal tests can be applied to both seized drug samples or to toxicological samples. The elimination pathway of amphetamines is such that 30–40% of the drug dose is excreted unchanged and may be detected in urine specimens.<sup>15, 16</sup> The gold chloride microcrystal tests for the identification and differentiation of these structurally related compounds and their stereoisomers has been described in depth by Fulton<sup>17</sup>. The microcrystal test for methamphetamine using acidified HAuCl<sub>4</sub><sup>-</sup> immediately precipitates numerous needles and blades. The same microcrystal test used on amphetamine produces large thin square plates. The acidified HAuCl<sub>4</sub><sup>-</sup> microcrystal test performed on ephedrine produces square and four-parted plates, but at a much slower rate than the two previous compounds. These microcrystal results are in

agreement with those for each product as described by Fulton.<sup>17</sup> Microcrystal tests are often excluded from the laboratory's battery of analytical techniques for a variety of reasons. Modern instrumental analysis, such as mass spectrometry and infrared spectrophotometry are considered preferred analytical techniques due to their high discriminating power. However, each has their drawbacks. A major reason that microcrystal tests are often overlooked in the general analytical scheme is the lack of research that supports an understanding of the crystal structure.<sup>18</sup> Another criticism of microcrystal tests is the empirical and subjective nature of the microchemical technique, which relies heavily upon the training, knowledge, and experience of the forensic scientist. Due to variations in sample matrices, interfering adulterants, by-products of incomplete reaction and sample purity; care must be taken in the preparation and interpretation of the resulting microcrystals. A poorly trained or inadequately prepared scientist could make identification errors. For this reason, microcrystal tests should be used to compliment additional techniques. The Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) recommends that microcrystal tests be combined with a "Category A" technique such as infrared spectroscopy, mass spectrometry, nuclear magnetic resonance, or X-ray diffractometry; or a combination of uncorrelated chromatographic techniques.<sup>19</sup> The single-crystal structures of the products of the interactions of ( $\pm$ )-amphetamine, (+)-methamphetamine, and ( $\pm$ )-ephedrine with gold(III) chloride (one of the most widely used metal complexation agents used to precipitate these drugs and produce the microcrystals for testing) has been determined by single crystal

X-ray diffractometry in order to gain further insight into the nature of these microcrystal tests.

## SUMMARY OF CRYSTAL STRUCTURES DETERMINED

- I. The Gold(III) Adduct of ( $\pm$ )-Amphetamine and two chloride ions.  
[DL-2-(2-Aminopropyl)phenyl- $\kappa^2 N,C^1$ ]dichloridogold(III)
- II. The Gold(III) Tetrachloride Salt of (+)-Methamphetamine  
d-Methyl-(1-phenylpropan-2-yl)azanium tetrachloridoaurate(III)
- III. The Gold(III) Tetrachloride Salt of ( $\pm$ )-Ephedrine  
DL-(1-hydroxy-1-phenylpropan-2-yl)-(methyl)azanium  
tetrachloridoaurate(III)

## EXPERIMENTAL

### Synthesis and crystallization:

( $\pm$ )-Amphetamine, (+)-methamphetamine, and ( $\pm$ )-ephedrine were purchased from Sigma Chemical.  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  was purchased from Fisher Chemical Co. Aqueous solutions (1.0 mL) of 0.2% of ( $\pm$ )- $\alpha$ -methylphenethylamine sulfate [for (I)], (+)- $N$ - $\alpha$ -dimethylphenethylamine hydrochloride [for (II)] or ( $\pm$ )-2-methylamino-1-phenylpropan-1-ol hydrochloride [for (III)] were mixed with 0.5% aqueous  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (1 mL) acidified with several drops of concentrated HCl. Crystals grew over a period of approximately 2–4 weeks by slow evaporation at room temperature.

Crystals of amphetamine (I) formed as an adduct with gold(III) as the central atom additionally bound to two chlorides, [D,L-2-(2-Aminopropyl)phenyl- $\kappa^2\text{N,C}1$ ]dichloridogold(III). Methamphetamine (II) formed a salt with an  $\text{AuCl}_4^-$  anion. The drug, ephedrine (III), also precipitated as a gold(III) chloride salt (Figure 2-1).

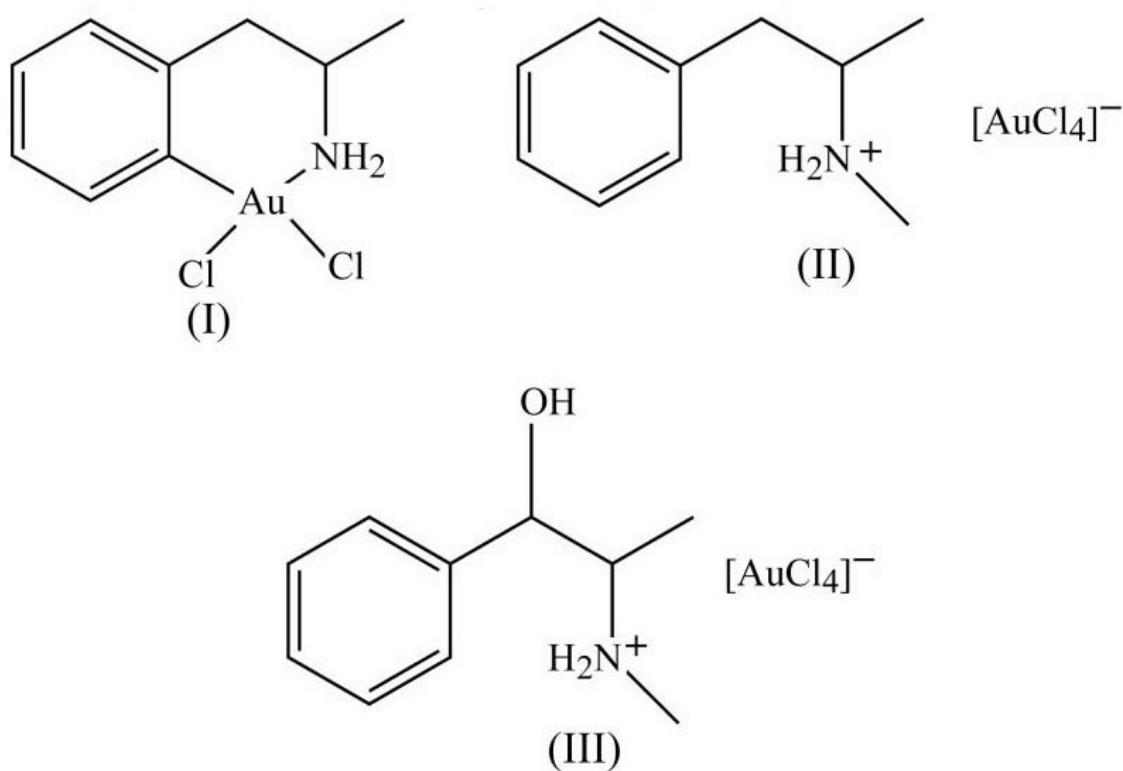


Figure 2-1. Diagrams of the gold(III) precipitation products of the three phenethylamines (amphetamine, methamphetamine, and ephedrine). (I) [D,L-2-(2-aminopropyl)phenyl- $\kappa$ 2N,C1] dichloridogold(III), (II) D-methyl(1-phenylpropan-2-yl)azanium tetrachloridoaurate(III).

**Table 2-1**

Experimental details.

	I	II	III
<b>Crystal data</b>	[ <i>D,L</i> -2-(2-Aminopropyl)phenyl- $\kappa^2$ <i>N,C</i> <sup>1</sup> ]dichloridogold(III)	<i>D</i> -Methyl(1-phenylpropan-2-yl)azanium tetrachloridoaurate(III)	<i>D,L</i> -(1-Hydroxy-1-phenylpropan-2-yl)(methyl)azanium tetrachloridoaurate(III)
Chemical Formula	[Au(C <sub>9</sub> H <sub>12</sub> N)Cl <sub>2</sub> ]	[C <sub>10</sub> H <sub>16</sub> N][AuCl <sub>4</sub> ]	[C <sub>10</sub> H <sub>16</sub> NO][AuCl <sub>4</sub> ]
<i>M</i> <sub>r</sub>	643.12	489	505
Crystal system, space group	Orthorhombic, <i>Pbca</i>	Monoclinic, <i>P2</i> <sub>1</sub>	Monoclinic, <i>P2</i> <sub>1</sub> /c
a, b, c (Å)	9.1323 (2), 8.9812 (2), 27.1824 (6)	7.3561 (1), 14.2394 (2), 13.9103 (2)	7.7537 (4), 25.0264 (13), 15.4587 (8)
$\alpha, \beta, \gamma$ (°)	90, 90, 90	90, 90.077(1), 90	90, 93.920 (2), 90
V (Å <sup>3</sup> )	2229.50 (9)	1457.05 (4)	2992.7 (3)
Z	8	4	8
Density Mg m <sup>-3</sup>	2.396	2.229	2.242
Radiation type		Cu $K\alpha$	
$\mu$ mm <sup>-1</sup>	28.84	25.52	24.93
Temperature (K)	100	100	100
Shape, color	Block, yellow	Parallelepiped, gold	Needle, yellow
Crystal size (mm)	0.42 × 0.30 × 0.24	0.24 × 0.17 × 0.10	0.38 × 0.11 × 0.06
<b>Data collection</b>			
Diffractometer	Bruker SMART CCD APEXII area-detector diffractometer		
Absorption correction	multi-scan: (SADABS; Sheldrick, 2008a) numerical (SADABS; Sheldrick, 2008a)		
T <sub>min</sub> , T <sub>max</sub>	0.029, 0.055	0.064, 0.189	0.038, 0.326
$\Theta_{\text{min}}$ , $\Theta_{\text{max}}$	3.3, 71.2°	4.4, 71.0°	3.4, 72.1°
No. of measured reflections	20023	13819	26603
No. of independent	2039	4846	5386

<b>reflections</b>			
No of observed reflections [ $I > 2[\sigma](I)$ ]	2014	4831	4874
$R_{\text{int}}$	0.051	0.041	0.053
<b>Refinement</b>			
$R[F^2 > 2\sigma(F^2)]$ , $wR(F^2)$ , S	0.042, 0.102, 1.14	0.029, 0.071, 1.15	0.04, 0.094, 1.12
No. of reflections	2039	4846	5386
No. of parameters	120	295	312
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	2.12, -2.79	1.35, -1.50	1.94, -1.35
Absolute structure	Flack, H. D. (1983). Acta Cryst. A39, 876-881.		
Friedel Pairs	2131		
Flack parameter	0.077 (12)		

### Refinement:

All O-, N-, and C bound H atoms for (I), (II) and (III) were found in difference electron density maps. The methyl H atoms were placed with C—H = 0.98 Å and with initial torsion angles determined using a local difference Fourier calculation, and were constrained to have  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . The torsion angle about the proximal C—C or C—N bond was permitted to vary during refinement. The methylene, methine, aromatic, and amine H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atoms, with C—H = 0.99, 1.00 and 0.95 Å , respectively. The N—H distances were constrained to 0.92 Å. The O-bound H atoms of (III) were placed in geometrically

idealized positions and constrained to ride on their parent O atoms, with O—H = 0.84 Å. All of these had  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ,  $1.2U_{\text{eq}}(\text{N})$  or  $1.5U_{\text{eq}}(\text{O})$ . For (III), the molecule labeled A had larger anisotropic displacement parameters (attributed to possible disordering), and one constraint was applied between two of the C atoms. For all compounds, data collection: APEX2<sup>20</sup>; cell refinement: APEX2; data reduction: SAINT<sup>21</sup>; program(s) used to solve structure: SHELXTL<sup>22</sup>; program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

X-ray data have been deposited in CCDC<sup>23</sup>: amphetamine gold(III) dichloride adduct (Refcode = “MEXWAP”) = 934609; methamphetamine gold(III) tetrachloride (Refcode = “MEXVUI”) = 934610; ephedrine gold(III) tetrachloride (refcode = “MEXVOC”)= 934611.

## RESULTS

The compound [*DL*-2-(2-aminopropyl)phenyl- $\kappa^2N,C^1$ ]dichloridogold(III), (I), is the adduct of gold(III) with ( $\pm$ )-amphetamine and two chloride ions, forming a square-planar complex. The *D*-Methyl-(1-phenylpropan-2-yl)azanium tetrachloridoaurate(III), (II), is the ionic salt formed when Au<sup>III</sup> crystallizes with (+)-methamphetamine, and *DL* -(1-hydroxy-1-phenylpropan-2-yl)-(methyl)azanium tetrachloridoaurate(III), (III), is the ionic salt formed between ephedrine and gold(III) chloride. In contrast with (II) and (III), which are tetrachloridogold(III) salts, (I) undergoes cycloaurate metallation to form a six-membered ring structure. In (I), the Au(III) atom is coordinated to the N atom and one of the *ortho* C atoms of the phenyl ring of the amphetamine ligand, as well as to two Cl atoms. This binding arrangement forms a cycloaurated, distorted square-planar coordination geometry with an r.m.s. deviation of the coordinated atoms from the best least-squares plane of 0.021 Å (). This result is in contrast with the previous studies, in which protonated amine ligands formed salts with the gold(III) chloride crystallizing reagent<sup>23, 24</sup>.

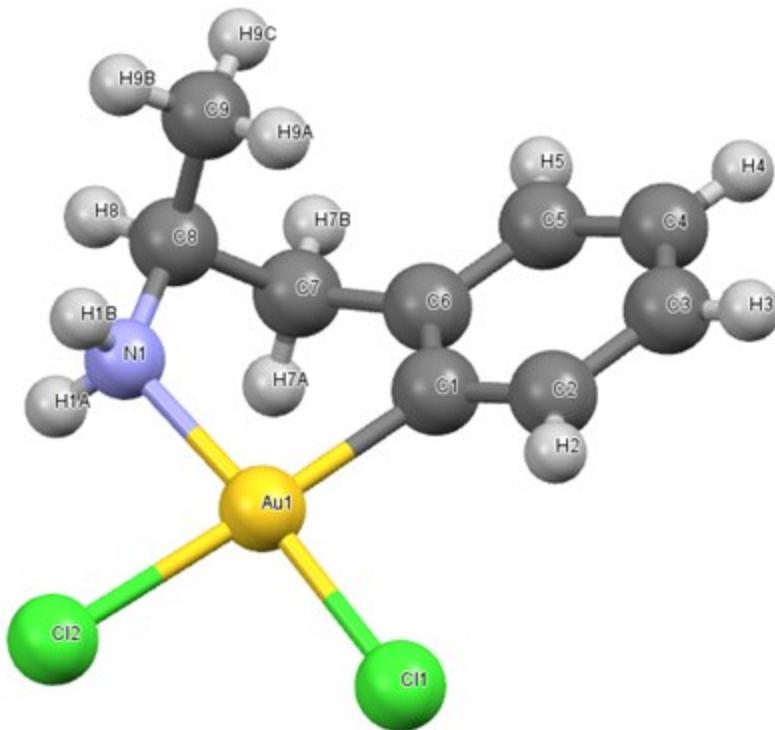


Figure 2-2. The asymmetric unit of (I), the gold(III) amphetamine dichloride adduct.

Several similar gold adducts have been studied for potential anti-tumor and anti-microbial applications. The first Au(III) six-membered *C,N*-cycloaurate derivatives of this type with 2-benzylpyridines ( $\text{NC}_5\text{H}_4-\text{CH}_2\text{Ph}-2$  and  $\text{NC}_5\text{H}_4-\text{CHMePh}-2$ ) was described by Cinelli *et al.*<sup>25</sup> Similarly, the reaction between these ligands and  $\text{HAuCl}_4$  at room temperature led to the formation of cycloaurated adducts. When the 2-benzylpyridine had two methyl groups on the bridging C atom ( $\text{NC}_5\text{H}_4-\text{CMe}_2\text{Ph}-2$ ) only the  $\text{AuCl}_4^-$  salt precipitated. In both of the cycloaurated Cinelli structures, the Au bridges the C and N atoms of the 2-benzylpyridine ligands to form a six-membered ring, i.e., a cycloaurate ring similar to that found in (I).

The *trans* effect<sup>26</sup> is a stretching of the bond distance of the ligand opposite the *trans*-influencing ligand. The *trans* influence makes the trans ligand more reactive. There is a strong *trans* influence found in (I), shown by the Au1—Cl2 bond length of 2.414 (2) Å versus the Au1—Cl1 bond length of 2.270 (2) Å. This 0.144 (3) Å difference reflects the stronger *trans* influence of the aryl C atom compared with the N-atom donor. The *trans* effect was compared with similar structures containing a six-membered cycloaurated *C,N*-motif, but having various heteroatoms opposite the Au atom in the ring (Table 2-2).<sup>25, 27, 28, 29, 30</sup> These complexes also demonstrate a *trans* influence, but to a much lesser extent. The Au—Cl2 bond length in (I) is the longest example of a bond with the *trans* influence among the *C,N*-cycloaurated ring systems found to date. Also, the difference in bond length between Au—Cl2 and Au—Cl1 in (I) is much larger than the next closest value to have been reported, and is much larger than the average of the five structures previously reported.

**Table 2-2**

*Trans* effect on bond length of comparable structures  
Comparison of bond distances (Å) for (I) and related compounds.

Heteroatom	Au—Cl2	Au—Cl1	Au—C	Au—N	Reference
C	2.414 (2)	2.270 (2)	2.057 (8)	2.069 (7)	This work
C	2.390 (1)	2.282 (1)	2.021 (3)	2.041 (3)	25
N	2.399 (7)	2.277 (7)	2.01 (2)	2.05 (2)	28
O	2.369 (5)	2.275 (4)	2.03 (2)	2.02 (1)	29
S	2.384 (4)	2.277 (4)	2.04 (2)	2.07 (1)	29
C=O	2.381 (2)	2.276 (2)	2.033 (7)	2.035 (5)	30

**Table 2-3**

*Trans* effect on "bite" angle of comparable structures  
Comparison of bond angles ( $^{\circ}$ ) for (I) and related compounds.

Hetero-atom	C—Au—N	Cl1—Au—Cl2	C—Au—Cl1	C—Au—Cl2	N—Au—Cl1	Au—Cl2	N— Au— Cl2	Refer- ences
C	92.8 (3)	91.01 (9)	91.2 (3)	177.8 (3)	175.4 (2)	85.0 (2)	This work	25
	85.7 (1)			177.4 (1)	176.2 (8)	91.9 (9)		
N	87.3 (9)	91.6 (4)	90.8 (1)	179.2 (7)	176.1 (6)	92.0 (6)	28	29
	86.6 (6)	90.1 (2)	90.5 (7)	177.7 (4)	175.2 (3)	91.7 (4)		
O	88.3 (6)	92.1 (2)	89.5 (4)	178.4 (5)	176.8 (5)	90.2 (4)	29	30
	89.5 (3)	91.9 (1)	89.6 (5)	177.4 (2)	176.2 (2)	92.0 (2)		
C=O		88.29 (7)	90.3 (2)	(2)				

The bidentate binding between the Au atom and the amphetamine also distorts the square planar coordination by increasing the angle, or 'bite' between the N1—Au1—C1 atoms to 92.8 (3) $^{\circ}$ . This is much larger than the average value of 87.48 $^{\circ}$  (range of 84.7- 86.2 $^{\circ}$ ) of similar cycloaurates<sup>31, 32, 33, 34</sup> and the 'bite' of 85.7(1) $^{\circ}$  found in Cinnelu's [Au{NC<sub>5</sub>H<sub>4</sub>(CMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)}Cl<sub>2</sub>].<sup>25</sup> For a comparison of the 'bite' and other angles around the gold center in similar structures, see Table 2-3. The six-membered cycloaurate ring in (I) is in a slightly distorted boat conformation, with a dihedral angle of 20.3 (6) $^{\circ}$  between the C1—Au1—N1 and N1—C8—C6—C1 planes and a dihedral angle of 57.0(6) $^{\circ}$  between the C6—C7—C8 and N1—C8—C6—C1 planes. The dihedral angle between the Au1—Cl1—Cl2—N1 plane and the plane of the phenyl ring (C1—C6) is 35.2(3) $^{\circ}$ . The structure of (I) is most similar to one published by Mack *et al.*<sup>35</sup>, in that their

ligand is 2-(N,N-dimethylaminomethyl) phenyl, referred to as “damp”, whereas ours is 2-(N-ethylaminomethyl) phenyl, both making a cycloaurate-bridged structure. However, the former ligand makes a five-membered ring and the latter produces a six-membered ring. The Mack structure also demonstrates the *trans* influence. Kilpin & Henderson<sup>36</sup>, Parish *et al.*<sup>37</sup> and Vicente *et al.*<sup>38</sup> have studied these five-membered C,N-chelated dichlorido cycloaurate(III) systems extensively. Damp(AuCl<sub>2</sub>) and a large number of structural analogues have been studied for their antitumor and antimicrobial properties, with results comparable to cisplatin in vitro and modest results in vivo.<sup>37</sup> Like cisplatin, these structures contain a central metal in a four-coordinate square-planar geometry, with two chloride ligands in mutually *cis* positions. The Au atom in gold complexes has a larger reduction potential than the Pt atom; this necessitates incorporating the Au atom in a ring structure of the general formula LAuX<sub>2</sub>, where ‘X’ is typically a Cl<sup>-1</sup> and L is a C,N bound ligand.<sup>36</sup> The observed *trans* effect preferentially releases one of the two Cl anions. The structural similarities between damp(AuCl<sub>2</sub>) and complex (I) indicate the potential for similar antitumor and antimicrobial properties and warrant further investigation of this and other analogues.

In the packing diagram of (I), Figure 2-3, the non-polar phenyl rings of the amphetamine-gold chloride adduct are oriented in such a way as to form alternating clusters with the gold and chlorine components of the molecule. The gold and chlorine atoms divide the unit cell in half along the c-axis and are located at each end.

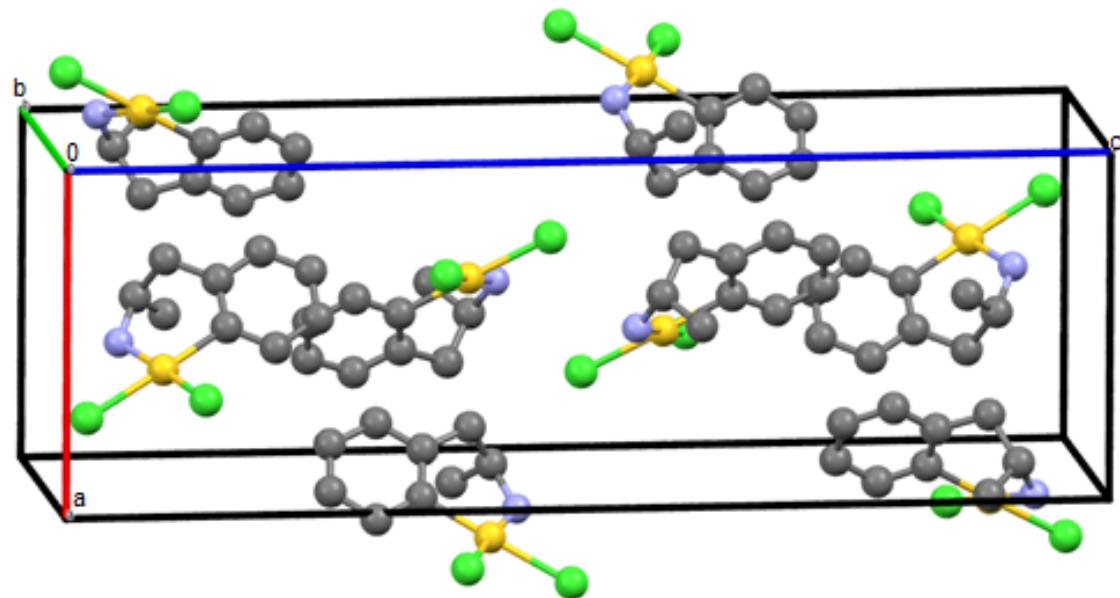


Figure 2-3. The packing diagram of (I) showing the clustering of the non-polar phenyl rings. Hydrogens have been removed for clarity.

Methamphetamine and amphetamine differ from each other by the single addition of a methyl group on the amine; however, the structure of the microcrystal products differs significantly. Methamphetamine tetrachloroaurate (II) precipitates as a salt from the reaction of methamphetamine and  $\text{HAuCl}_4^-$ . Two protonated methamphetamine cations and two  $\text{AuCl}_4^-$  anions exist in the asymmetric unit (Figure 2-4). The two anions are essentially square planar, with r.m.s. deviations of 0.025 and 0.008 Å from the best least-squares planes for the Au1 and Au2 atoms, respectively.

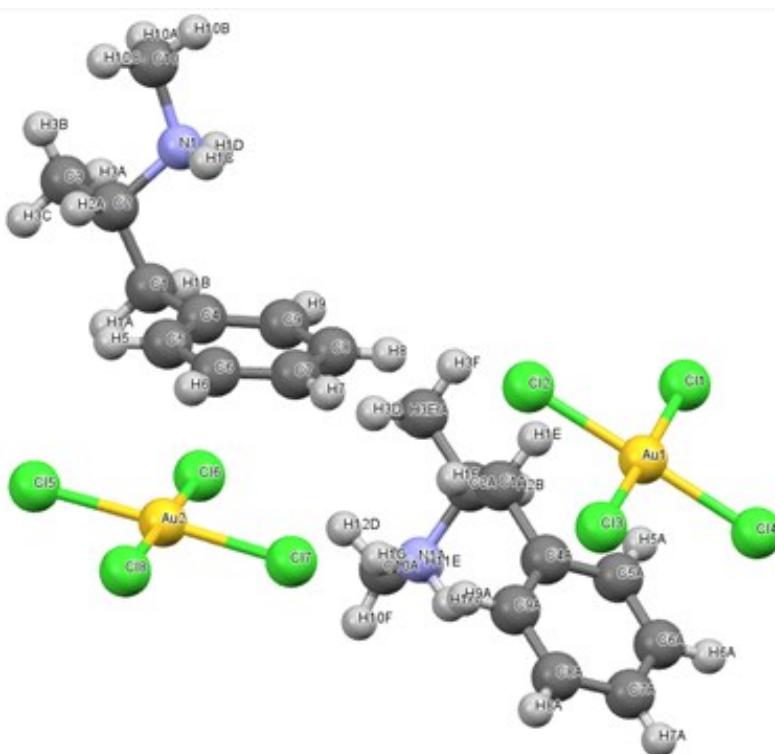


Figure 2-4. The asymmetric unit of (II), methamphetamine gold(III) tetrachloride salt.

Collier *et al.*<sup>4</sup> described two distinct conformations of structurally similar ephedrine cations that result from different torsion angles around a bond adjacent to a single chiral center. The ‘folded’ conformer is found for the chiral center having a torsion angle between 49 and 72°, whereas the ‘extended’ conformer has torsion angles between 163 and 178° in the molecules studied. We find that both of the cations in the asymmetric unit of (II) are in the ‘extended’ conformation, with torsion angles C1—C2—N1—C10 = 178.0 (9)° and C1A—C2A—N1A—C10A = 179.6 (8)°. There are a number of hydrogen bonds formed between the azonium group and the Cl atoms (Table 2-4); these are mainly with symmetry-related molecules, but one is within the same asymmetric unit. Two sets of these are bifurcated, *viz.* N1—H1C...{Cl5,Cl6}(x - 1, y, z), and N1A—

$\text{H1H}\dots\{\text{Cl1}, \text{Cl2}\}$ - ( $x + 1, y, z$ ). Not surprisingly, these hydrogen bonds are all longer than those reported by Hakey *et al.*<sup>39</sup> for the related chloride salt, where the two independent N...Cl distances are 3.069 and 3.116 Å.

**Table 2-4**

H-bonds formed between the azanium group and the Cl atoms.  
Hydrogen-bond geometry (Å) and (°)for (II).

D-H...A	D-H	H...A	D...A	D-H...A
N1—H1C...Cl5 <sup>i</sup>	0.9	2.58	3.324 (8)	138
N1—H1C...Cl6 <sup>i</sup>	0.9	2.79	3.465 (8)	131
N1—H1D...Cl8 <sup>ii</sup>	0.9	2.47	3.334 (8)	156
N1A—H1G...Cl7	0.9	2.51	3.410 (9)	167
N1A—H1H...Cl1 <sup>iii</sup>	0.9	2.62	3.432 (9)	147
N1A—H1H...Cl2 <sup>iii</sup>	0.9	2.75	3.244 (8)	115

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x + 1, y - 1/2, -z + 1$ ; (iii)  $x + 1, y, z$

Alternating  $[\text{AuCl}_4]^-$  anions and phenyl rings from the cation form stacks parallel to the  $a$  axis (Figure 2-5). The planes of the anions and phenyl groups are nearly parallel to (100), with the Au atoms located near  $a/3$  and  $2a/3$ . The coordination planes of Au1 and Au2 are inclined at 11.04 (6) and 13.20 (6)°, respectively, to the [100] direction. The anions are positioned slightly away from a line drawn between the centroids of the phenyl rings of the methamphetamine cations separated by one unit cell in  $a$ , as shown for Au1. In the adduct with the Au1 anion, the (cation ring centroid)—Au1—(cation ring centroid) angle is 17.9° and the Au1 atom is 0.58 Å from the line joining the two centroids. In the case of the Au2 fragment, the (cation ring centroid)—Au2—(cation ring centroid) angle is 6.6° and the Au2 atom is 0.21 Å from the line joining the two centroids. For Au2,

the phenyl ring is shown sandwiched between Au2 and Au2C( $x-1, y, z$ ) (Figure 2-5B).

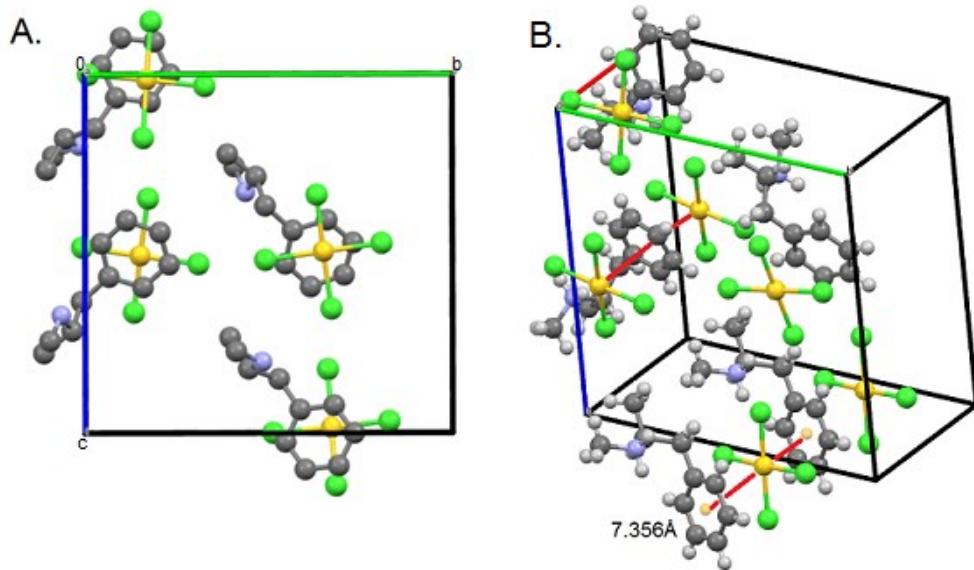


Figure 2-5. Two views of the packing diagram of (II), methamphetamine gold(III) tetrachloride.

For (III), the two  $[\text{AuCl}_4]^-$  anions are again essentially square planar (Figure 2-6), with Au—Cl bond lengths ranging from 2.2734 (18) to 2.2846 (18) Å, and angles ranging from 88.86 (7) to 91.55 (7)° and from 176.04 (7) to 178.99 (7)°. Concerning the planarity of the two  $[\text{AuCl}_4]^-$  anions, the r.m.s. deviations of the atoms from the best least-squares planes are 0.054 and 0.016 Å for the Au1 and Au2 planes, respectively. One of the cations in the asymmetric unit is in the ‘folded’ state, with a C1—C2—N1—C10 torsion angle of -57.2 (8)°, and the second cation is in the ‘extended’ conformation, with a C1A—C2A—N1A—C10A torsion angle of 179.4 (9)°.<sup>4</sup> There is one intramolecular N—H...O contact in each cation (Table 2-5): N1...O1 = 2.716 (9) Å and N1A...O1A = 2.658 (11) Å. There are also six N—H...Cl hydrogen bonds of varying lengths and one

intermolecular hydroxy–hydroxyl hydrogen bond [O1—H2...O1A ( $x + 1$ ,  $-y + 1/2$ ,  $z + 1/2$ )], with an O...O distance of 3.264 (12) Å.

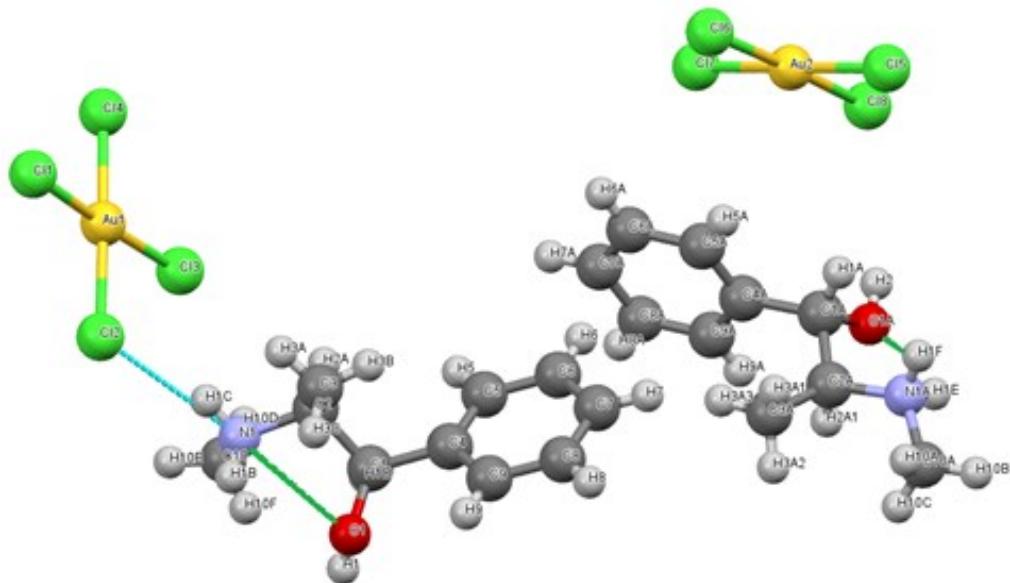


Figure 2-6. The asymmetric unit of (III), ephedrine gold(III) tetrachloride salt with numbering. An intramolecular H bond is shown by the green, dashed line and the H bond from the protonated N atom to the chloride is shown by the dashed, teal line.

**Table 2-5**

H-bonds formed between the azanium group and the Cl atoms.

Hydrogen-bond geometry ( $\text{\AA}$ ) and ( $^{\circ}$ ) for (III).

D-H...A	D-H	H...A	D...A	D-H...A
O1—H1...Cl6i	0.84	2.59	3.399 (6)	161
O1—H1...Cl7i	0.84	2.72	3.256 (6)	124
N1—H1B...O1	0.92	2.38	2.716 (9)	101
N1—H1B...Cl8ii	0.92	2.54	3.371 (7)	151
N1—H1C...Cl2iii	0.92	2.4	3.292 (7)	163
N1A—H1E...O1A	0.92	2.27	2.658 (11)	105
N1A—H1E...Cl5iv	0.92	2.55	3.410 (7)	156
N1A—H1F...Cl6v	0.92	2.56	3.413 (7)	155
O1A—H2...O1vi	0.84	2.53	3.264 (12)	146

Symmetry codes: (i)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (iii)  $x - 1, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (iv)  $-x + 2, -y, -z + 1$ ; (v)  $-x + 1, -y, -z + 1$ ; (vi)  $x + 1, -y + \frac{1}{2}, z + 1$

Figure 2-7 shows the packing diagram for (III), viewed down the  $a$  axis. The two sets of  $[\text{AuCl}_4]^-$  anions are located near the (020) planes, intercalating between the ephedrine cations which are clustered around  $b/3$  and  $2b/3$ . The nonpolar portions of the ephedrine ligand tend to group together, away from the  $[\text{AuCl}_4]^-$  anions. This results in a molecular bilayer of alternating polar and nonpolar clusters in the cell. The Au1 anion is essentially parallel to the ac plane [found near  $(1/2, 0, 0)$ ] and is separated from its symmetry-generated counterpart at  $(-x + 1, -y, -z)$  by  $4.2115 (6)$   $\text{\AA}$ . The second anion (Au2) is nearly parallel to the ab plane, and its closest symmetry related congener at  $(-x + 1, -y, -z + 1)$  is at a distance of  $4.0341 (6)$   $\text{\AA}$ . There is one close contact of  $3.3925 (19)$   $\text{\AA}$  between atom Cl5 and atom Au2 at  $(-x + 1, -y, -z + 1)$ .

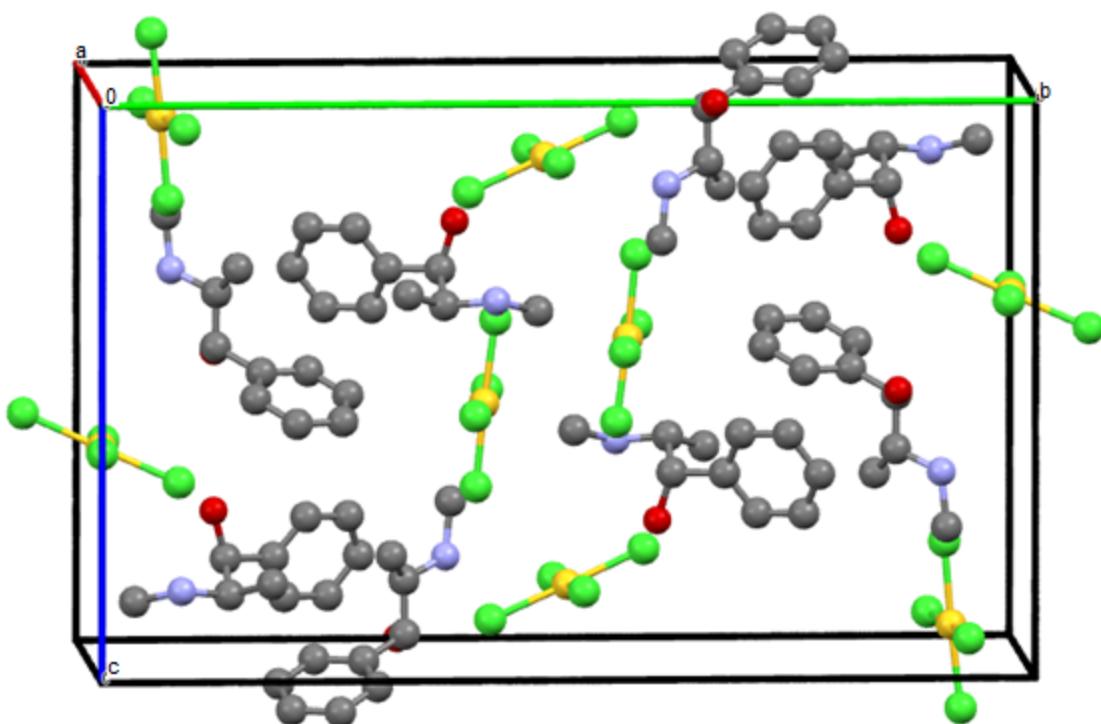


Figure 2-7. The packing diagram of (III) ephedrine gold(III) tetrachloride showing the stratified arrangement of the gold tetrachloride anions and protonated N atoms of the cation between congregated phenyl rings.

## CONCLUSION

Microcrystal tests of suspected drugs of abuse can be a powerful tool in the analytical scheme of the forensic drug laboratory. A small battery of these tests can quickly screen a number of commonly encountered substances and when used by the experienced and trained analyst on a polarized light microscope, the microcrystal test can even distinguish optical isomers of enantiomeric substances. Historically, microcrystal tests have been used simply based on the empirical observation of the uniqueness of the precipitates' color, morphology, and optical characteristics under the microscope. Little information has been available regarding the formation or internal atomic arrangement of the resultant.<sup>40</sup> The three complexes described in this section, the first a cycloaurated adduct, and the other two being tetrachloroaurate(III) salts, all involve the same class of stimulants that are prevalent in illicit drug use. These structures are important additions to the understanding of the microcrystal tests for these drugs that have been employed for well over 150 years. Despite the close structural resemblance between amphetamine, methamphetamine, and ephedrine, each compound produces distinct microcrystal precipitates (Figure 2-8) when reacted with the traditional gold chloride (5% auric chloride in acidified aqueous solution) test reagent<sup>41</sup>.



Figure 2-8. The precipitates of the HAuCl<sub>4</sub>- crystal test with a) amphetamine, b) ephedrine, and c) methamphetamine. Photomicrographs from the McCrone Research Institute.

The distinct differences in the microscopic analysis of the amphetamine, methamphetamine, and ephedrine microcrystals are clearly reflected in the single crystal structures of each. Amphetamine incorporates the gold chloride in a 6-membered cycloaurated adduct, bidentate to the *ortho* carbon of the phenyl ring and the N-atom of the amine. With both methamphetamine and ephedrine, as well as other gold chloride microcrystal tests studied<sup>23, 24, 42</sup>, the gold chloride remains as an anion to the protonated ligand cation.

In the amphetamine-gold chloride product, the adduct packs in the unit cell with the nonpolar phenyl rings oriented towards each other between regions of gold and chloride anions where the two remaining chloride atoms are pointed away from the hydrophobic clusters. The arrangement of the adduct is such that the chloride opposite the aryl carbon experiences a *trans* effect elongating the Cl-Au bond and making the chloride more reactive or susceptible to loss. Surprisingly, this adduct is closely related to a series of cycloaurate compounds being investigated for their anti-tumor and anti-microbial properties.

Although differing from amphetamine by the addition of a single methyl group to the amine, methamphetamine crystalizes with gold chloride in a significantly different manner. This microcrystal test precipitates a complex salt consisting of the protonated methamphetamine cation and the  $\text{HAuCl}_4^-$  anion. The torsion angle about the single chiral center is in the “extended” conformation for all cations in the asymmetric unit, with the N-methyl pointed outward from the rest of the ion. The internal crystal packing arrangement involves the gold chloride anion alternating with the phenyl ring of the methamphetamine in unique stacks along the  $a$ -axis. This is in stark contrast to other examples where the gold chloride anions are clustered together or among other charged species.

The  $\text{HAuCl}_4^-$  anions for both the methamphetamine and ephedrine complex salts are proximally located near the protonated N-atom and they are relatively square planar showing only slight out-of-plane distortion. Unlike the methamphetamine salt where the anions interleave with the phenyl rings of the cations, the anions found in the ephedrine unit cell form layers independent of the phenyl moieties of the cations. This results in separate and distinct layers along the  $b$ -axis within the cell.

The contrasting crystal features of the three closely related phenethylamines provides much needed insight into the internal atomic structure and dramatic evidence for the differentiation of the microcrystal reaction products.

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## CHAPTER 3. BATH SALTS<sup>1</sup>

### INTRODUCTION

In the illicit drug market, the names ‘Bath Salts’, ‘Plant Feeders’, and ‘Plant Food’ refer to a class of novel psychoactive substances (NPS) that belong to a group of β-ketone amphetamine-type stimulants. These are analogs or derivatives of the central nervous system (CNS) stimulant cathinone. The term ‘bath salts’, is not to be confused with legitimate personal hygiene products <sup>1</sup>, but is used in an attempt to avoid prosecution and deceive law enforcement. Clandestine drug manufacturers have created synthetic analogs of the banned or controlled substance cathinone, a naturally occurring stimulant found in khat (*Catha edulis*) <sup>2</sup>. Designers of these types of illicit compounds make slight modifications to the parent cathinone skeleton in attempts to circumvent existing drug regulations (Figure 3-1). Simple modifications of the parent cathinone make synthesis of these drugs particularly difficult to regulate due to the wide array of possible analogues.

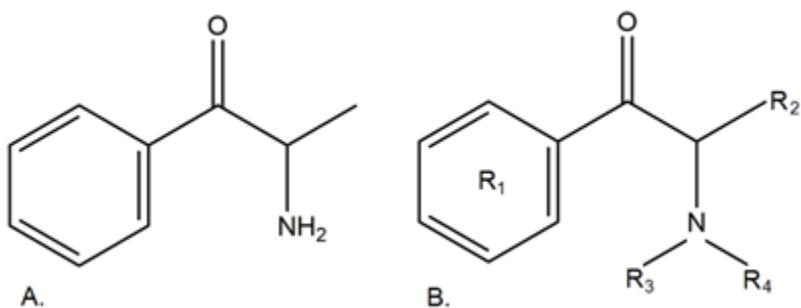


Figure 3-1. Diagrams of the A. parent cathinone and B. locations of 'designer cathinone' modifications.

<sup>1</sup> Adapted from previously published work. 9, 28, 31

Designer cathinones are readily available through grey-market internet retailers. This unrestricted access has caused a dramatic rise in abuse as recreational drugs and, as a result, hospital emergency room visits <sup>3</sup>, and fatalities. The newly synthesized stimulants arrive on the market unregulated and with little to no reliable pharmacological or analytical data available to guide hospitals, emergency medical personnel, law enforcement, or forensic science laboratories.<sup>4</sup> Recent studies have shown that emergency medical personnel have a lack of awareness or understanding of the scope and nature of the novel psychoactive substances abuse and clinical manifestations.<sup>5</sup> Another study, surveying attendees at an electronic music festival, reported that nearly half of the attendees who admitted to using what they believed was “ecstasy” (3,4-methylenedioxymethamphetamine or MDMA), had detectable levels of other synthetic cathinones in their system.<sup>6</sup> The recreational drug users may have been misled or unaware of the products they are actually consuming.

A problem for forensic science laboratories is that most of these compounds reach the community without warning. Forensic labs must quickly determine the absolute chemical structure, develop methods and drug standards, and create reference libraries for mass spectrometry, infrared spectrophotometry, X-ray powder diffraction, and other analytical techniques. Additionally, many of these compounds are isomers of each other, making spectral interpretation difficult. The structures of many of these modified cathinones are just now being solved by single crystal X-ray diffraction,<sup>7, 8, 9</sup> as partnerships between academic

institutions and forensic laboratories combine resources and expertise to combat the growing public health crisis.

In the course of this research project, the absolute structure of six synthetic cathinones, MDPV, Ethylone,  $\alpha$ -Pyrrolidinovalerophenone ( $\alpha$ -PVP), Pentylone, Dibutylone, and Ephylone have been determined by single crystal X-ray diffraction. All six drugs (Figure 3-2) were recovered from actual law enforcement seizures and they represent a small example of the array of cathinone modifications.

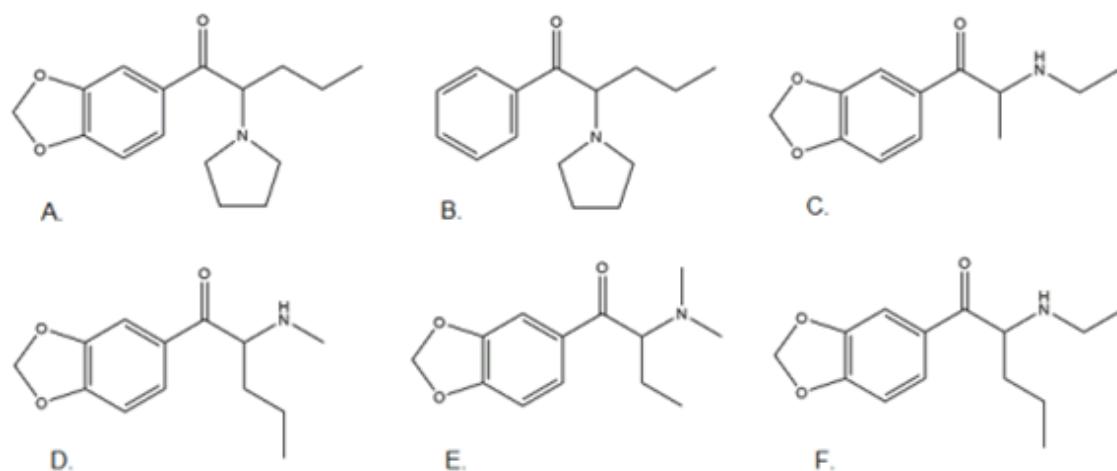


Figure 3-2. Diagrams of six designer cathinones. A. MDPV, B.  $\alpha$ -PVP, C. Ethylone, D. Pentylone, E. Dibutylone, and F. Ephylone

Research into the pharmacology and toxicology of designer cathinones is progressing, primarily focusing on structure-activity relationships (SAR). In general, cathinones have shown inhibitory effects on monoamine transporters and receptors (norepinephrine, dopamine, and serotonin) causing neurotransmitter uptake inhibition or effecting monoamine release <sup>10</sup>. However, significant differences in the potency, as indicated by the ratio of dopamine to

serotonin transport inhibition of the various substituted cathinones have been observed *in vitro*. For a further review of the available literature, the interested reader is directed to the comprehensive review article <sup>11</sup> and the citations contained therein.

MDPV [(RS)-1-(1,3-benzodioxol-5-yl)-2-(pyrrolidin-1-yl)pentan-1-one], also known as 3,4-methylenedioxypyrovalerone, is one of the most potent of these new designer cathinones. Retailers refer to MDPV by various slang terms such as “super coke”, “ivory wave”, or “cloud nine”, in attempts to conceal the nature of the dangerous substance. MDPV is commonly seen in drug samples as its hydrochloride salt ( $C_{16}H_{21}NO_3 \cdot HCl$ ), in either the hydrated or the anhydrous forms, but has also been seen in forensic lab submissions as the hydrobromide or mixed hydrobromide/hydrochloride salts. In 1969, Boehringer Ingelheim investigated several 1-[(3,4-methylenedioxy)phenyl]-2-pyrrolidino-1-alkanones as stimulants for potential medicinal uses including the synthesis and patent of MDPV <sup>12</sup>; no legitimate clinical uses were ever developed. However, in the mid-2000’s MDPV re-emerged as a popular alternative to ecstasy and cocaine. MDPV has been categorized as a pyrovalerone–cathinone due to its ability to block catecholamine uptake, which has been linked to higher addiction risks in humans. <sup>13</sup> In 2011, the US Drug Enforcement Administration added three ‘bath salts’: MDPV, 4-methylmethcathinone (mephedrone) and 3,4-methylenedioxymethcathinone (methylone) <sup>14</sup>, to the list of Schedule I Controlled Substances ‘due to their high potential for abuse, and lack of medical use’. <sup>15</sup>

MDPV is synthesized by the Grignard reaction of piperanol to form the substituted 3,4-methylenedioxybenzyl alcohol, oxidation to the  $\beta$ -ketone, bromination, and then displacement of the bromine by the pyrrole (**Error! Not a valid bookmark self-reference.**). This reaction pathway may account for the presence (or partial presence) of bromide as a counter ion in two of the seized drug samples that were structurally determined.

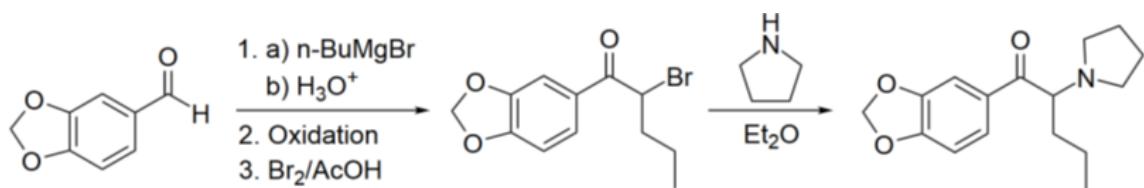


Figure 3-3. The synthetic route for MDPV

Law enforcement samples analyzed by X-ray crystallography demonstrated three different forms of the MDPV salt that were found in drug seizures: two forms of the HCl salt, one as a mixed bromide/chloride salt, C<sub>16</sub>H<sub>22</sub>NO<sub>3</sub><sup>+</sup> · 0.343Br<sup>-</sup>/0.657Cl<sup>-</sup> [systematic name: 1-(benzo[d][1,3]dioxol-5-yl)-2-(pyrrolidin-1-ium-1-yl)pentan-1-one bromide/chloride (0.343/ 0.657)], and the other with a H<sub>7</sub>O<sub>3</sub><sup>+</sup> cation, as well as a second HCl counter-ion [systematic name: hydroxonium 1-(benzo[d][1,3]-dioxol-5-yl)-2-(pyrrolidin-1-ium-1-yl)pentan-1-one dichloride], H<sub>7</sub>O<sub>3</sub><sup>+</sup> · C<sub>16</sub>H<sub>22</sub>NO<sub>3</sub><sup>+</sup> · 2Cl<sup>-</sup>; and one salt exclusively with a bromide counterion C<sub>16</sub>H<sub>22</sub>NO<sub>3</sub><sup>+</sup> · Br<sup>-</sup>, [systematic name: 1-(benzo- [d][1,3]dioxol-5-yl)-2-(pyrrolidin-1-ium-1-yl)pentan-1-one bromide]. In addition to seized samples, the tetrachloridoaurate salt of this drug, (C<sub>16</sub>H<sub>22</sub>NO<sub>3</sub><sup>+</sup>) [AuCl<sub>4</sub><sup>-</sup>] was crystallized with the forensic gold chloride test reagent, 5% aqueous gold(III) chloride slightly acidified with HCl. The microcrystal reagent, HAuCl<sub>4</sub> has been used for over a

150 years to identify common drugs of abuse containing a protonated nitrogen moiety via microscopic identification (**Error! Reference source not found.**).

Ethylone, also known as BK-MDEA and MDEC, (3,4-methylenedioxyethylcathinone), is regularly sold and abused as its hydrochloride salt (systematic name: N-{1-[*[(benzo[d][1,3]dioxol-5-yl)carbonyl]ethyl*]}ethanaminium chloride, C<sub>12</sub>H<sub>16</sub>NO<sub>3</sub><sup>+</sup>·Cl<sup>-</sup>). As popular cathinones slowly get banned or controlled, new iterations are designed to take their place, exploiting loopholes or deficiencies in the legal system. The rise in abuse of ethylone is a result of these regulatory efforts banning previous generations of cathinones. This novel drug compound is nothing more than a slight chemical modification of the banned drug methylone (3,4-methylenedioxymethcathinone), extending the N-alkyl substituent by one -CH<sub>2</sub>- in length. Ethylone's presence was confirmed in nine deaths reported in toxicology samples analyzed by the Forensic Toxicology Laboratory at the University of Florida.<sup>16</sup> As seen with other cathinones, ethylone has CNS effects similar to both cocaine and ecstasy, non-selectively inhibiting the monoamine transporters with potency comparable to or lower than that of cocaine (mean IC<sub>50</sub>, 2.5–5.7); and releasing serotonin (mean EC<sub>50</sub>, 9.9 μM) similar to MDMA and other entactogens.<sup>10</sup>

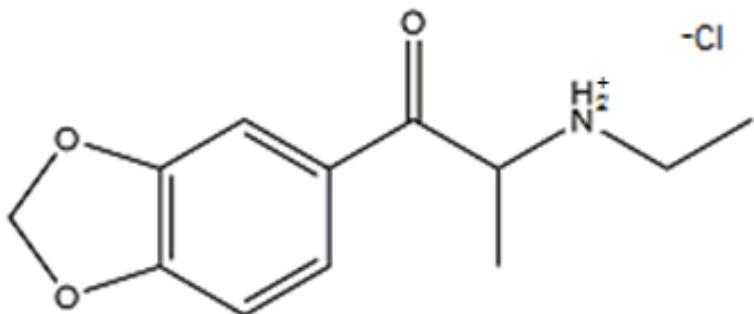


Figure 3-4. Diagram of Ethylone Hydrochloride Salt

$\alpha$ -Pyrrolidinovalerophenone ( $\alpha$ -PVP), also known as  $\alpha$ -pyrrolidinopentiophenone, a dangerous designer drug, is now being marketed around the world as a so called ‘legal high’ or harmLess ‘bath salt’, when in reality it is a powerful  $\beta$ -ketone phenethylamine stimulant. The drug compound itself is similar in structure to the naturally occurring stimulant cathinone, but has a pyrrole ring in place of the amine group of the cathinone and a propyl group on the  $\alpha$ -C atom. Unlike other cathinones that are typically sold in crystal or crystalline form, the majority of law enforcement seizures of  $\alpha$ -PVP have been of the free base form. A sample of the free base from a recent law-enforcement seizure was crystallized as the partially hydrated HCl salt [systematic name: 1-(1-oxo-1-phenylpentan-2-yl)pyrrolidin-1-i um chloride 0.786-hydrate],  $C_{15}H_{22}NO^+ \cdot Cl^- \cdot 0.786 \cdot H_2O$  (Figure 3-5).

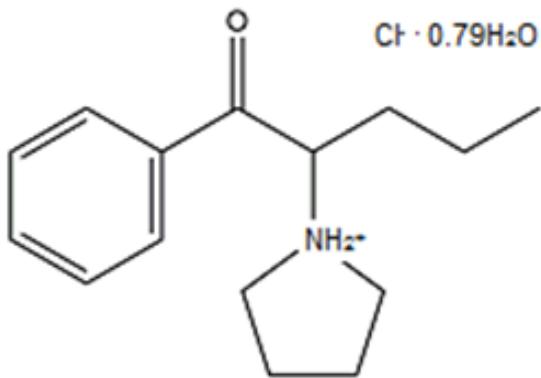


Figure 3-5. Diagram of  $\alpha$ -PVP Hydrochloride 0.79 Hydrate.

$\alpha$ -PVP can be synthesized from benzonitrile via the Heffe synthesis.<sup>17, 18</sup> The Grignard reaction of benzonitrile followed by acid hydrolysis yields the  $\beta$ -ketone, pentiophenone. Subsequent bromination over aluminum chloride leads to the  $\alpha$ -bromoketone. The reaction is completed by reacting with pyrrolidine to produce  $\alpha$ -PVP.

Little reliable information exists regarding the physiological effects of  $\alpha$ -PVP and similar cathinones, beyond postings on internet drug-forum websites and hospital case studies.<sup>19</sup> Meltzer *et al.*<sup>18</sup> investigated the use of  $\alpha$ -PVP and other pyrovalerophenone analogues for use as a treatment for the abuse of substances such as cocaine. Previous findings have shown that similar cathinones and amphetamine-type stimulants interact with dopamine, serotonin, and norepinephrine receptors and may be effective in replacement type therapies. However, this group found  $\alpha$ -PVP to be 10–12 times more potent than cocaine in the inhibition of both dopamine and norepinephrine transport and re-uptake, and because of the low ratio of inhibition of dopamine transport to re-uptake inhibition, it is a poor cocaine antagonist. As with MDPV and other

pyrrole substituted cathinones, α-PVP was found to have a mixed cocaine/methamphetamine-type stimulatory effect in rodent studies.<sup>20</sup> Numerous reports of psychotic episodes, delirium, paranoia, and hallucinations have been described in news stories of α-PVP abuse and overdoses as well as incidences of aggressive attacks, self-mutilation, and suicides. In emergent medical treatment, this drug has led to cardiac arrest and kidney failure.

Pentylnone, (±)-1-(1,3-benzodioxol-5-yl)-2-(methylamino)pentan-1-one; dibutylone, (±)-1-(1,3-benzodioxol-5-yl)-2-(dimethylamino)butan-1-one; and ephylone, (±)-1-(1,3-benzodioxol-5-yl)-2-(ethylamino)pentan-1-one represent the three most recently encountered designer cathinones, appearing in law enforcement seizures since 2015 (Figure 3-6). These compounds are among the latest derivatives of synthetic cathinones to attempt to evade criminal prosecution while profiting from an expanding stimulant market. Like other “bath salts”, all three compounds are produced from minor modifications of the naturally occurring stimulant cathinone found in “Khat”, *Catha edulis*.<sup>2</sup> As of this 2017 writing, only pentylnone is controlled, banned, or regulated in several countries; dibutylone and ephylone use and abuse has not yet reached levels that have drawn regulatory attention as other previous cathinone analogs. All three of these emerging compounds represent new iterations of the designer drug threat to the community and danger to recreational drug users.

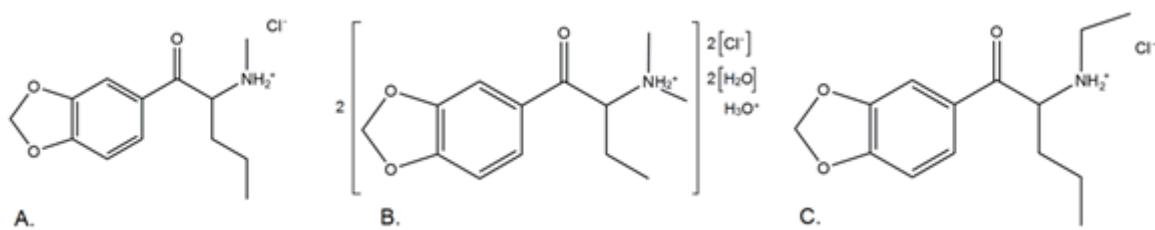


Figure 3-6. Hydrochloride salts of three novel cathinones: A. Pentyline Hydrochloride, B. Dibutylone Dichloride Hydrate, C. Ephylone Hydrochloride.

Several of the latest novel psychoactive substances have been indicated in recent arrests and fatalities. In a series of fatal intoxication cases in Florida (USA), pentyline, along with other illicit drugs, was reported by Montgomery County Coroner's Office/Miami Valley Regional Crime Laboratory in the post-mortem toxicology results of three decedents.<sup>19</sup> In Europe, the United Nations Office on Drugs and Crime (UNODC) received several reports of emerging NPS, which included both pentyline and dibutylone.<sup>21</sup> As an example of the scope of the synthetic cathinone epidemic, pentyline was seized from retail shops in Poland<sup>22</sup> and Germany<sup>23</sup> and laboratory analysis by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and both EI and CI mass spectrometry, revealed the compound in "NRG" branded products marketed as alternative "legal highs" in the UK.<sup>24</sup> The European Monitoring Centre for Drugs and Drug Addiction (EMCDDA) ranked synthetic cathinones as the second largest group of substances being monitored by that organization. Since 2009, 103 new cathinone analogs, derivatives, or isomers have been reported by law enforcement or public health entities<sup>25</sup>. In their report, the EMCDDA described over 8000 seizures of synthetic cathinones, totaling more than 1000 kg of the drug materials. Due to the lack of physiological and

emergency treatment information, these new psychoactive substances present an urgent public health emergency.

Pentylone has been most commonly seized as the hydrochloride salt. In preparing this compound for single crystal X-ray diffraction, material from drug arrests was dissolved in 10% HCl solution and recrystallized with acetone. The resulting complex was a pentylone hydrochloride monohydrate salt (Figure 3-6A).

In the US Drug Enforcement Administration's "Emerging Threat Report", <sup>26</sup> dibutylone was the most commonly reported cathinone in the first quarter of 2016. Dibutylone is closely related to butylone, adding a second methyl substituent on the amine to convert it from a secondary to a tertiary amine. It is also closely related to dimethylone and dipentylone, having one more –CH<sub>2</sub>– within the α-carbon alkyl chain of the former and one less in the latter tertiary amines. Due to the paucity of pharmacological and toxicological research on this compound, all assumptions regarding the human physiological effects are drawn from comparison to the above three structurally similar compounds. Still, demand for dibutylone remains consistently high among recreational drug users. By the end of 2016, dibutylone remained the most commonly reported designer cathinone, followed by ephylone (n-ethylpentylone). <sup>27</sup> Single crystals of dibutylone suitable for single crystal X-ray diffraction precipitated from acetone after acidification by 10% hydrochloric acid as the 1.5 hydrate of the hydrochloride salt (Figure 3-6B).

The most recent synthetic cathinone to make its way into forensic drug testing laboratories is ephylone. Ephylone began appearing in law enforcement

seizures as recently as November of 2015. The use of ephylone continues to rise <sup>26</sup>, <sup>27</sup> despite unfavorable user reports on recreational drug user bulletin boards. The increase in use may be related to increased availability from traffickers, low cost, or the success of regulatory efforts to control previous generations of designer cathinones, which have not yet been applied to this cathinone. Most of the information regarding desirable and undesirable effects of this drug are only available on the internet from “user” reports and should be relied upon cautiously. Despite the recent rise in popularity, to date there are no published studies on the pharmacological and toxicological effects of ephylone. Crystals for X-ray diffraction studies were grown from law enforcement collected dibutylone by dissolution in 10% HCl and precipitation from acetone (Figure 3-6C).

## SUMMARY OF CRYSTAL STRUCTURES DETERMINED

- I. The mixed bromide/chloride salt of 3,4-methylenedioxypyrovalerone  
1-(Benzo[d][1,3]dioxol-5-yl)-2-(pyrrolidin-1-i um-1-yl)pentan-1-one  
bromide/chloride (0.343/ 0.657).
- II. The hydrated chloride salt of 3,4-methylenedioxypyrovalerone  
Hydroxonium 1-(benzo[d][1,3]-dioxol-5-yl)-2-(pyrrolidin-1-i um-1-yl)pentan-1-one dichloride.
- III. The bromide salt of 3,4-methylenedioxypyrovalerone  
1-(Benzo- [d][1,3]dioxol-5-yl)-2-(pyrrolidin-1-i um-1-yl)pentan-1-one  
bromide.
- IV. The gold tetrachloride salt of 3,4-methylenedioxypyrovalerone  
1-(Benzo- [d][1,3]dioxol-5-yl)-2-(pyrrolidin-1-i um-1-yl)pentan-1-one gold  
tetrachloride.
- V. The hydrochloride salt of 3,4-methylenedioxyethylcathinone  
N-{1-[(benzo[d][1,3]dioxol-5-yl)carbonyl]ethyl}ethanaminium chloride
- VI. The hydrochloride salt of  $\alpha$ -Pyrrolidinovalerophenone  
1-(1-oxo-1-phenylpentan-2-yl)pyrrolidin-1-i um chloride 0.786-hydrate
- VII. The monohydrated chloride salt of pentylone  
( $\pm$ )-1-(1,3-benzodioxol-5-yl)-2-(methylamino)pentan-1-one chloride
- VIII. The 1.5-hydrated chloride salt of dibutylone  
( $\pm$ )-1-(1,3-benzodioxol-5-yl)-2-(dimethylamino)butan-1-one chloride
- IX. The monohydrated chloride salt of ephylone  
( $\pm$ )-1-(1,3-benzodioxol-5-yl)-2-(ethylamino)pentan-1-one chloride

## EXPERIMENTAL

### Synthesis and crystallization:

Samples of the illicit compounds (I), (II), and (IV) were obtained from law enforcement seizures. The identities of these materials were confirmed by routine mass spectrometric analyses as part of the usual forensic analytical protocol, and then were purified by recrystallization from aqueous solution to yield X-ray-quality crystals. Compound (V) was isolated from a similar procedure using aqueous HCl. For (III), a sample of the seized illicit street drug 3,4-methylenedioxypyrovalerone was dissolved in water to make a 0.2% solution. To 1 mL of this drug solution was added 1 mL of a 0.5% solution of HCl-acidified HAuCl<sub>4</sub>. Crystals of (III) grew over a period of approximately 2–4 weeks by slow evaporation at room temperature.<sup>28</sup>

The free base of α-PVP was obtained from law-enforcement seizures resulting from investigations of illicit bath salts. The identity was confirmed by gas chromatography/mass spectrometry (GC–MS) and compared with published data.<sup>29, 30</sup> The amorphous white powder (~50 mg) was dissolved in 10% HCl (2 mL) and this was allowed to go to dryness. Acetone (2 mL) was then added and single crystals of (VI) suitable for X-ray analysis were obtained from slow room-temperature evaporation of this solution.<sup>31</sup>

Samples of (VII), (VIII), and (IX) were also obtained from law enforcement seizures of suspected “bath salts”. The reaction of cathinones with a common, non-specific, law-enforcement field test consisting of 5% formaldehyde in concentrated sulfuric acid gives a bright yellow color when the reagent is added

dropwise. The identities of (VII), (VIII), and (IX) were confirmed by gas chromatography/mass spectrometry and verified by published data for both (VII)<sup>24</sup> and (VIII)<sup>32</sup>; for (IX), structural elucidation was the main method of identification. All three samples were recrystallized by dissolution in 10% HCl followed by the addition of acetone. Single crystals suitable for X-ray analysis were obtained from slow evaporation of each solution, at room temperature, over several days.<sup>9</sup>

Refinement:

Suitable crystals of each sample were mounted on a Bruker-AXS SMART APEX II CCD diffractometer at 100(1)K. The cell dimensions and the intensities were all collected with CuK $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). Data processing, Lorentz-polarization, and face-indexed numerical absorption corrections were performed using SAINT, APEX, and SADABS computer programs.<sup>33, 34, 35</sup> The structures were solved by direct methods and refined by full-matrix least-squares on F<sup>2</sup>, using the SHELXTL V6.14 program package.<sup>36, 37</sup> Non-hydrogen atoms were refined anisotropically. Crystal data, data collection, and structure refinement details are summarized in Table 3-1. The H atoms for all of the structures were found in electron-density difference maps. The numbers in parentheses are the errors in the least significant digit. The coordinates of all of the N-bound H atoms were allowed to refine freely. The methyl H atoms were placed in ideally staggered positions, with C—H = 0.98 Å and U<sub>iso</sub>(H) = 1.5U<sub>eq</sub>(C). The methylene, methine, and aromatic H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atoms, with C—H =

0.99, 1.00 and 0.95 Å, respectively; H atoms involved in hydrogen bonds were allowed to refine. All of the above had  $U_{iso}(H) = 1.2U_{eq}(C)$  or  $1.2U_{eq}(N)$ . For (I), the Cl and Br positions were restrained by EADP and EXYZ, while the occupancies were allowed to refine; when the occupancy was determined, then the EADP and EXYZ were refined while the occupancies of these two ions were held constant. In (VI) there is a positive residual electron density of  $1.35 \text{ e } \text{\AA}^{-3}$  located 0.86 Å from the chloride anion; this is partially counter balanced by electron density of  $0.29 \text{ e } \text{\AA}^{-3}$  located 0.76 Å on the other side of Cl1.

X-ray data have been deposited in CCDC<sup>38</sup>: MDPV mixed Cl<sup>-</sup>/Br<sup>-</sup> salt (Refcode "GUBJAQ") = 1035663; MDPV Hydrobromide (Refcode "GUBJEU") = 1035664; MDPV Gold(III) Tetrachloride salt (Refcode "GUBJIY") = 1035665; MDPV Hydrochloride Hydrate (Refcode "GUBJUK") = 1035667; ethylone HCl (Refcode "GUBJOE") = 1035666; α-PVP HCl (Refcode "PAGCOS") = 141976; pentylone (Refcode "In Press") = 1504571; dibutylone (Refcode "In Press") = 1504572; ephylone (Refcode "In Press") = 1504573.

**Table 3-1**

	MDPV mixed Cl/Br Salt (I)	MDPV Hydrobromide (II)	MDPV Gold(III) Chloride (III)
Experimental details.			
Crystal data			
Chemical formula	$C_{16}H_{22}NO_3^+ \cdot 0.343Br^- \cdot 0.657Cl^-$	$C_{16}H_{22}NO_3^+ \cdot Br^-$	$(C_{16}H_{22}NO_3)[AuCl_4]$
M <sub>r</sub>	327.06	356.25	615.11
Crystal system, space group	Orthorhombic, <i>Pbca</i>	Monoclinic, <i>P2<sub>1</sub>/c</i>	Orthorhombic, <i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>
a, b, c (Å)	7.0133 (5), 17.8399 (13), 25.0044 (18)	7.1280 (1), 21.3335 (5), 10.5243 (2)	10.5046 (4), 11.1534 (4), 17.5193 (6)
α, β, γ (°)	90, 90, 90	90, 95.118 (1), 90	90, 90, 90
V (Å <sup>3</sup> )	3128.5 (4)	1594.00 (5)	2052.60 (13)
Z	8	4	4
Density Mg m <sup>-3</sup>	1.389	1.485	1.99
Radiation type	Cu K $\alpha$	Cu K $\alpha$	Cu K $\alpha$
μ (mm <sup>-1</sup> )	2.73	3.6	18.4
Temperature (K)	100	293	100
Shape, color	Plate, colorless	Needle, colorless	Rod, orange
Crystal size (mm)	0.50 × 0.22 × 0.05	0.43 × 0.18 × 0.06	0.23 × 0.19 × 0.11
Data collection			
Diffractometer	Bruker APEXII CCD area-detector diffractometer		
Absorption correction	Numerical ( <i>SADABS</i> ; Sheldrick, 2008a)		
T <sub>min</sub> , T <sub>max</sub>	0.400, 0.896	0.307, 0.813	0.101, 0.237
θ <sub>min</sub> , θ <sub>max</sub>	3.5°, 70.2°	4.1°, 69.8°	4.7°, 69.5°
No. of measured, independent and observed [I > 2σ(I)] reflections	27721, 2859, 2600	14889, 2942, 2813	24150, 3554, 3479
R <sub>int</sub>	0.037	0.021	0.047
(sin Θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.61	0.609	0.608
Refinement			

R[F <sup>2</sup> >2σ(F <sup>2</sup> )], wR(F <sup>2</sup> ), S	0.025, 0.066, 1.04	0.042, 0.134, 1.06	0.039, 0.096, 1.08
No. of reflections	2859	2942	3554
No. of parameters	204	194	250
No. of restraints	0	1	37
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement		
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.23, -0.17	0.69, -1.24	1.66, -2.42
Absolute structure	—	—	Refined as an inversion twin.
Friedel Pairs			
Flack parameter	—	—	0.45 (3)
Computer programs: [APEX2 (Bruker, 2006), (Bruker, 2009). Bruker AXS Inc., Madison, Wisconsin, USA.], [SAINT (Bruker, 2005), (Bruker, (2009) SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.], [SHELXTL (Sheldrick, 2008), SHELXT (Sheldrick, 2015), SHELXL2014 (Sheldrick, 2015)].			

Table 3-1 (continued)	Ethylene Hydrochloride (IV)	MDPV Dihydrochloride Hydrate (V)	α-PVP Hydrochloride (VI)
<b>Experimental details.</b>			
Crystal data			
Chemical formula	C <sub>12</sub> H <sub>16</sub> NO <sub>3</sub> <sup>+</sup> ·Cl <sup>-</sup>	H <sub>7</sub> O <sub>3</sub> <sup>+</sup> ·C <sub>16</sub> H <sub>22</sub> NO <sub>3</sub> <sup>+</sup> ·2Cl <sup>-</sup>	C <sub>15</sub> H <sub>22</sub> NO <sup>+</sup> ·Cl <sup>-</sup> ·0.786H <sub>2</sub> O
M <sub>r</sub>	257.71	402.3	281.95
Crystal system, space group	Monoclinic, P2 <sub>1</sub> /c	Monoclinic, P2 <sub>1</sub> /c	Monoclinic, P2 <sub>1</sub> /c
a, b, c (Å)	10.6159 (4), 7.1060 (3), 17.6348 (6)	15.8084 (3), 11.4143 (2), 11.6289 (2)	13.9428 (3), 9.3285 (2), 13.6865 (3)
α, β, γ (°)	90, 105.3310 (18), 90	90, 107.4200 (9), 90	90, 119.273 (1), 90
V (Å <sup>3</sup> )	1282.97 (9)	2002.10 (6)	1552.82 (6)
Z	4	4	4
Density Mg m <sup>-3</sup>	1.334	1.335	1.206
Radiation type	Cu Kα	Cu Kα	Cu Kα
μ (mm <sup>-1</sup> )	2.62	3.18	2.14

Temperature (K)	100	100	100
Shape, color	Block, colorless	Plate, colorless	Parallelepiped, colorless
Crystal size (mm)	0.33 × 0.31 × 0.15	0.46 × 0.35 × 0.06	0.59 × 0.13 × 0.07
<b>Data collection</b>			
Diffractometer	Bruker APEXII CCD area-detector diffractometer		
Absorption correction	Numerical (SADABS; Bruker, 2009)		
T <sub>min</sub> , T <sub>max</sub>	0.475, 0.696	0.322, 0.827	0.363, 0.867
θ <sub>min</sub> , θ <sub>max</sub>	4.3°, 70.1°	2.9°, 68.6°	3.6°, 68.6°
No. of measured, independent and observed [I >2σ(I)]	9602, 2253, 2097	18712, 3588, 3393	14334, 2756, 2455
R <sub>int</sub>	0.03	0.022	0.032
(sin Θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.61	0.604	0.604
<b>Refinement</b>			
R[F <sup>2</sup> >2σ(F <sup>2</sup> )], wR(F <sup>2</sup> ), S	0.039, 0.107, 1.20	0.048, 0.151, 1.09	0.048, 0.115, 1.09
No. of reflections	2253	3588	2756
No. of parameters	162	231	183
No. of restraints	2	0	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement		
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.36, -0.26	1.53, -0.39	1.35, -0.84
<b>Absolute structure</b>			
Friedel Pairs	—		
Flack parameter	—		

Table 3-1 (continued)	Pentylone Hydrochloride (VII)	Dibutylone Hydrochloride 1.5 hydrate (VIII)	Ephylone Hydrochloride (IX)
<b>Experimental details.</b>			
Crystal data			
Chemical formula	$C_{13}H_{18}NO_3^+Cl^- \cdot H_2O$	$C_{26}H_{36}N_2O_6^{2+} \cdot 2Cl^- \cdot 3H_2O$	$C_{14}H_{20}NO_3^+Cl^-$
$M_r$	289.75	597.52	285.76
Crystal system, space group	Monoclinic, P21/c	Orthorhombic, P212121	Monoclinic, P21/n
$a, b, c$ (Å)	10.9795(6), 11.4679(6), 11.4490(6)	7.2737(1), 14.6615(3), 28.1196(5)	14.5901(3), 7.2805(1), 14.8937(3)
$\alpha, \beta, \gamma$ (°)	90, 100.618(1), 90	90, 90, 90	90, 112.649(1), 90
$V$ (Å <sup>3</sup> )	1416.88(13)	2998.77(9)	1460.05(5)
$Z$	4	4	4
Density Mg m <sup>-3</sup>	1.358	1.323	1.3
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
$\mu$ (mm <sup>-1</sup> )	2.487	2.391	2.355
Temperature (K)	100	100	100
Shape, color	Block, Colorless	Block, Colorless	Block, Colorless
Crystal size (mm)	0.183 x 0.211 x 0.256	0.076 x 0.131 x 0.198	0.240 x 0.305 x 0.428
Data collection			
Diffractometer	Bruker APEXII CCD area-detector diffractometer		
Absorption correction	Numerical (SADABS; Bruker, 2009)		
$T_{min}, T_{max}$	0.472, 0.608	0.487, 0.721	0.531, 0.698
$\theta_{min}, \theta_{max}$	5.5°, 69.0°	3.1°, 68.5°	3.6°, 68.5°
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	10325, 2343, 2221	27718, 5248, 4830	13114, 2599, 2567
$R_{int}$	0.031	0.039	0.024
$(\sin \Theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.605	0.604	0.604
Refinement			

R[ $F^2 > 2\sigma(F^2)$ ],	0.026, 0.072,	0.034, 0.087,	0.024, 0.061,
wR( $F^2$ ), S	1.06	1.033	1.052
No. of reflections	2343	5248	2599
No. of parameters	191	383	181
No. of restraints	3	8	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement		
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	0.215, -0.223	0.498, -0.320	0.233, -0.181
Absolute structure			
Friedel Pairs			
Flack parameter	-	0.46(5)	-

## RESULTS

Methylenedioxypyrovalerone (MDPV) has been recovered from law enforcement investigations as the mixed HCl:HBr (65.7:34.3%) salt, (I), and also as the HBr salt.<sup>28</sup> In the study of this compound, it was found that the synthetic route to produce MDPV involves the bromination of 3,4-methylenedioxypentylphenone.<sup>12</sup> It is likely that poor purification techniques leave residual bromine resulting in the mixed or HBr salts. Both of these salts were received and analyzed in the anhydrous form, whereas the hydrochloride salt was crystallized during the course of this research project as the hydroxonium chloride salt  $[C_{16}H_{21}NO_3HCl][H_7O_3^+Cl^-]$ , (V).<sup>28</sup>

The monomer of the HCl:HBr salt of MDPV ( $C_{16}H_{21}NO_3 \cdot 0.343HBr:0.657HCl$ ), (I), crystallizes in the space group Pbca with eight molecules per cell. The asymmetric unit was determined to contain 34.3(2)% HBr salt and 65.7(2)% HCl salt with the anions located in the same coordinate position but having different anisotropic parameters (Figure 3-7).

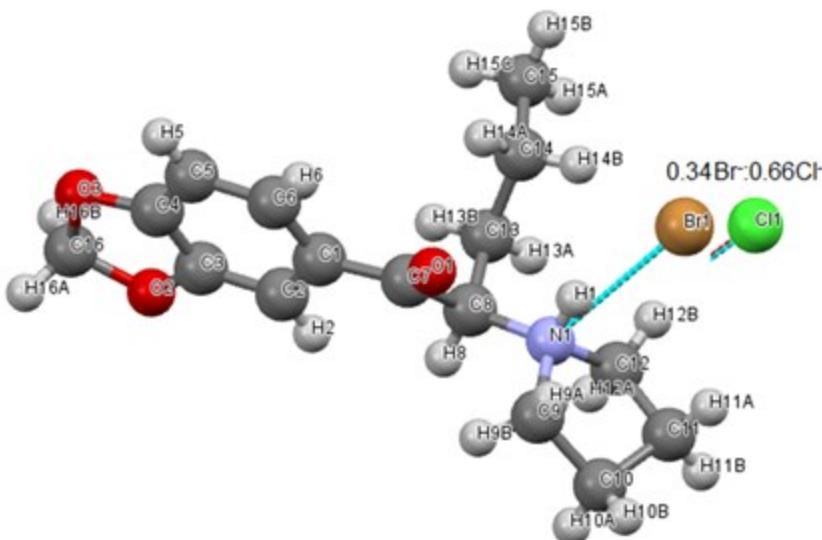


Figure 3-7. The asymmetric unit of (I). Both the chloride (66%) and the bromide (34%) counter ions are located in the same, overlapping coordinate position with the close contact to the protonated N atom shown.

A search of the Cambridge Structural Database<sup>38, 39</sup> of well refined compounds (R factor <7.5%) led to seven other examples of compounds containing both  $\text{Cl}^-$  and  $\text{Br}^-$  anions together in the same crystal lattice: CASGEK<sup>40</sup>, FENJOY and FENJUE<sup>41</sup>, HIYNOS<sup>42</sup>, MIPPUX<sup>43</sup>, VIZNAT<sup>44</sup>, and YIDJAW<sup>45</sup>. Each of these examples contained protonated N atoms as counter ions to the dihalide anions. Of these, only two, FENJOY and FENJUE, contain different, but isotopic, halide anions.<sup>41</sup> As with these two examples, MVDP has the  $\text{Cl}^-$  and  $\text{Br}^-$  ions in essentially the same coordinate positions, though with slightly different anisotropic parameters for each; however, both FENJOY and FENJUE contain two quaternary amines within the molecule; MDPV is a monocation, as is shown in Figure 3-7.

The bond lengths and bond angles for (I), as well as for the other MDPV salts presented here are all in the usual ranges. It is interesting to note that in (I), (III) and (V) the alkyl side chain extends away from the plane of the dioxole-phenyl rings at a nearly perpendicular angle, see Figure 3-7. Only (II), the MDPV bromide salt, shows the side chain folded back towards the rings. The MDPV mixed Cl<sup>-</sup>/Br<sup>-</sup> salt, (I), contains a single hydrogen bond from the protonated N atom to the counterion. In the predominant Cl<sup>-</sup>, the bond distance is 3.136(3) Å and the angle is 155.6(13)<sup>°</sup> (Table 3-2).

**Table 3-2**

Hydrogen bonding for designer cathinones, also known as "Bath Salts"

Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ ) for (I) MDPV mixed Chloride/Bromide Salt				
$D\text{---H}\cdots A$	$D\text{---H}$	$H\cdots A$	$D\cdots A$	$D\text{---H}\cdots A$
N1—H1···Cl1	0.902 (18)	(18)	3.136 (3)	(13)
Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ ) for (II) MDPV Hydrobromide				
$D\text{---H}\cdots A$	$D\text{---H}$	$H\cdots A$	$D\cdots A$	$D\text{---H}\cdots A$
N1—H1···Br1	0.87 (2)	2.34 (2)	3.198 (2)	171 (3)
Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ ) for (III) MDPV Gold(III) Tetrachloride				
$D\text{---H}\cdots A$	$D\text{---H}$	$H\cdots A$	$D\cdots A$	$D\text{---H}\cdots A$
N1—H1···Cl4	0.92 (1)	2.57 (7)	3.41 (1)	151 (11)
Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ ) for (IV) Ethylone Hydrochloride				
$D\text{---H}\cdots A$	$D\text{---H}$	$H\cdots A$	$D\cdots A$	$D\text{---H}\cdots A$
N1—H1A···Cl1	0.90 (2)	2.24 (2)	3.103 (2)	161 (2)
Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ ) for (V) MDPV Hydrochloride Hydrate				
$D\text{---H}\cdots A$	$D\text{---H}$	$H\cdots A$	$D\cdots A$	$D\text{---H}\cdots A$
N1—H1···Cl1	0.95 (4)	2.34 (4)	3.234 (2)	157 (3)
O4—H4A···Cl1i	0.88	2.29	3.166 (2)	173
O4—H4B···Cl2	0.88	2.25	3.108 (2)	165
O5—H5A···Cl1i	0.88	2.23	3.107 (2)	177
O5—H5B···Cl2ii	0.88	2.36	3.240 (2)	176
O6—H6A···Cl2	0.88	2.07	2.948 (2)	173
O6—H6B···O5	0.89	1.65	2.525 (3)	168
O6—H6C···O4iii	0.88	1.61	2.482 (3)	168
Symmetry codes: (i) $-x+1, -y+1, -z$ ; (ii) $-x, y+1/2, -z+1/2$ ; (iii) $x, -y+1/2, z+1/2$				
Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ ) for (VI) $\alpha$ -PVP Hydrochloride				
$D\text{---H}\cdots A$	$D\text{---H}$	$H\cdots A$	$D\cdots A$	$D\text{---H}\cdots A$
N1—H1···Cl1	0.94 (3)	2.21 (3)	3.0997 (18)	157 (2)
O2—H2A···Cl1	0.84 (5)	2.22 (5)	3.064 (2)	176 (4)
O2—H2B···Cl1 <sup>i</sup>	0.85 (5)	2.45 (5)	3.291 (3)	175 (4)
Symmetry code: (i) $-x, -y, -z$ .				
Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ ) for (VII) Pentyline Hydrochloride				
$D\text{---H}\cdots A$	$D\text{---H}$	$H\cdots A$	$D\cdots A$	$D\text{---H}\cdots A$
N1—H3A···Cl1	0.91	2.31	3.1241(11)	159
N1—H4···O4 <sup>i</sup>	0.91	1.91	2.7674(14)	157

O4-H1···Cl1 <sup>ii</sup>	0.820(1)	2.345(2)	3.163(1)	175(2)
O4-H2···Cl1 <sup>iii</sup>	0.820(1)	2.425(6)	3.2111(11)	161(2)
Hydrogen-bond geometry (Å, °) for (VIII) Dibutylone Hydrochloride 1.5Hydrate				
D—H···A	D—H	H···A	D···A	D—H···A
N1-H1···Cl1	0.8600(14)	2.298(13)	3.104(2)	156(3)
N2-H2···O7	0.8602(14)	1.987(19)	2.756(4)	148(3)
O7-H1A···Cl2	0.8201(14)	2.375(11)	3.171(2)	164(4)
O7-H2A···O8	0.8200(14)	1.996(13)	2.785(4)	161(4)
O8-H3A···Cl1	0.8202(14)	2.291(5)	3.108(3)	174(4)
O8-H4A···Cl2 <sup>i</sup>	0.8200(14)	2.390(4)	3.208(3)	175(4)
O9-H5A···Cl2	0.8204(14)	2.383(11)	3.190(3)	168(5)
O9-H6A···Cl1	0.8203(14)	2.335(12)	3.136(3)	166(5)
Hydrogen-bond geometry (Å, °) for (IX) Ephylene				
D—H···A	D—H	H···A	D···A	D—H···A
N1-H1A···Cl1	0.880(1)	2.231(3)	3.098(1)	168.1(12)
N1-H1B···Cl1 <sup>iv</sup>	0.880(1)	2.370(5)	3.203(1)	158.1(11)
Symmetry Codes: (i) 1+x, y,z; (ii) 1-x,1-y,1-z; (iii) 1-x,1/-y,1/+z; (iv) 1/2-x,-1/2+y,1/2-z				

The packing diagram (Figure 3-8) shows two interesting features. The first is the alignment of the plane of the pyrrole functions nearly parallel to and along the c-axis alternating between 1/3 and 2/3 the cell length in b. The second is the interaction of the two dioxole-phenyl rings at the center of symmetry. The rings are also nearly parallel to each other and the related C-atoms of each phenyl ring are separated only by 3.639 Å +/-0.015 within the range of 3.3-3.8 Å described for π-π interactions by Janiak.<sup>46</sup>

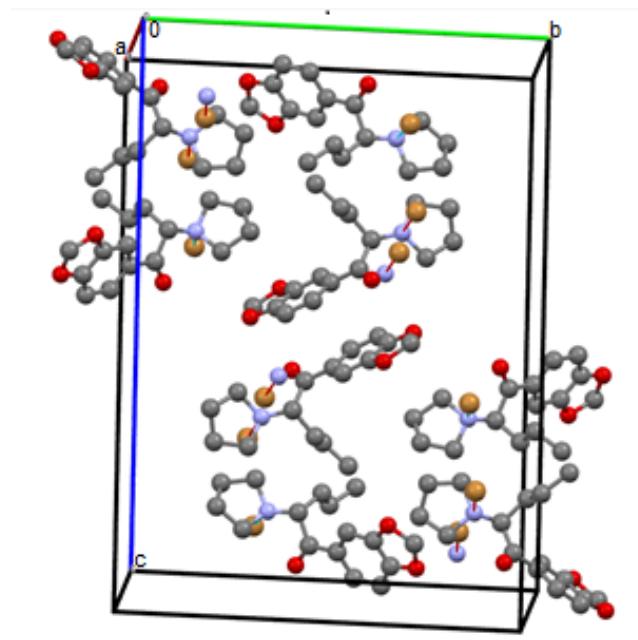


Figure 3-8. The packing diagram of (I) with the H atoms removed for clarity. The isotopic position of the 0.66Cl:0.34Br anions are indicated only by the brown colored bromide.

Figure 3-9 shows the asymmetric unit of the hydrobromide salt of MDPV, (II) ( $C_{16}H_{21}NO_3 \cdot HBr$ ), with its numbering. This molecule crystallizes in the  $P2_1/c$  space group, with  $Z = 4$  and  $Z' = 1$ . The only hydrogen bond exists between the protonated N atom and the bromide at a distance of  $3.198(2)$  Å, [N1-Br1] and the angle [N1—H1...Br1] of  $171^\circ(3)$  (Table 3-2). This is the only MDPV salt in this study in which the alkyl side chain is folding back towards the molecule rather than extended outward perpendicular to the plane of the dioxole-phenyl rings. The packing diagram of (II) (Figure 3-10) is fairly unremarkable. It shows similarities with the packing diagram of the mixed salt (Figure 3-8) in that the H bonded anion is nearly perpendicular to the pyrrole.

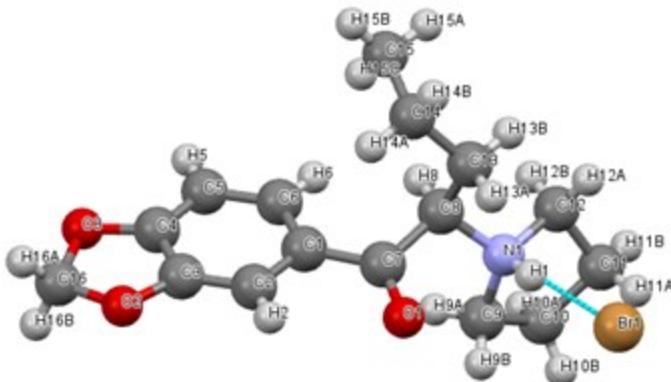


Figure 3-9. The asymmetric unit of (II). The hydrobromide salt of MDPV showing the close contact between the protonated N atom and the bromide anion. The alkyl side chain is seen bending back towards the methyldioxyphenyl rings.

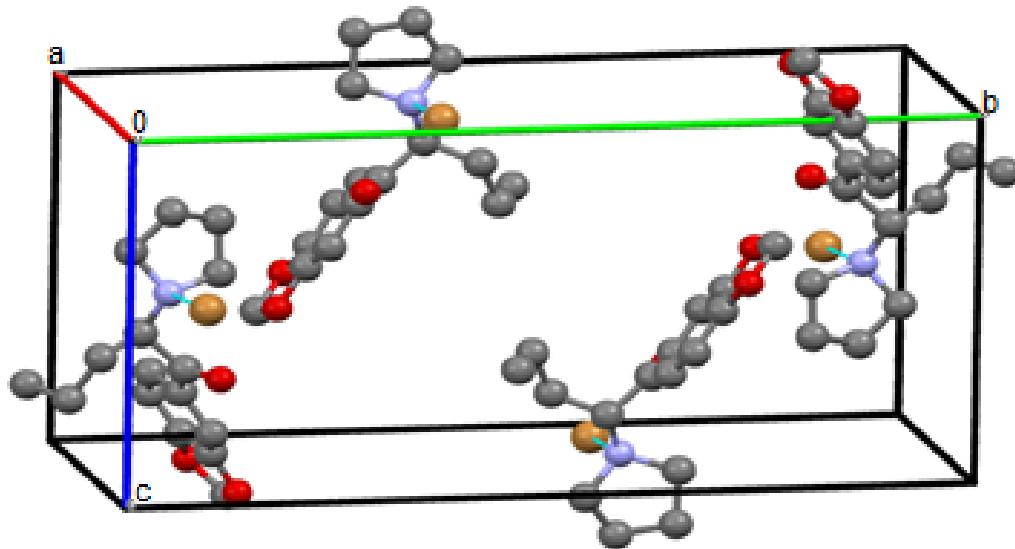


Figure 3-10. The packing diagram of (II) MDPV hydrobromide. The H atoms have been removed for clarity.

The aqueous reagent of acidified gold(III) chloride ( $\text{HAuCl}_4$ ) has been applied to the forensic analysis of drugs of abuse for over 150 years. This reagent has been shown to precipitate unique crystals of cocaine, heroin,

methamphetamine and other “classic” drugs of abuse; however recently this reagent has been used to identify novel psychoactive substances such as the modified cathinones, including 3,4-methylenedioxypyrovalerone (studied here) and mephedrone.<sup>47</sup> Little is known about the resulting microcrystals beyond the characteristics (morphology, color, birefringence, and other optical properties) observed under the polarized light microscope.<sup>48</sup>

Law enforcement submitted samples of MDPV were tested with the HAuCl<sub>4</sub>·3H<sub>2</sub>O as a forensic crystallizing agent in the same manner as previously tested samples. As MDPV HCl and HBr salts all contained quaternary nitrogen atoms, albeit within the pyrrole ring, it was expected that MDPV would crystallize as the tetrachloridoaurate(III) salt, (III). Figure 3-11 gives the atom-numbering scheme for the gold ionic complex (III). The successful production and structural elucidation of the MDPV gold(III) tetrachloride crystals further demonstrates the utility of this reagent for forensic identification via chemical microscopy.<sup>49, 50, 51</sup> As with previously examined drugs (amphetamine being the lone exception), HAuCl<sub>4</sub> forms a complex salt between the N-protonated cation and the gold(III) tetrachloride anion.

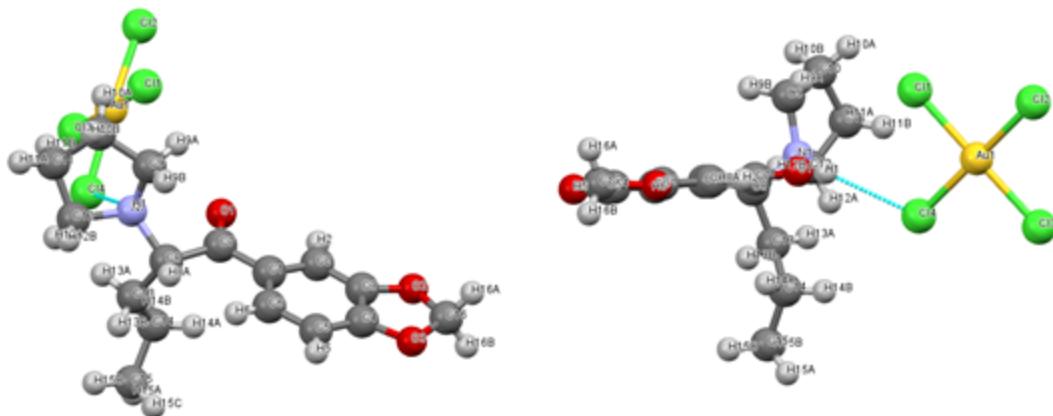


Figure 3-11. Two perspectives of the asymmetric unit of (III), the gold(III) tetrachloride salt of MDPV. The view on the left shows the full extension of the alkyl chain. The view on the right show the close contact between the chlorine (Cl4) and the protonated N atom. The disorder of atoms C13, C14, and C15 and their associated H atoms has been removed for clarity.

Law enforcement samples of suspected ‘bath salts’ were tested by conventional forensic laboratory methods, including gas chromatography-mass spectrometry and compared to published data.<sup>52</sup> The confirmed MDPV samples were then recrystallized using slightly acidified gold(III) chloride reagent. Both the MDPV gold(III) tetrachloride salt (III) and dibutylone hydrochloride (VIII) are the only two of the nine cathinones to crystallized in a Sohncke space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, with Z = 4, the latter (VIII) as a kryptoracemate. In (III) the anion, [AuCl<sub>4</sub>]<sup>-</sup>, is relatively planar, with the r.m.s. deviation of all atoms from the best least-squares plane being 0.045 (3) Å. MDPV gold(III) tetrachloride has only one H bond between N1-Cl4 at 3.41(1) Å, with an N1—H1...Cl4 angle of 151°(11) (Table 3-2). Although it appears to extend outward from the main body of the cathinone, the propyl group was disordered in the crystal at a ratio of 0.64(3):0.36(3). Additionally, the crystal was racemically twinned with a refined

ratio of 0.45(2):0.55(2). The disorder is shown in the packing diagram, Figure 3-12.

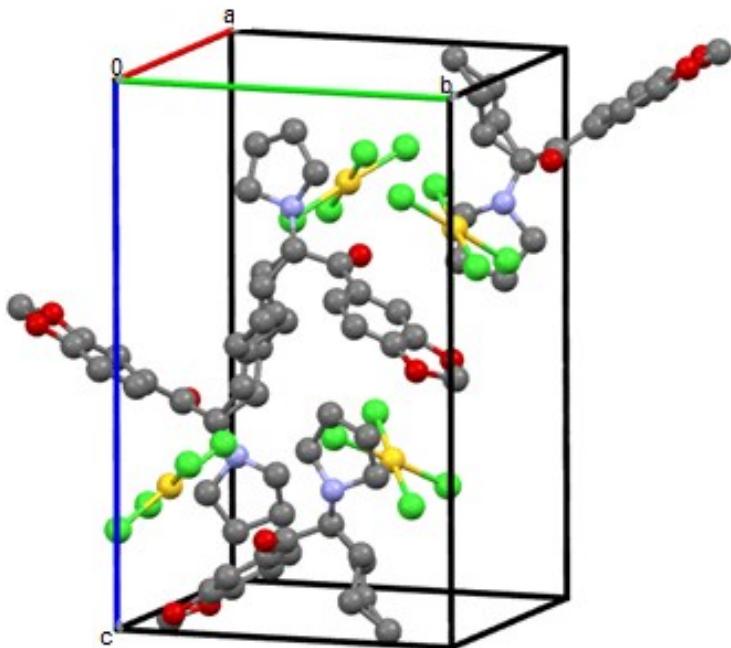


Figure 3-12. The packing diagram of (III), the gold(III) tetrachloride salt of MDPV. H atoms have been removed for clarity. The disorder on the propyl chain can be seen in this diagram.

Ethylone was submitted to the Ocean County, NJ (USA) Sheriff's Department laboratory as a well-crystallized, hydrochloride salt, (IV). This cathinone is structurally similar to methylone in which the methyl group on the amine of methylone has been converted to an ethyl group; at the time of our initial publication<sup>28</sup>, it was not regulated; however, it is now banned in the United States due to its lack of medical use and high potential for abuse. As with other cathinones that have a dioxole substituent on the phenyl ring, Simmler *et al.*<sup>10</sup> categorized the pharmacological effect of ethylone as cocaine–MDMA–mixed

cathinone, based on its inhibition of monoamine uptake inhibitors similar to cocaine and serotonin releasers such as MDMA (3,4-methylenedioxymethamphetamine). As with many of the latest designer drugs, there is very little reliable pharmacological information available. Many of the notions regarding the physiological effects or medical treatment of ethylone rely on inference to similar compounds such as methylmethoxyamphetamine (MDEA), or other cathinones such as methylone. Ethylone HCl crystallizes in the  $P2_{1/c}$  space group with a  $Z = 4$ , and one molecule in the asymmetric unit. Figure 3-13 shows the atom numbering for (IV). As seen with several of the quaternary nitrogen drugs and hydrochloride salts, there is a single H bond between N1 and Cl1 with a length of 3.103(2) Å, and an N1—H1A...Cl1 angle of 161°(2) (Table 3-2).

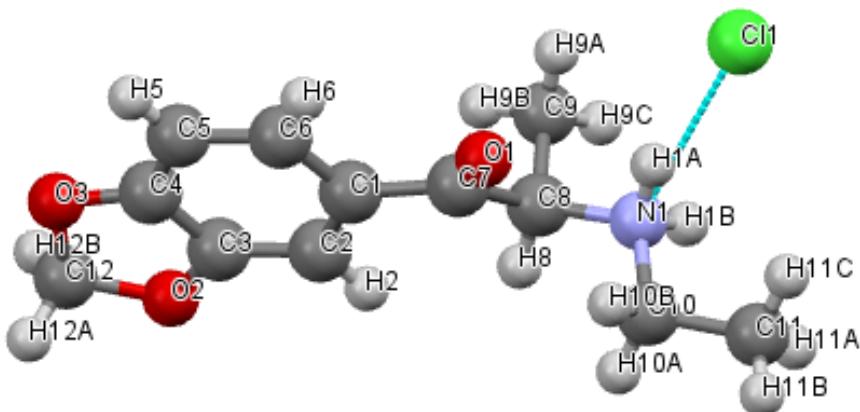


Figure 3-13. The asymmetric unit of (IV), the hydrochloride salt of ethylone. The single close contact from the chloride anion to the protonated N atom of the cation is shown.

The packing diagram of (IV) shows closely parallel planes of the phenyl rings lying within  $3.618\text{\AA} \pm 0.023$  of each other about the unit cell's center of

symmetry. This falls within the previously described range of  $\pi$ -interactions (3.3 – 3.8 Å). The alternating  $\sim 90^\circ$  propagation of the N to Cl close contact can be also be seen extending into adjacent unit cells in the packing diagram (Figure 3-14).

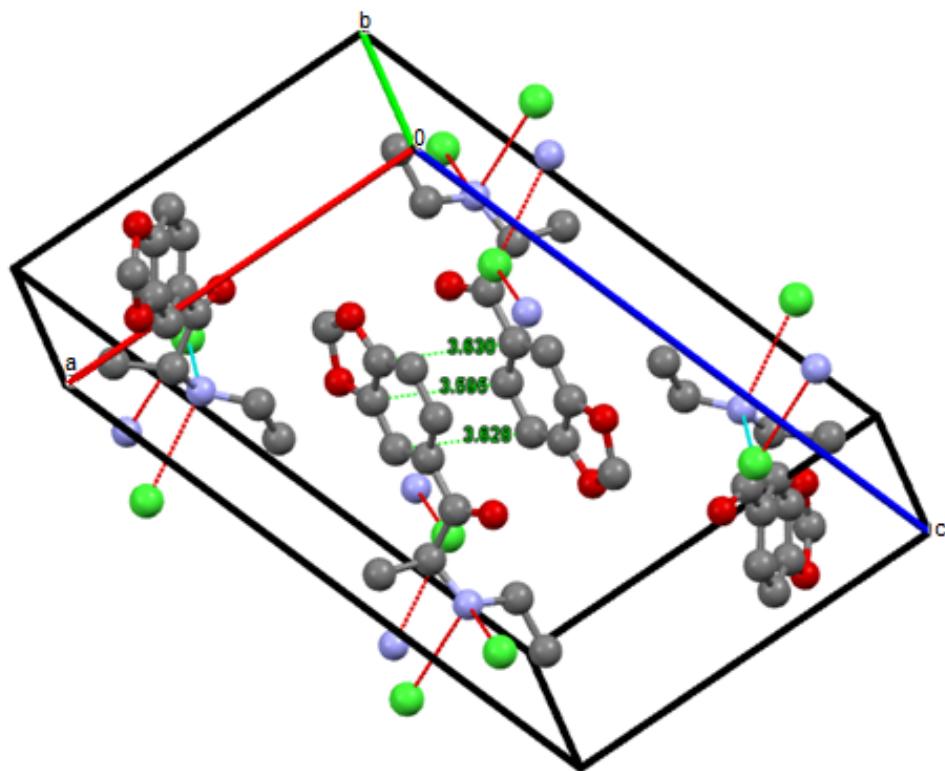


Figure 3-14. The packing diagram of (IV) with H atoms removed. The close contacts between N and Cl atoms are shown as well as the interaction of the phenyl rings about the center of symmetry.

The MDPV gold(III) tetrachloride salt (V) differs from the typical 1:1 cation to anion pairs seen in other drug & gold(III) chloride precipitates. This crystal example contains two chlorides, two waters of hydration and one hydronium ion for charge balance (Figure 3-15). Based upon the hydrogen bond configuration of the  $\text{H}_3\text{O}^+$  cation and two waters of crystallization, the hydroxonium cation

present in this lattice has elemental composition  $\text{H}_7\text{O}_3^+$ .  $\text{MDPV}\cdot\text{HCl}\cdot\text{H}_7\text{O}_3^+\text{Cl}^-$  crystallizes in the space group  $\text{P}2_{1/c}$ , with  $Z = 4$ .

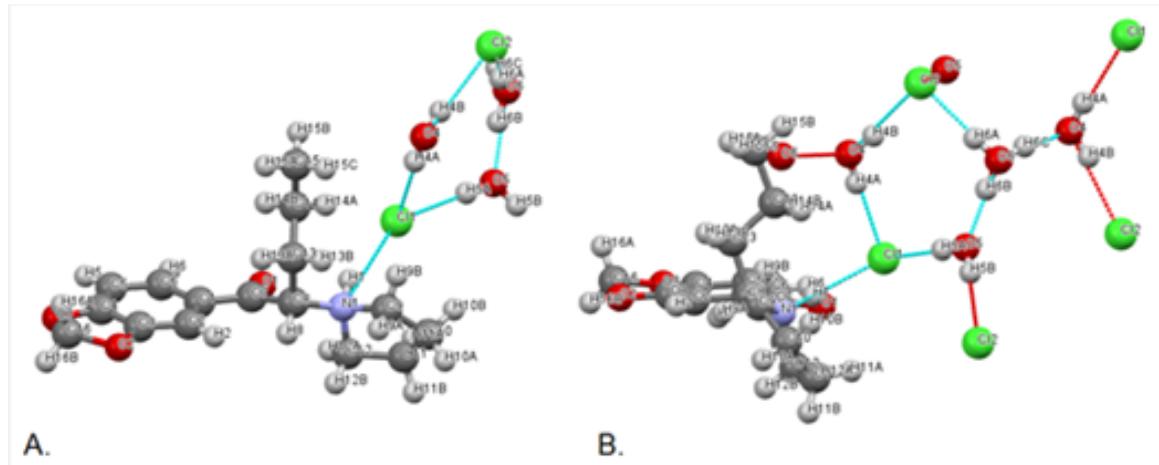


Figure 3-15. A. The asymmetric unit of (V) the hydrated MDPV hydrochloride salt (A) with an additional perspective (B) of the hydrogen bonding network which includes one water molecule and two chloride ions related by symmetry [x, 1.5 y, 1/2+z]. The additional perspective shows the  $\text{H}_3\text{O}^+$  (O6) being flanked by two waters (O4 and O5).

The crystal complex of MDPV with the  $\text{H}_7\text{O}_3^+$  cation is one of a very few structures which is an example of a precisely determined hydroxonium cation. In a 2014 review<sup>53</sup> of the Cambridge Structural Database<sup>38</sup>, the number of reliable structures ( $R < 7.0$ ) of cations with overall composition  $\text{H}_7\text{O}_3^+$  is 11 (CBZSUL01<sup>54</sup>, GIDZEZ<sup>55</sup>, HAZCAN<sup>56</sup>, JOTQOY03<sup>57</sup>, NITRAN01<sup>58</sup>, ODEBOO<sup>59</sup>, SALSUL<sup>60</sup>, SINNAF<sup>61</sup>, SLBZAC10<sup>62</sup>, SOJZOH<sup>63</sup> and XUMQIF<sup>64</sup>), out of a total number of cations with composition  $\text{H}_x\text{O}_y^+$  (with  $x = 2n + 1$  and  $y = n$ ) of 1406 located in the CSD database.<sup>38</sup> In (V), the configuration of the  $\text{H}_7\text{O}_3^+$  H bonding is described in a 2014 study and review by Bernal & Watkins.<sup>53</sup> They found that there are three possible geometrical isomers of the hydroxonium cation with composition,  $\text{H}_7\text{O}_3^+$ . The first arrangement, is seen in (V) where the charged

hydronium cation is evenly spaced between two hydrogen bonded waters in a "V" configuration, i.e.  $\text{H}_2\text{O}-\text{H}_3\text{O}^+-\text{H}_2\text{O}$  (see Figure 3-15b). The second arrangement, a Zundel cation,  $\text{H}_5\text{O}_2^+-\text{H}_2\text{O}$ , where the additional proton is centered evenly between the center water and one of the end waters, the positive charge being essentially shared evenly between two of the three H bonded waters. The third configuration has the extra proton clearly located on one of the end of the chain of waters to produce  $\text{H}_3\text{O}^+-\text{H}_2\text{O}-\text{H}_2\text{O}$ . All three configurations can be distinguished by their respective O...O bond H bond distances. For a more in depth discussion of  $\text{H}_x\text{O}_y^+$  species, see Bernal & Watkins<sup>53</sup> for further details.

Figure 3-15b and Figure 3-16 (the packing diagram), give a graphic representation of the extensive hydrogen-bonding network that contains the previously described  $\text{H}_7\text{O}_3^+$  in (V) and includes the interactions with the drug molecule and the chloride anions. Within the network of hydrogen-bonded hydronium cations and waters, the chlorides make additional contacts to the cations at the protonated nitrogens at opposite ends of the unit cell along the *a*-axis. The network continues into adjacent cells, however; only a small portion in a single unit cell is shown here in Figure 3-16.

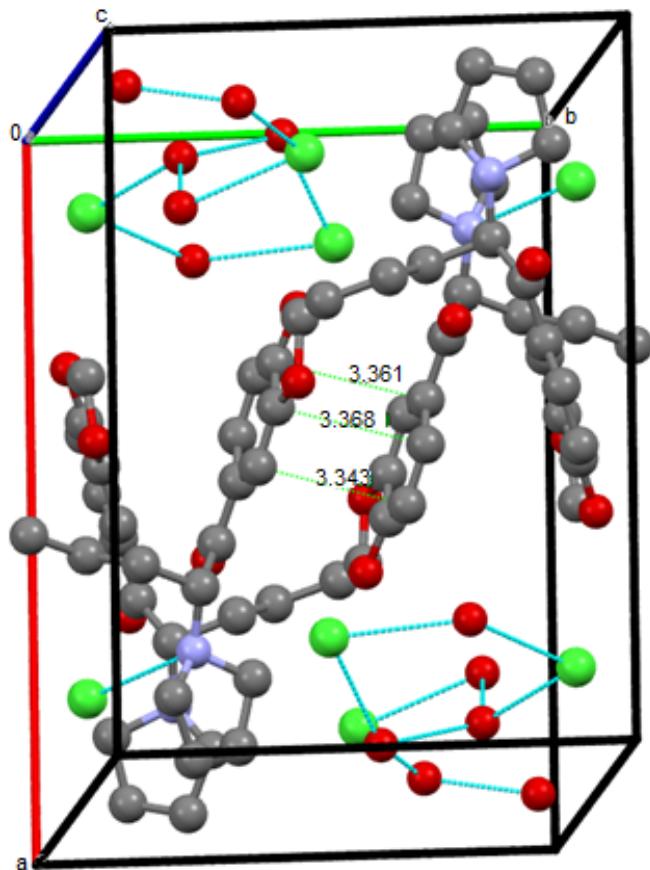


Figure 3-16. The packing diagram of (V) showing the H-bonding/close contact network and proximity of ring moieties at center of symmetry. Hydrogens have been removed for clarity.

All four of the MDPV crystal structures have their quaternary N-containing cations in close contact through a hydrogen bond to either a Cl-, a Br-, or an [AuCl<sub>4</sub>]<sup>-</sup> anion (see Table 3-2 for the values for each individual structure). The hydrogen-bond distance between the quarternary N1 atom and the Cl1 ion in the MDPV gold(III) tetrachloride hydrate structure is 3.234 (2) Å and the N1—H1...Cl1 angle is 157° (3); the remaining H bond and close contact distances and angles are given in Table 3-2. The packing diagram also shows the planes of the

rings parallel and separated by only 3.354Å +/-0.011 at the center of symmetry as seen with other π interactions in previous investigated cathinones.

The X-ray powder diffraction patterns of the MDPV salts, those found in law enforcement seizures, and those obtained after precipitation of the gold(III) chloride microcrystal test, show unique and reproducible patterns that can be obtained in under thirty minutes. The patterns (Figure 3-17) show that even closely related salts, such as MDPV hydrobromide and MDPV hydrobromide(0.34):hydrochloride(0.66) can readily be distinguished.

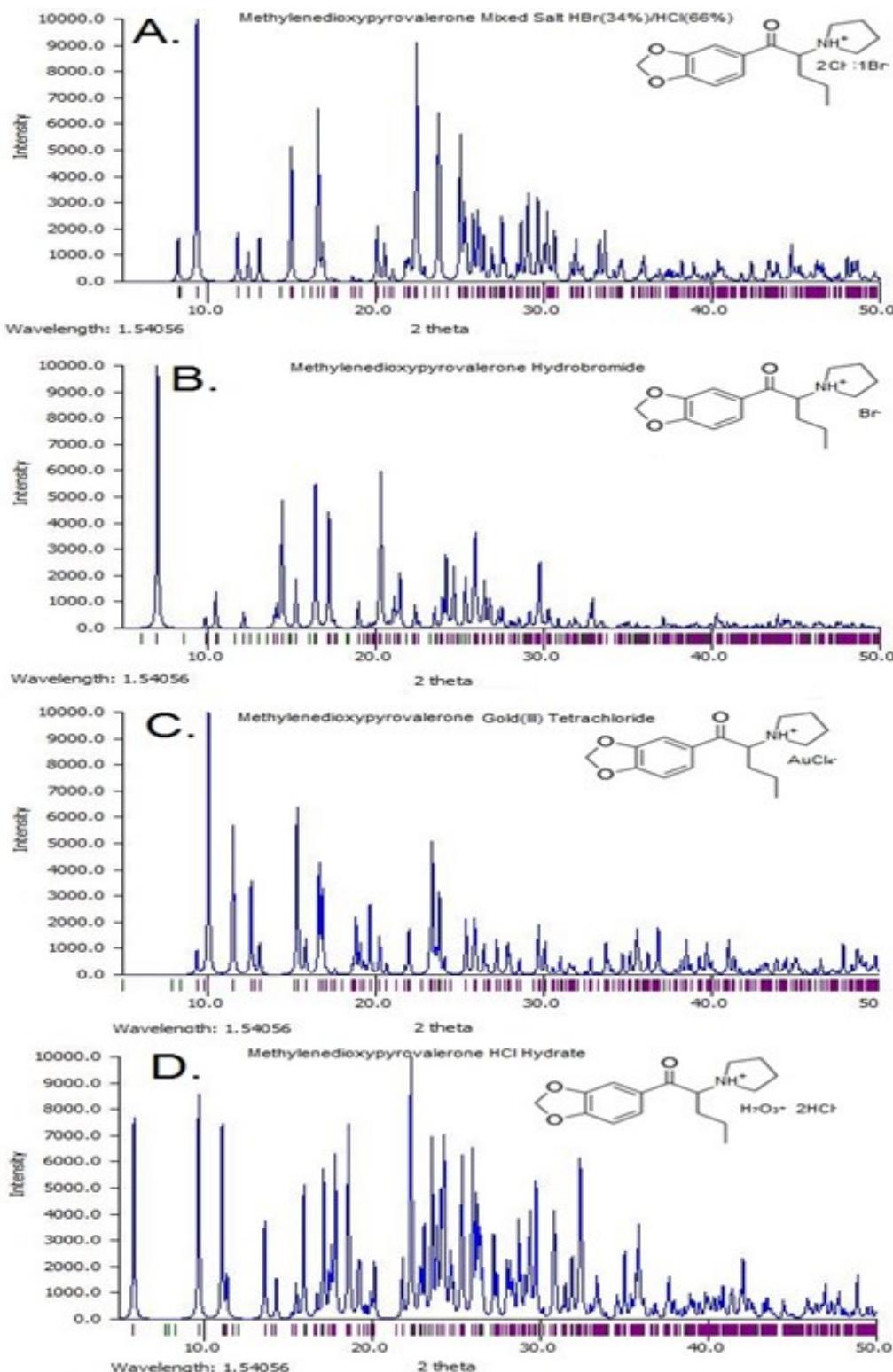


Figure 3-17. The powder diffraction patterns of four salts of methylenedioxypyrovalerone(MDPV). A. MDPV mixed HBr/HCl salt, B. MDPV HBr, C. MDPV HAuCl<sub>4</sub> and D. MDPV HCl Hydrate.

$\alpha$ -Pyrrolidinovalerophenone ( $\alpha$ -PVP) is potentially the most dangerous of the synthetic cathinones to reach the illicit drug market. It shares the same parent cathinone structure having a phenethylamine base with a ketone function on the  $\beta$ -C atom. Similar to the previously described MDPV,  $\alpha$ -PVP has a propyl alkyl chain attached to  $\alpha$ -C; however, this cathinone lacks the 3,4-methylenedioxy substituent on the phenyl ring.

In the crystal structure of  $\alpha$ -PVP hydrochloride 0.786-hydrate, (VI), the propyl chain extends away from the phenyl ring at nearly a  $90^\circ$  angle to both the plane of the phenyl ring [dihedral angle between the mean plane through atoms C8–C12 and that through the phenyl ring =  $82.93^\circ(14)$ ] and carbonyl unit ([dihedral angle between the mean plane through atoms C8–C12 and that through atoms C1/O1/C2/C8) =  $87.78^\circ(12)$ ] (Figure 3-18). The asymmetric unit shows the chloride anion (Cl1) hydrogen bonded to the quaternary N1 atom and also bound to two different water molecules, distances and angles given in Table 3-2.

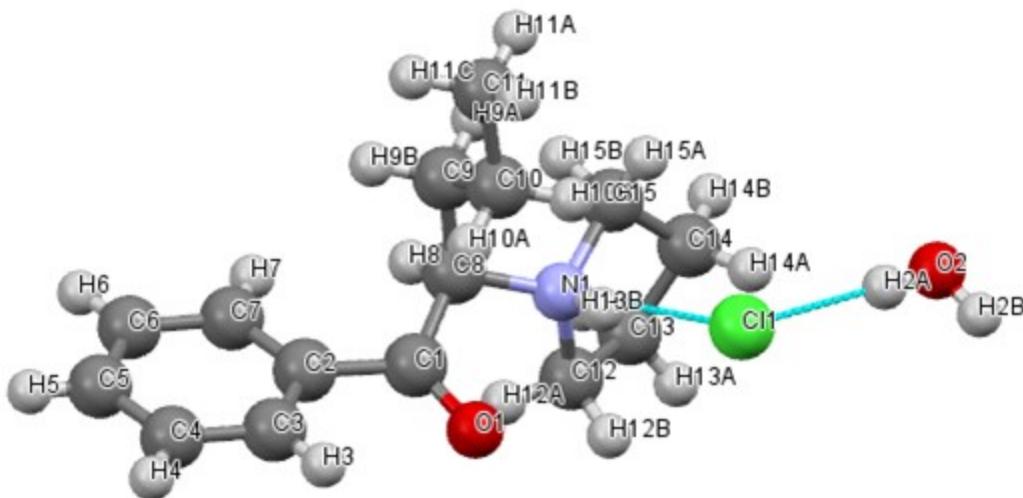


Figure 3-18. The asymmetric unit of (VI)  $\alpha$ -PVP with numbering. The close contact from the protonated N atom to the chloride anion to the water is indicated by the teal colored lines.

The effect of the hydrogen bonding network is to form a centrosymmetric dimer across multiple cells at the origin of the unit cell. Figure 3-19 depicts this dimer configuration of the  $\alpha$ -PVP cation, the two engaged  $\text{Cl}^-$  anions, and the partial (0.786) water. The waters and chlorides form opposite corners of a parallelogram with angles:  $\text{H2A} \dots \text{Cl1} \dots \text{H2B}(-x, -y, -z) = 76.6^\circ(14)$  and  $\text{H2A} \dots \text{O2} \dots \text{H2B} = 102^\circ(4)$ .

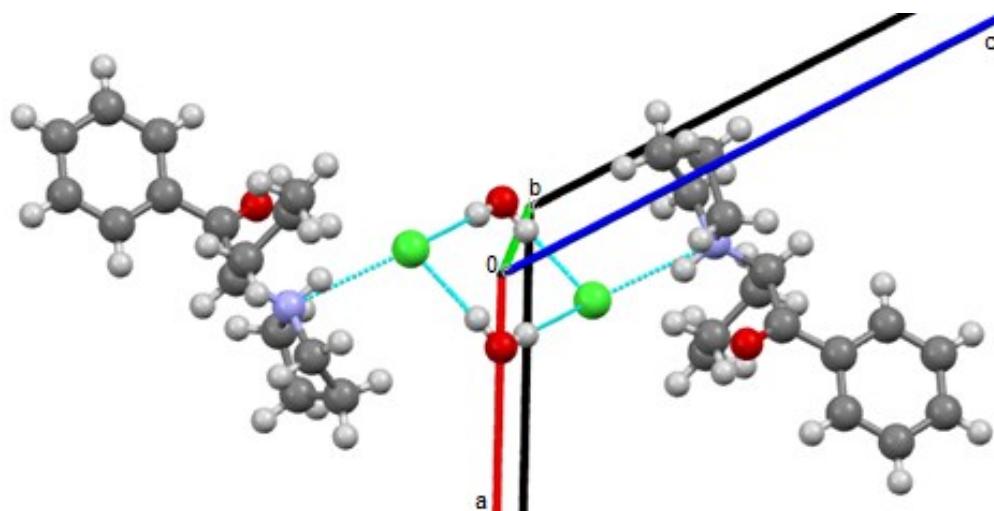


Figure 3-19. Depiction of the dimer formed by two waters, two chloride anions and two  $\alpha$ -PVP anions at the origin of the cell.

Figure 3-20 is the packing diagram of  $\alpha$ -PVP that shows the phenyl rings of the cation lying essentially through the middle of the unit cell in the  $a$  dimension ( $a/2$ ), with the propyl alkane chains nearly perpendicular to the plane of these rings. There are no  $\pi$ - $\pi$  interactions between the aromatic rings in contrast to the interactions seen in the packing of other cathinones studied. The pyrrole rings all tend to point outward towards the edges of the ac plane.

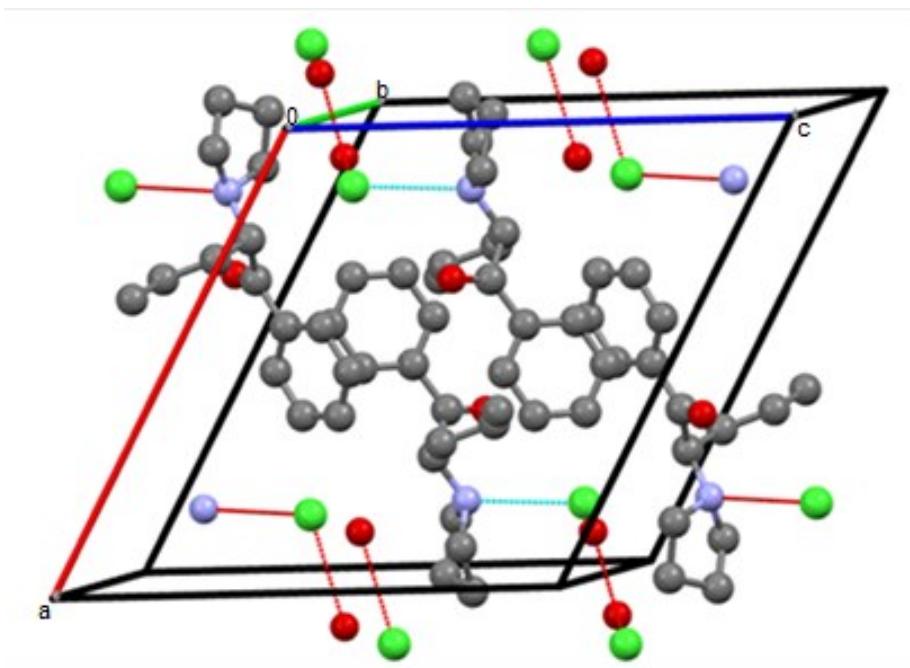


Figure 3-20. The packing diagram of (VI), the hydrochloride salt of  $\alpha$ -PVP. H-atoms have been removed for clarity.

In comparing the conformation of this structure with those of MDPV (previously described) and bath salts published by other research groups<sup>38, 54</sup>, even though the bond between the phenyl group and the ketone group (C1...C2) has free rotation, the conformation within the crystal structures is essentially consistent between all cathinones. In all of the following modified cathinone "bath salt" structures, the carbonyl plane formed by atoms C1/O1/C2/C8, is approximately 20° (range 4.57° - 23.58°) out of plane with the aromatic phenyl or dioxole-phenyl rings: MDPV [3,4-methylenedioxypyrovalerone, (RS)-1-(1,3-benzodioxol-5-yl)-2-(pyrrolidin-1-yl)pentan-1-one];<sup>28</sup> ethylone [(RS)-1-(1,3-benzodioxol-5-yl)-2-(ethylamino) propan-1-one],<sup>28, 55</sup> metaphedrone (mephedrone, 4-MMC, [(RS)-2-methylamino-1-(4-methylphenyl)propan-1-one],<sup>8</sup> pentadrone [()-1-phenyl-2-(methylamino)pentan-1-one]<sup>8</sup>; methylone [()-2-

methylamino-1-(3,4-methylenedioxyphenyl)propan-1-one]<sup>7</sup>, 3,4-DMMC [()<sup>-</sup>1-(3,4-dimethylphenyl)-2-(methylamino)propan-1-one];<sup>7</sup> and 4-MEC [(RS)-2-ethylamino-1-(4-methylphenyl)propan-1-one];<sup>7</sup> pentylone[ $(\pm)$ -1-(1,3-benzodioxol-5-yl)-2-(methylamino)pentan-1-one chloride], (unpublished), dibutylone[ $(\pm)$ -1-(1,3-benzodioxol-5-yl)-2-(dimethylamino)butan-1-one chloride, (unpublished), and ephylone[ $(\pm)$ -1-(1,3-benzodioxol-5-yl)-2-(ethylamino)pentan-1-one chloride, (unpublished)]. It is likely that the conformation is energetically favorable and that may it contribute to the similar observed physiological effects if the receptors rely the position of these functional groups for receptor binding. Likewise, for immunoassay toxicology testing, these structural similarities may cause cross-reactivity in certain assays.

Regardless of the similarities in structural aspects of the molecule, the differences in the internal arrangement within the crystal lattice can be seen quickly by comparison of the powder X-ray diffraction patterns without the need for a full structural determination of the crystals. Once the single crystal structure has been solved, the powder diffraction pattern can be electronically calculated and deposited into a searchable database to aid others in the drug identification. The powder patterns of ethylone HCl and  $\alpha$ -PVP are shown in Figure 3-21.

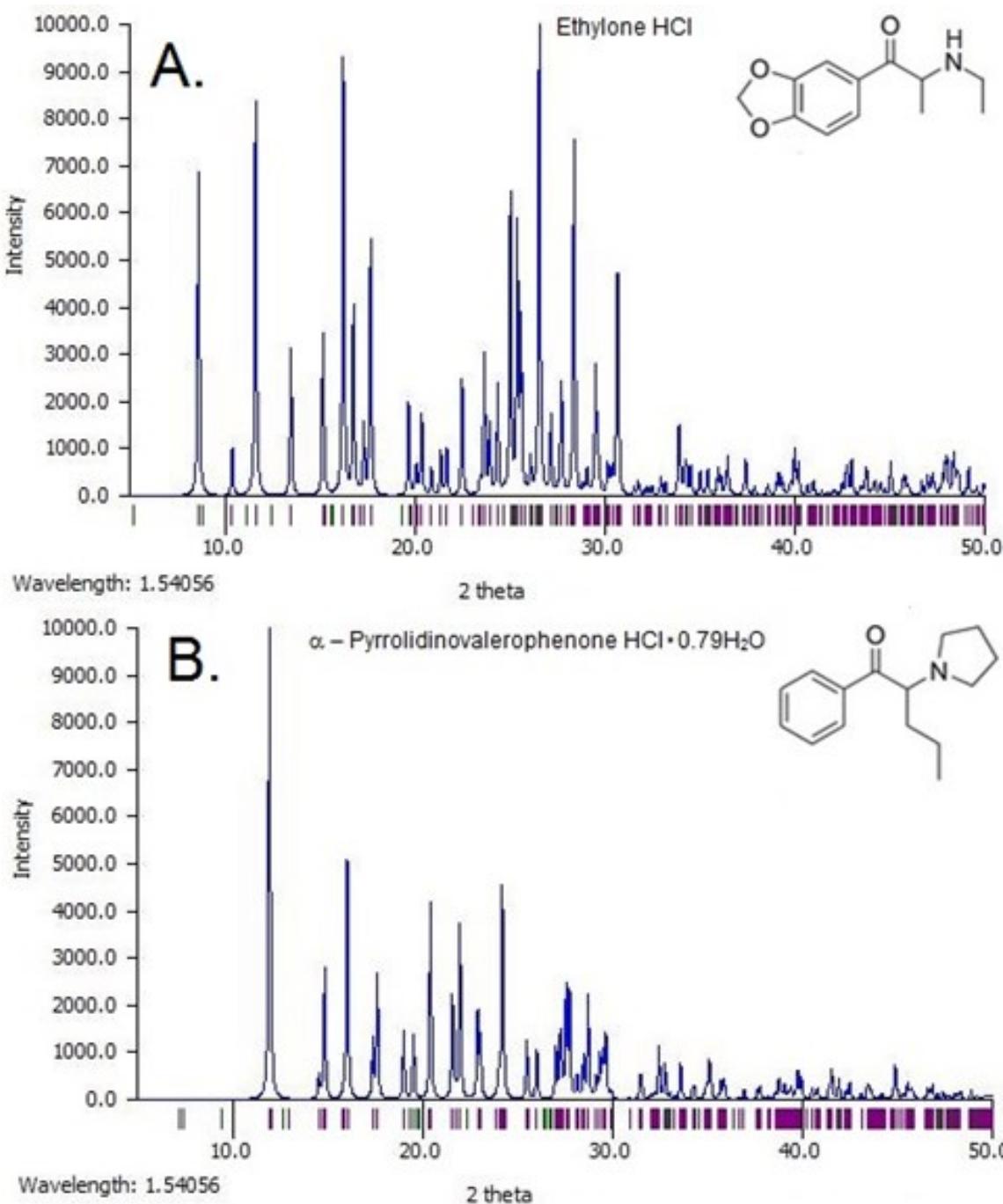


Figure 3-21. The X-ray powder diffraction patterns of (A.) Ethylone HCl and (B.)  $\alpha$ -PVP HCl 0.79 Hydrate.

Pentylone (VII),  $C_{13}H_{20}ClNO_3 \cdot H_2O$ , crystallizes in the  $P2_1/c$  space group with a  $Z=4$  and  $Z'=1$ . There is a single unit of the protonated pentylone cation in

the asymmetric unit with a chloride for charge balance and a single water molecule. The pentylone cation is another example cathinone where the propyl chain extends perpendicularly from the remaining structure and the carbonyl ketone nearly planar with the dioxole-phenyl rings. Figure 3-22 shows the asymmetric unit and hydrogen bonding within the crystal structure. The H-bonding goes from the quarternary N1 atom to Cl1 [3.1241(11) Å], and to the O4 of the water [2.7686(15) Å]; the water, in turn, is H bonded to two different Cl counterions (by symmetry) [3.2107(11) and 3.1641(11) Å] to make an extensive H-bonded lattice.

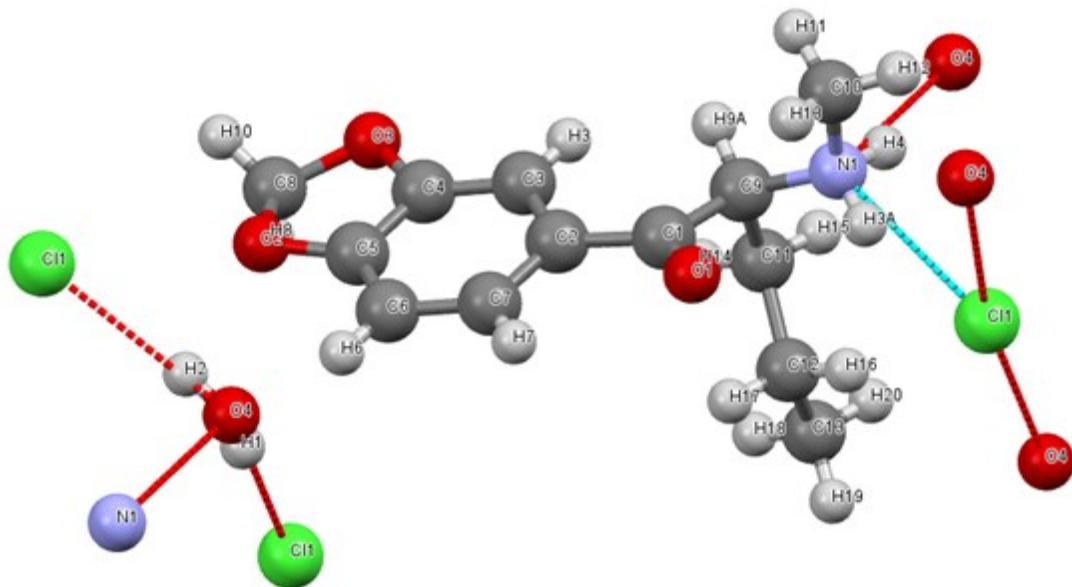


Figure 3-22. The asymmetric unit of (VII), pentylone hydrochloride monohydrate. The figure shows hydrogen bonding from the protonated nitrogen to the chloride, as well as H bond to other symmetry-related waters and chloride anions. The dashed, teal colored line indicates H bonds within the asymmetric unit. The dashed red lines indicate H bonds to symmetry related atoms.

At the origin of the cell, these H bonds cross very close to a center of symmetry, resulting in an interesting hexagonal chair conformation of hydrogen bonds (N1 [1-x, -1/2+y, 1/2-z] to Cl1 [-1+x, 1/2-y, -1/2+z] to O4 [-x, -1/2+y, 1/2-z] to N1' [-1+x, 1/2-y, -1/2+z] to O4' [x, 1/2-y, -1/2+z] to Cl1' [1-x, -1/2+y, 1/2-z] back to N1. See Figure 3-23A for a depiction of the hydrogen bonding network and Table 3-2 for H bond angles and distances.

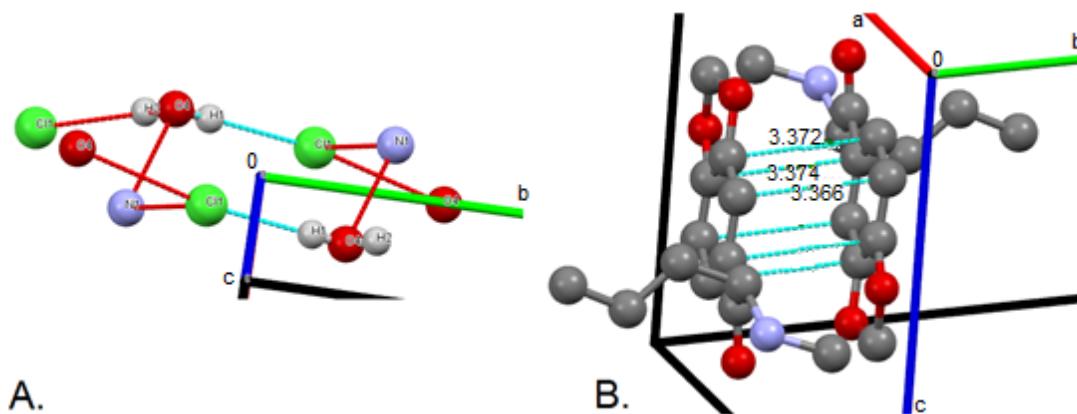


Figure 3-23. An illustration of (A) the hydrogen bonding network at the origin of the cell resulting in a six-membered ring in a chair configuration and (B) the  $\pi$ - $\pi$  interactions between symmetry related cation, phenyl rings across the AC plane. Extraneous atoms have been removed for clarity of the diagram.

Elsewhere in the unit cell, the pentylone cation is positioned such that two cations lie in close proximity to each other within the range of  $\pi$ - $\pi$  interactions between the phenyl rings from a pair of symmetry-related molecules. The plane of one ring system, defined by C2-C3-C4-C5-C6-C7, interacts with the equivalent plane of another molecule at symmetry position [1-x, -y, 1-z] to produce contacts ranging from 3.3659(18) to 3.3740(18) Å, and a centroid-to-centroid distance of 3.365 Å. See Figure 3-23B for a representation of the  $\pi$ - $\pi$  stacking of these phenyl groups between molecules.  $\pi$ - $\pi$  interactions are manifested in three

configurations. Pentylylone stacked in the “sandwich” configuration, which is the least common of three aromatic ring configurations, where the two rings are positioned directly, face-to-face. The other two are offset stacking (parallel displaced) and T-stacking (edge-to-face), where the second ring is perpendicular to the first ring. According to Hunter & Sanders <sup>56</sup>, electrostatic forces are responsible for the interaction between the aromatic rings. However, Wheeler & Houk <sup>57</sup> have suggested that dispersive forces contribute to repulsion of the rings favoring either the T-stacking or the offset configuration with multiple substituents on the phenyl ring lowering the repulsive forces and supporting the sandwich configuration.

Dibutylone (VIII),  $C_{13}H_{17}ClNO_3 \cdot 1.5H_2O$ , is similar in structure to two cathinones described by other research groups, butylone <sup>58</sup> and dimethylone <sup>59</sup>. This compound has a second methyl group on the amine function compared to butylone, hence the “di” terminology, and an extension of the  $\alpha$ -methyl group to an ethyl group of the dimethylone resulting in the “butyl-” name. Illicit users and clandestine labs do not use any standardized naming conventions, but rather name these new compounds based on similarities to previously designed drugs, often with confusing or ambiguous nomenclature (Figure 3-24). Many of the natural or active drug compounds display chirality because they contain either asymmetric or dissymmetric entities. If they are natural products, they normally appear in pure chiral form. “Man-made” chemicals, unless made with considerations to achieve chirality in mind, typically crystallize in one of the non-Sohncke space groups. If the molecule does not contain a chiral center, then the

common centrosymmetric space groups are significantly more likely hosts than the Sohncke space groups  $P2_12_12_1$  and  $P2_1$  by a factor of 8:1.<sup>60</sup> Crystals of achiral compounds are a mixture of both hands of the molecule.

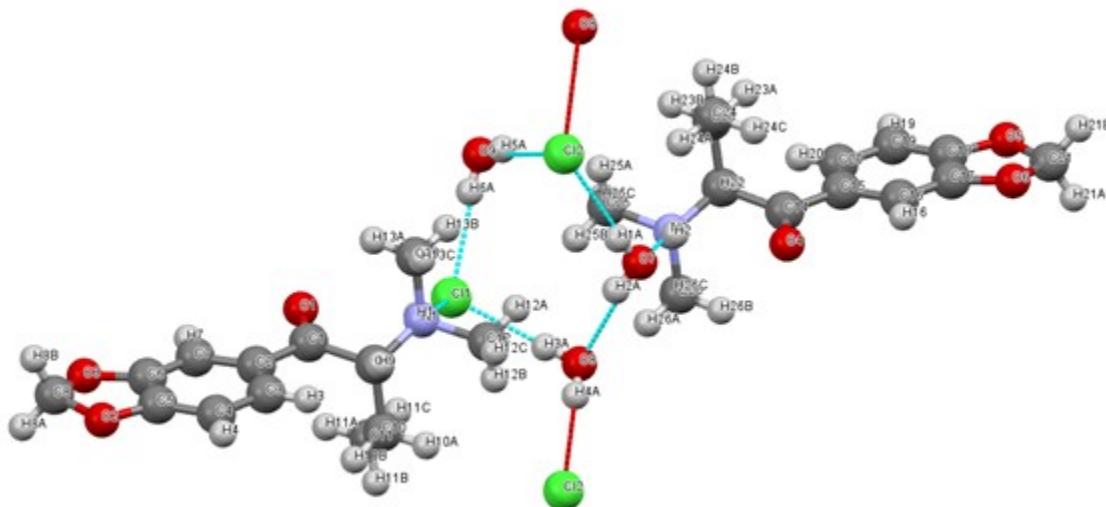


Figure 3-24. The asymmetric unit of (VIII), dibutylone hydrochloride 1.5 hydrate. The figure shows the H bonding within the asymmetric unit (teal dashed line) and H bonding to a symmetry related water and chloride (red dashed lines).

Kryptoracetates are compounds that contain pairs of racemic molecules, but crystallize in Sohncke space groups typically reserved for enantiomerically pure chiral compounds. This phenomenon was recently recognized by Dr. Ivan Bernal, co-author on several of the papers contributing to this manuscript.<sup>61</sup> Dibutylone is a unique example of a kryptoracetate in which both independent cations each have a hydrogen bond to their respective  $\text{Cl}^-$  counter-ion, but share three waters of hydration. Crystal structures of this nature are rare; however, it is difficult to assess the actual number that has been characterized due to limitations in database searching and the relative naissance of the recognition of

kryptoracemates. From Figure 3-24, it would suggest that packing influences, such as waters of hydration or hydrogen bonding networks, could override the preferred space group or behaviors of racemic pairs in some certain cases.

The configuration of both the ketone and the extended alkyl chain remains consistent with the dihedral angles reported for other cathinones. In one molecule of dibutylone, the phenyl group (C2 through C7) makes a 13.20(14) $^{\circ}$  dihedral angle with the ketone moiety (C1,C2,C9,O1) and a dihedral angle of 82.7(2) $^{\circ}$  to the ethyl group on C9 (C9,C10,C11). The other molecule has dihedral angles within a few degrees of the first: the phenyl group (C15 through C20) makes a 14.82(14) $^{\circ}$  dihedral angle with the ketone moiety (C14,C15,C22,O4) and a dihedral angle of 80.0(2) $^{\circ}$  to the ethyl group located on C22 (C22,C23,C24).

The  $\pi$ - $\pi$  interaction in this crystal structure is not as direct as seen in pentylone or ephylone. The phenyl rings are slightly offset from each other, by approximately 33.95 $^{\circ}$ . The phenyl ring to symmetry-related phenyl ring [C2.....C7 (1/2 - x, 1 - y, -1/2 + z)] centroid distance is 3.791 $\text{\AA}$  and the line between the ring centroids is 146.05 $^{\circ}$  relative to the plane of the rings. The face-to-face stacking aligns both the five-membered dioxole ring above the complementary phenyl ring. The offset nature of the C atoms suggests that the strong influence of the additional substituents affects the character of the pi orbital over the surface of the phenyl ring (Figure 3-25).

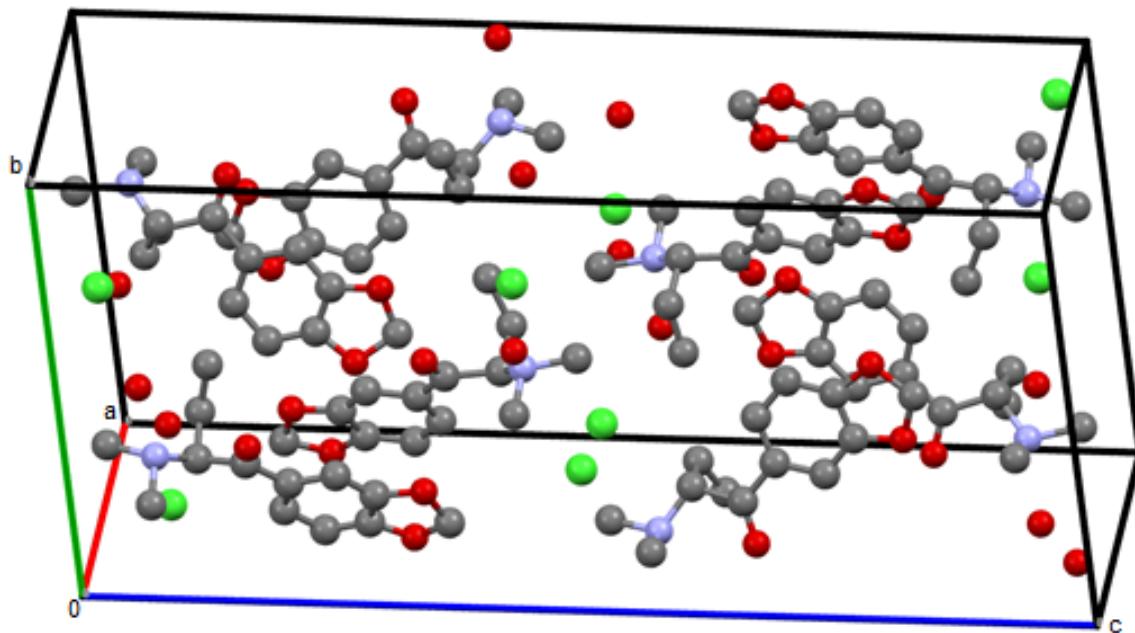


Figure 3-25. The packing diagram of (VIII) dibutylone hydrochloride 1.5 hydrate. The figure shows the stacking arrangement of the overlapping ring structures.

In addition to the arrangement of the ring structures, the packing diagram shows the protonated N atoms, the waters of hydration, and the chloride anions are clustered at the center and ends of the unit cell along the c-axis. Each of the two independent molecules in the asymmetric unit of (VIII) has a  $\text{Cl}^-$  counterion H bonded to the quaternary N atom of the associated cation. The three waters of hydration, shared between the two molecules, contribute a number of hydrogen bonds: two of the three water molecules (O8) and (O9) are each H bonded to both chloride ions ( $\text{Cl1}$ ) and ( $\text{Cl2}$ ). The other water (O7) is bound to the protonated amine, one water (O8), and one chloride ( $\text{Cl2}$ ). These three water molecules link together with the two chloride counterions to make a 5-membered H-bonding ring whose sequence is: [ $\text{Cl1...H6A-O9-H5A...Cl2...H1A-O7-H2A...O8-H3A...Cl1}$ ] (Figure 3-24 above) and Table (3-2).

Ephylone (IX), C<sub>14</sub>H<sub>20</sub>CINO<sub>3</sub>, (also known as N-ethyl-pentylone, BK-Ethyl-K, and BK-EBDP) is another structurally related cathinone. This designer drug substitutes an N-ethyl alkyl for the N-methyl of pentylone (Figure 3-26). The propyl chain (C9, C10, C11, and C12) is pointed outward at a 88.45(7) $^{\circ}$  dihedral angle from the phenyl group (C2 through C7) and the ketone function is at an 18.11(8) $^{\circ}$  dihedral angle to the phenyl group as well. These positions remain consistent throughout all but one of the designer cathinones examined, MDPV hydrobromide (II). The protonated amine of the cation makes a hydrogen bond with the chloride anions, which continues indefinitely alternating between symmetry related cations and anions in an interesting “zig-zag” pattern (Figure 3-27).

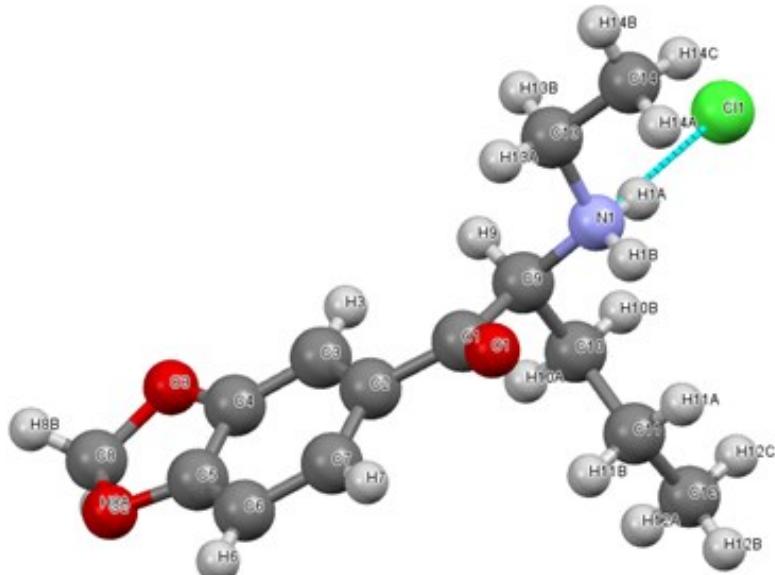


Figure 3-26. The asymmetric unit of (IX) ephylone hydrochloride with numbering. The figure shows the hydrogen bond from the protonated N atom to the Cl anion.

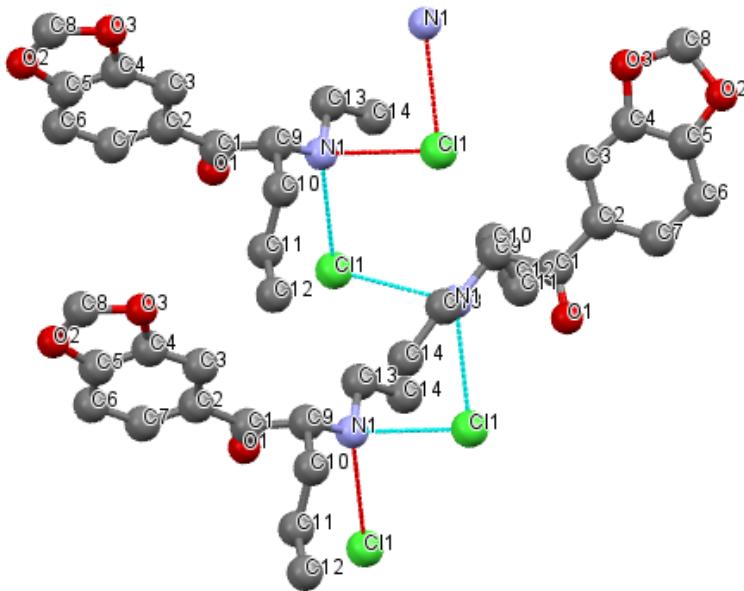


Figure 3-27. The asymmetric unit of (IX) ephylone hydrochloride with numbering. The figure shows the 'zig-zag' pattern of the hydrogen bonds involving the protonated N atoms and the Cl anions.

The phenyl group (C2 through C7) creates a "π-π stacking" arrangement through the unit cell's center of symmetry. The distances between the complimentary C atoms range between 3.5289 and 3.5331 Å. The phenyl ring centroid-to-centroid distance is 3.53 Å, well within the range established<sup>46</sup> for π-π interactions (Figure 3-28). The phenyl rings are face-to-face and nearly parallel, the angle between the line drawn through the centroids and the plane of the phenyl rings is 91.35°. While the overlapping of the π-orbitals are maximized, substituent effects of the methylene moieties and remainder of the cation stabilize the electrostatic and dispersion forces.

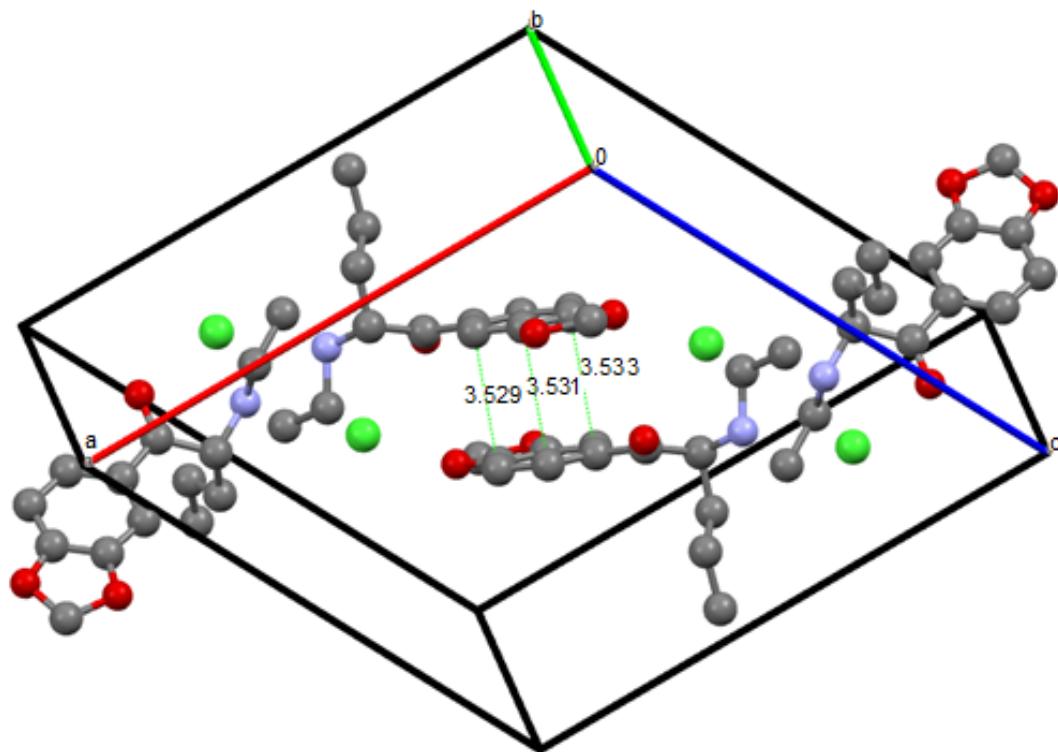


Figure 3-28. The packing diagram of (IX). The diagram shows the  $\pi - \pi$  stacking of the centrosymmetric phenyl rings with distances in Å. Hydrogen atoms have been removed for clarity.

This is another example of packing in cathinone structures (MDPV hydrobromide, ethylone hydrochloride, pentylone hydrochloride, dibutylone hydrochloride hydrate, and ephylone hydrochloride) where the drug compounds demonstrate “sandwich”  $\pi$ - $\pi$  stacking interactions (the phenyl rings of the cations are stacked face-to-face with each other within  $\sim 3.8\text{\AA}$ ).

When encountered in routine forensic laboratory work, the cathinones can be identified using X-ray powder diffraction and compared to patterns calculated from single crystal work, such as seen with the following patterns of pentylone, dibutylone, and ephylone (Figure 3-29).

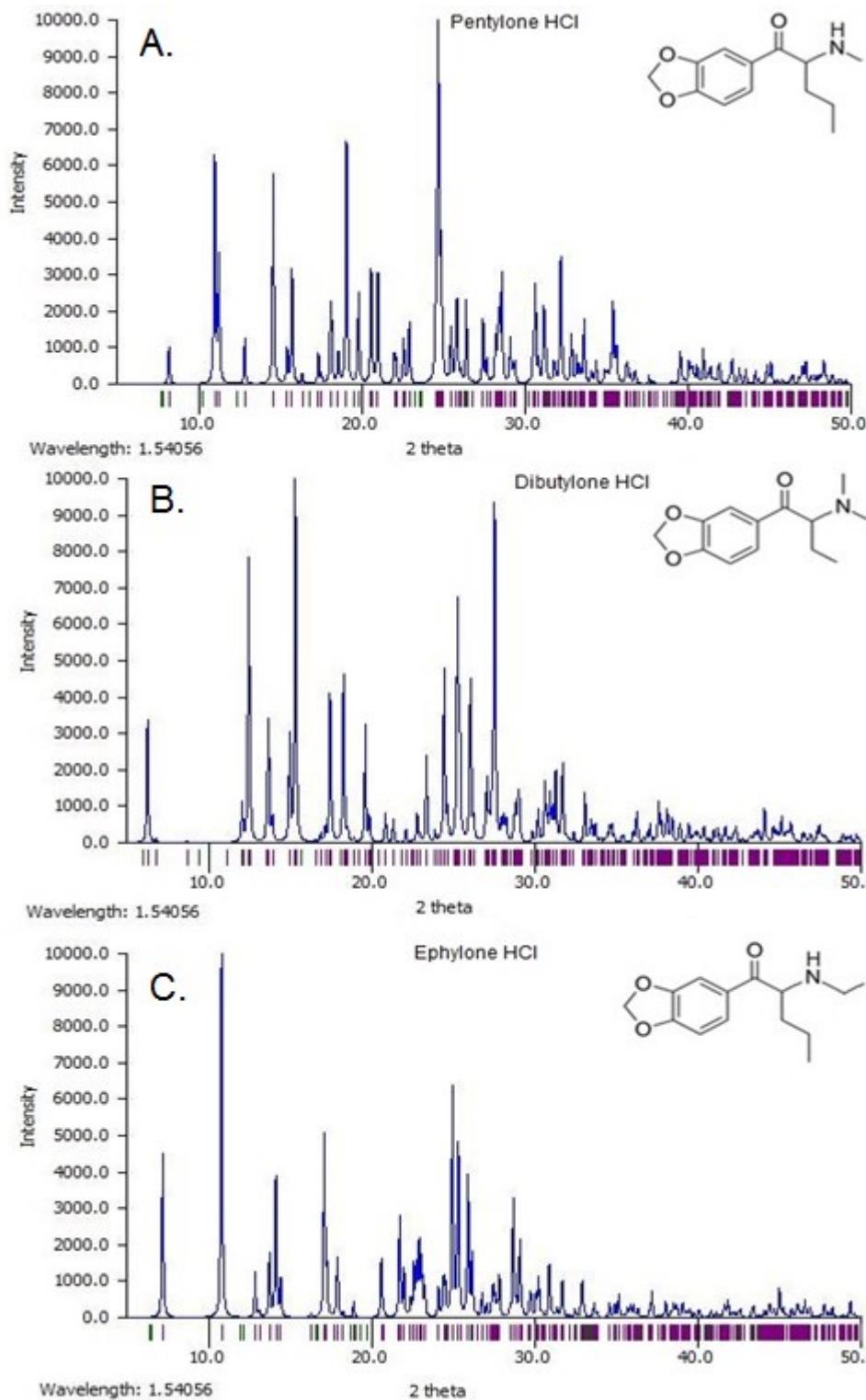


Figure 3-29. The X-ray powder diffraction patterns of (A.) pentylylone HCl, dibutylone HCl 1.5Hydrate, and (C.) ephylone HCl.

## CONCLUSION

The dramatic release of novel psychoactive stimulants onto the recreational drug scene has created an urgent need for the rapid and absolute identification of these new drugs of abuse. The structural elucidation of these six cathinones and their salts along with the determination of the powder X-ray diffraction spectra will speed the forensic laboratory analysis of these compounds when encountered in law enforcement seizures and toxicology samples. Understanding the absolute structure of designer drug compounds is the key to developing new drug standards and understanding the analytical profile of these drugs. Additionally, the provided powder X-ray diffraction patterns will allow labs to utilize a SWGDrug<sup>62</sup> recommended method of analysis that is rapid and requires very little sample preparation.

This chapter provides the absolute structural determination of six new synthetic cathinones, along with three additional salts of one of the cathinones, MDPV. One of the salts, MDPV gold(III) chloride is the product of a routine forensic drug microcrystal test and demonstrates the utility of the test, the uniqueness of the resulting precipitate, and the powder diffraction pattern which can be used to confirm the test results. It is intended that this information will benefit the forensic and medical practitioners in the rapid and efficient recognition of these drugs. Furthermore, the results of this study will contribute to the knowledge of medical personnel by improving the understanding of the pharmacological properties of the compound and will assist forensic investigators in the analysis of toxicological samples, and seized drug material. The results of

this structural analysis have demonstrated unique features of each cathinone; however, it has also shown features that are consistent among the group of stimulants. Aromatic rings, as those found on cathinones and other amphetamine-type stimulants, have been shown to interact with various serotonin receptor residues, specifically phenylalanine and tryptophan “within the likelihood of  $\pi$ - $\pi$  interactions” <sup>46</sup>. Specifically, MDPV,  $\alpha$ -PVP, ethylone, and pentylone showed norepinephrine uptake inhibition consistent with other cathinones, but increased serotonin uptake inhibition and mild serotonin release, physiological properties found in both cocaine and MDMA. Understanding how these unique and common features affect receptor binding, drug metabolism, and correlate to structure–activity relationships, will enable medical practitioners to have insight into proper preventative treatments and medical aid that may mitigate the undesirable effects of these drugs.

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## CHAPTER 4. ERDMANN'S SALT<sup>1</sup>

### INTRODUCTION

In the interest of researching an alternative complexing reagent to use for crystallizing and investigating seized drug material, Erdmann's salt, K[Co(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>4</sub>], was considered due to its lower cost and ease of synthesis.

Erdmann's salt, the ammonium tetrani<sup>t</sup>ro-diammine-cobaltiate, was first described in 1866.<sup>1</sup> The synthesis of the ammonium salt was improved by Jorgensen.<sup>2</sup> The crystal structure of the potassium Erdmann's salt, *trans*-[Co(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>4</sub>]<sup>-</sup>, was initially determined by X-ray diffraction using FeK<sub>α</sub> ( $\lambda=1.937\text{\AA}$ ) in 1956.<sup>3</sup>

An example of one drug compound from each of the previously described categories, (cocaine, methamphetamine, and methylone) was allowed to form crystal precipitates by the simple addition of a 10% aqueous solution of the potassium Erdmann's salt and a few milligrams of the target drug compound (Figure 4-1). Representative samples were selected from available law enforcement seizures in order to demonstrate the practical use of the reagent. All three of the drug compounds which have been shown to form cations via protonation of the amine moiety, were received as chloride salts, and, as expected, crystallized readily with the Erdmann's anion.

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<sup>1</sup> Unpublished work

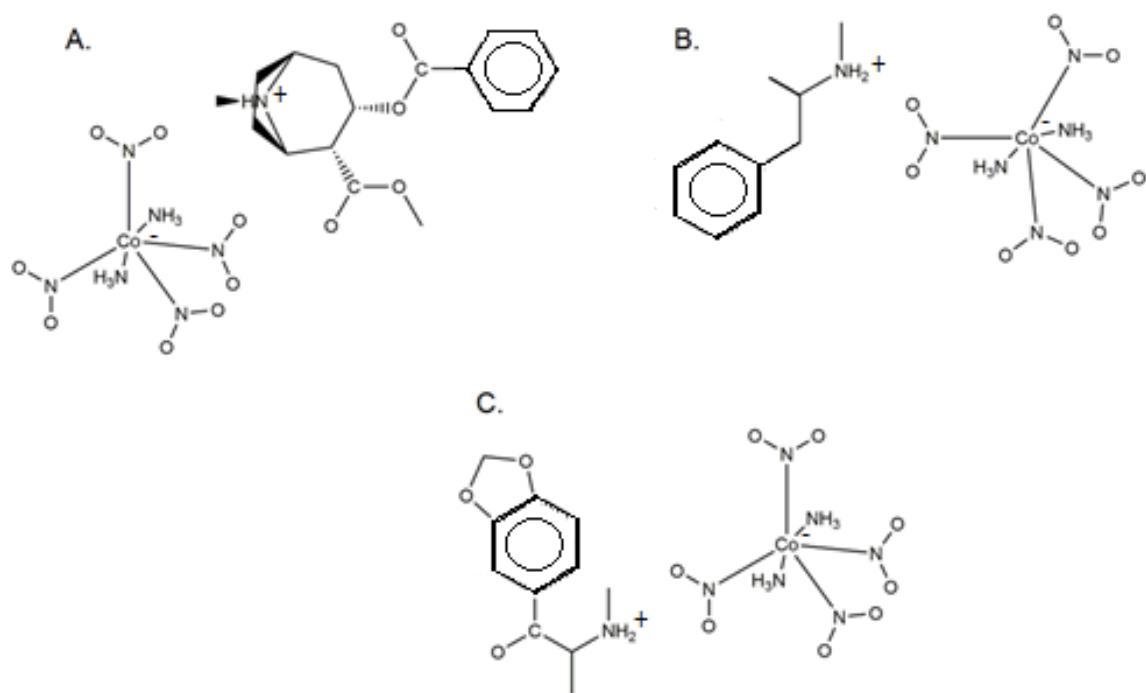


Figure 4-1. Diagrams of the Erdmann's salts of (A.) Cocaine, (B.) Methamphetamine, and (C.) Methylone.

SUMMARY OF CRYSTAL STRUCTURES DETERMINED

I. The Erdmann's Salt of Cocaine

(1R,2R,3S,5S,8S)-3-benzoyloxy-8-methyl-8-azabicyclo[3.2.1]octane-2-carboxylate tetranitrodiammine cobaltiate

II. The Erdmann's Salt of Methamphetamine

d-Methyl-(1-phenylpropan-2-yl)azanium tetranitrodiammine cobaltiate

III. The Erdmann's Salt of Methylone

1-(1,3-benzodioxol-5-yl)-2-(methylamino)-1-propanone tetranitrodiammine cobaltiate

## EXPERIMENTAL

### Synthesis and crystallization

The potassium salt of Erdmann's anion  $K[Co(NH_3)_2(NO_2)_4]$  (MW = 316.12 g/mol) was prepared by weighing 40.00g of  $CoCl_2 \cdot 6H_2O$  (0.1265 moles) dissolved in 100 mL of distilled water with stirring. In a separate beaker, 60.00g  $NaNO_2$  (MW = 69.01 g/mol) (0.869 moles) and 35.00g  $NH_4Cl$  (MW = 53.492 g/mol) (0.654 moles) were dissolved in 288 mL of distilled water with stirring and slight heating. This second solution was filtered through a glass-frit filter. To the second solution, 12 mL (0.180 moles) of conc.  $NH_4OH$  (15 M) was added with stirring. Both solutions were combined in a side-arm flask fitted with a rubber stopper and a glass tube (1 cm in diameter) to allow air to be drawn into the mixture. Air was bubbled vigorously through the mixture for 90 minutes. To the mixture was added 30 g KCl (MW = 74.55 g/mol) (0.402 moles) after which it turned from brown to brownish-red. The product was transferred to an evaporating dish where it was left for 2-3 days. It yielded a yellow-brown precipitate and a red-orange liquid. The solid was filtered using glass-frit filter and the precipitate was dissolved in 300 mL of distilled  $H_2O$  at 60°C. After 2 minutes, the solution was filtered through a glass-frit filter, and then cooled in an ice bath. The resulting crystals were recovered using a glass-frit filter.

A sample of a few milligrams of cocaine HCl from a law enforcement seizure was added to a glass slide with a single drop of a 5% Erdmann's potassium salt solution. Crystals of cocaine-tetranitrodiammine-cobaltiate(III)

began to form as yellow needles through slow evaporative condensation at room temperature. A suitable crystal was chosen for single crystal X-ray analysis.

Several milligrams of methamphetamine HCl was reacted with a drop of the previously prepared potassium Erdmann's salt on a pre-cleaned microscope slide. Yellow rods precipitated from solution and were allowed to grow at room temperature until they reached a size necessary for X-ray diffraction.

The synthetic cathinone, methylone, was also crystallized using the potassium Erdmann's salt reagent. A few crystals of methylone HCl were mixed on a glass slide with the test reagent and small yellow rods quickly grew out of the solution. A sample suitable for the single crystal X-ray diffraction experiment was chosen for analysis.

The identities of all three illicit drug specimens were previously confirmed by standard gas chromatography-mass spectrometry practices at the Ocean County Sheriff's Office forensic science laboratory.

The crystals were mounted on a Cryoloop using Paratone-N. The crystals were mounted on a 360° goniometer head on a Bruker Smart Apex using an Apex2 detector with a copper X-ray source. All of the diffraction patterns were obtained at 100 K. Experimental details are shown in Table 4-1.

**Table 4-1**

Experimental details.	Erdmann's Salt of Cocaine (I)	Erdmann's Salt of Methamphetamine (II)	Erdmann's Salt of Methylone (III)
<b>Crystal data</b>			
Chemical formula	$C_{17}H_{22}NO_4 \cdot CoH_6$ $N_6O_8$	$C_{10}H_{16}N \cdot CoH_6$ $N_6O_8$	$2(C_{11}H_{14}NO_3) \cdot CoH_6$ $N_6O_8$
$M_r$	581.39	427.27	693.5
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1$	Triclinic, $P\bar{1}$
$a, b, c$ (Å)	6.2403 (3), 11.0319 (4), 18.9421 (7)	6.3873 (2), 13.0182 (3), 21.6772 (5)	7.0440 (4), 10.3157 (7), 10.7700 (7)
$\alpha, \beta, \gamma$ (°)	106.450 (2), 93.831 (2), 92.655 (2)	90.94.6700 (17), 90	90.709 (4), 106.326 (4), 107.983 (4)
$V$ (Å <sup>3</sup> )	1244.94 (9)	1796.50 (8)	2052.60 (13)
$Z$	2	4	1
Density Mg m <sup>-3</sup>	1.551	1.580	1.622
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
$\mu$ (mm <sup>-1</sup> )	6.07	8.01	5.5
Temperature (K)	100	100	100
Shape, color	Needle, yellow	Rod, yellow	Rod, yellow
Crystal size (mm)	0.23 × 0.09 × 0.04	0.50 × 0.10 × 0.06	???
<b>Data collection</b>			
Diffractometer	Bruker APEXII CCD area-detector diffractometer		
Absorption correction	Numerical (SADABS; Sheldrick, 2008a)		
$T_{min}, T_{max}$	0.347, 0.772	0.440, 0.619	0.220, 0.682
$\theta_{min}, \theta_{max}$	2.4°, 69.3°	4.0°, 69.4°	4.3°, 49.8°
No. of measured, independent and observed [ $ I  > 2\sigma(I)$ ] reflections	9894, 5432, 4513	15772, 5875, 4066	6742, 1301, 1111
$R_{int}$	0.030	0.074	0.03
$(\sin \Theta/\lambda)_{max}$ (Å <sup>-1</sup> )	0.607	0.610	0.495

Refinement			
R[ $F^2 > 2\sigma(F^2)$ ],	0.038, 0.087,	0.057, 0.073,	
wR( $F^2$ ), S	0.95	0.90	0.070, 0.141, 1.09
No. of reflections	5432	5875	1301
No. of parameters	675	471	209
No. of restraints	3	1	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement		
$\Delta\rho_{\max}, \Delta\rho_{\min}(\text{e } \text{\AA}^{-3})$	0.43, -0.39	0.65, -0.48	0.53, -0.46
Absolute structure	-0.003 (4)	0.024 (6)	-
Friedel Pairs			
Flack parameter	-	-	-
Computer programs: <i>APEX 2</i> (Bruker, 2006), <i>APEX 2, SAINT</i> (Bruker, 2005), <i>SHELXTL</i> (Sheldrick, 2008b), <i>SHELXL2014/7</i> (Sheldrick, 2014), <i>SHELXTL</i> .			

#### Refinement:

All O-, N-, and C bound H atoms for (I), (II) and (III) were found in difference electron density maps. The methyl H atoms were placed with C—H = 0.98 Å and with initial torsion angles determined using a local difference Fourier calculation, and were constrained to have  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ . The torsion angle about the proximal C—C or C—N bond was permitted to vary during refinement. The methylene, methine, aromatic, and amine H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atoms, with C—H = 0.99, 1.00 and 0.95 Å , respectively. The N—H distances were constrained to 0.92 Å. All of the O-bound H atoms were placed in geometrically idealized positions and constrained to ride on their parent O atoms, with O—H = 0.84 Å. All of these had  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ,  $1.2U_{\text{eq}}(\text{N})$  or  $1.5U_{\text{eq}}(\text{O})$ . For all compounds, data collection: APEX2<sup>4</sup>; cell refinement: APEX2<sup>4</sup>; data reduction: SAINT<sup>5</sup>; program(s) used to solve structure: SHELXTL<sup>6</sup>; program(s) used to

refine structure: SHELXTL<sup>6</sup>; molecular graphics: SHELXTL<sup>6</sup>; software used to prepare material for publication: SHELXTL<sup>6</sup>.

## RESULTS

The absolute structures of three forensically important drugs were determined by precipitation with Erdmann's salt followed by single crystal X-ray diffraction. Cocaine, methamphetamine, and methylone were all encountered as the hydrochloride salts from law enforcement seizures. In each instance, the drug existed as the N protonated cation with a Cl anion. The Erdmann's anion from the potassium salt readily replaced the chloride when a drop of 10% aqueous solution of the Erdmann's salt was applied to a few milligrams of the drug compound. The resulting precipitates are the complex salt formed by the protonated cation and the anion in which the four NO<sub>2</sub> groups and the two *trans* NH<sub>3</sub> groups remained tightly bound to the central Co(III).

The Erdmann's salt of cocaine crystallizes in the P1 triclinic space group with two cocaine cations and two Erdmann's anions in the asymmetric unit (Figure 4-2). As seen in both cocaine gold(III) tetrachloride <sup>7</sup> and norcocaine <sup>8</sup>, there is an intramolecular hydrogen bond in each cation from the quaternary N to the carbonyl O of the methoxy carbonyl moiety. O3...H1A-N1 2.841Å and O15...H14A-N14 2.802Å. Both cations also have H bonds to symmetry related anions from the same quaternary N atoms, N1-H1A...O9 3.015Å [-1+x, y, z] and N14-H14A...O20 3.048Å [-1+x, y, z]. The first cation also has an H bond to an amine (N3) of the nearest Erdmann's anion O3...H3B-N3 3.058Å. Between the anions, both independently form chains that extend indefinitely with H bonds from N3 of one anion to O7 3.018Å of a symmetry [-1+x, y, z] related anion, and in the second anion O21...N8 3.045Å with the same symmetry [-1+x, y, z]. The

hydrogen bond between N3 and O7 passes between two hydrogens, H3A and H3C, at equal angles and distances, therefore it is difficult to determine which H participates in the H bond. The second Co<sub>2</sub> anion has an additional N9-H9A...O18 3.020Å [-1+x, y, z] H bond. See Table 4-2 for a list of the atoms, bond distances, and angles involved in the H bonding.

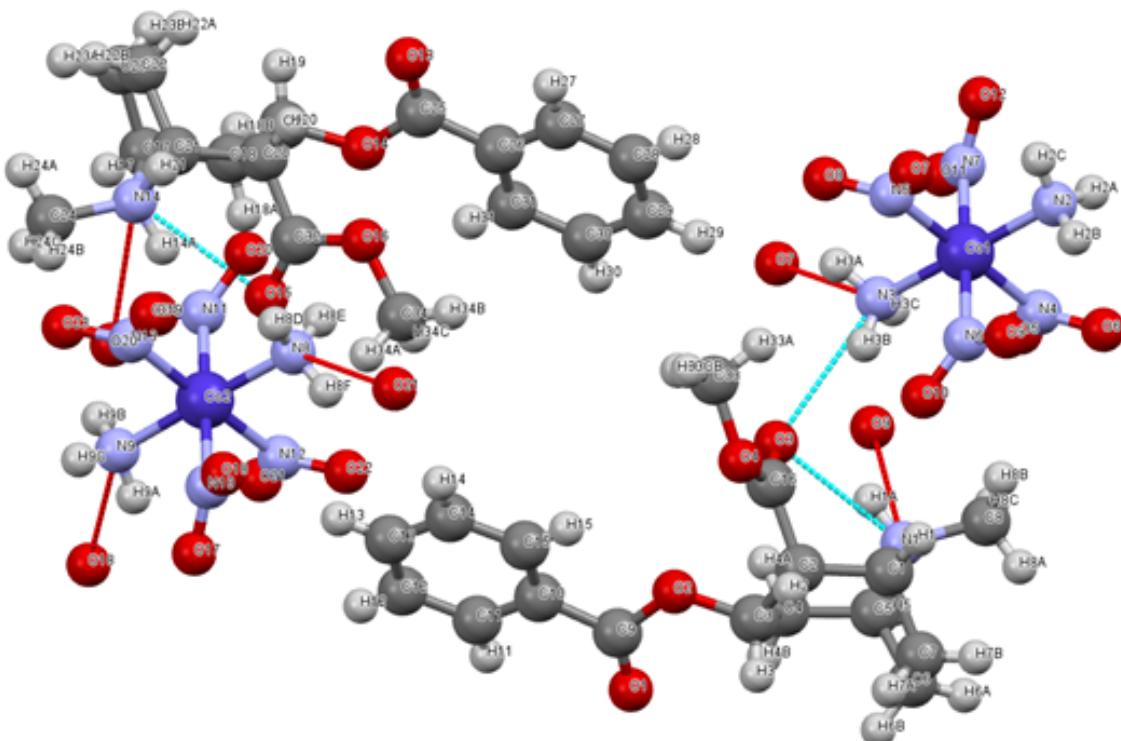


Figure 4-2. The asymmetric unit of (I) the Erdmann's Salt of cocaine with numbering. The figure shows the hydrogen bonding (teal dashed lines) within the asymmetric unit and additional H bonding to symmetry [-1+x, y, z] related atoms (red dashed lines).

The Erdmann's salt of methamphetamine crystallizes in the monoclinic space group P2<sub>1</sub> with Z = 4. One of the Erdmann's anions, with Co1 as the central cobalt, makes a hydrogen bond with the protonated N atom of one of the methamphetamine cations in the asymmetric unit N13-H13B...O1 2.887Å. The

2<sup>nd</sup> anion (Co2) makes a H bond to a symmetry related cation [-x, 1/2+y, -z] N14-H13A...O13 2.848 Å. In this crystal, both Erdmann's anions share two close contacts O1...O12 and O7...O13 between each other (figure 4-3).

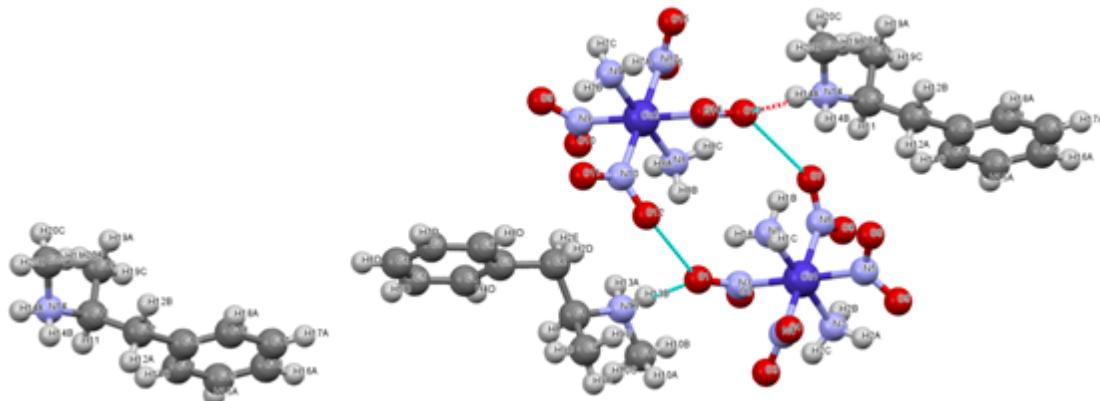


Figure 4-3. The asymmetric unit of (II) the Erdmann's salt of methamphetamine with numbering. An additional symmetry related cation was added to demonstrate the H bond (red dashed line) to the protonated N atom. H bonds and close contacts within the asymmetric unit are indicated (teal dashed lines).

The packing diagram (figure 4-4) shows the hydrogen bonding within the unit cell and highlights the close contacts between sets of Erdmann's anions.

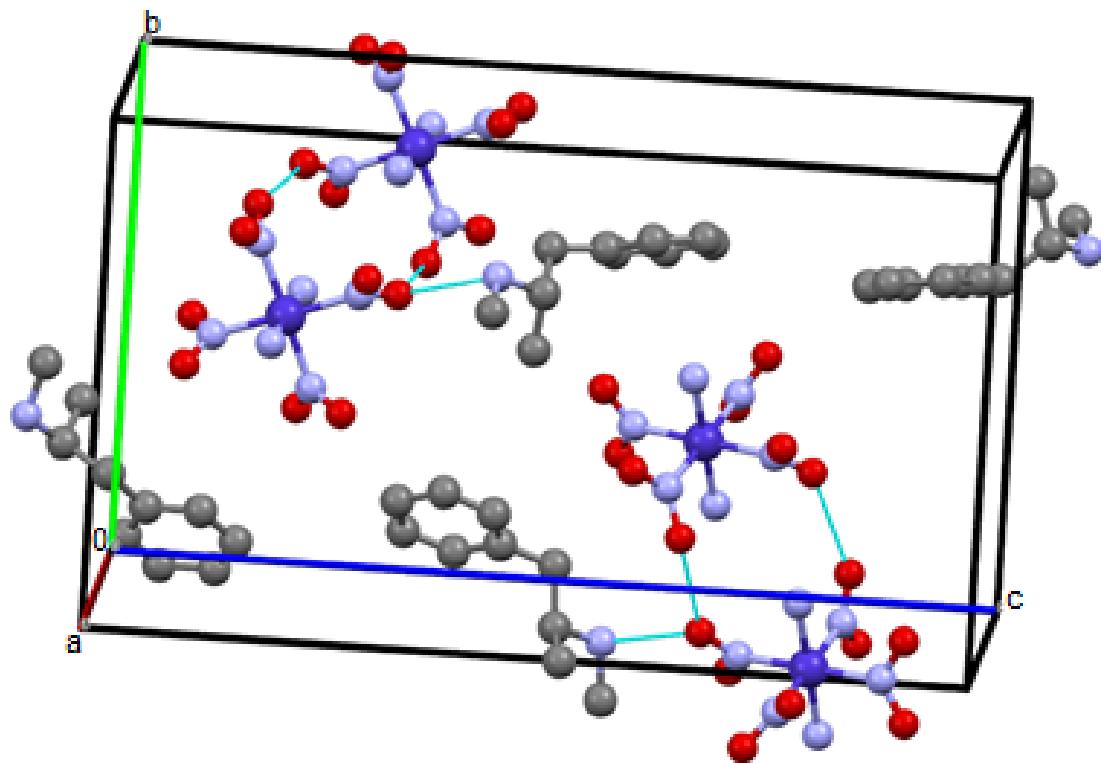


Figure 4-4. The packing diagram of (II) illustrates the sets of close contacts between Erdmann's anions and the H bonding to the methamphetamine cations.

**Table 4-2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I) The Erdmann's Salt of Cocaine

D—H…A	D—H	H…A	D…A	D— H…A
N1—H1A…O3	0.93	2.068	2.841(5)	139.5
N14—H14A…O15	0.93	2.023	2.802(6)	140.3
N1—H1A…O9 <sup>i</sup>	0.93	2.393	3.015(6)	124.1
N14—H14A…O20 <sup>i</sup>	0.93	2.497	3.048(6)	118.1
N3—H3B…O3	0.91	2.251	3.058(7)	147.5
N3—H3A(or C)…O7 <sup>i</sup>	0.91	2.615	3.018(6)	107.6
N8—H8F…O21 <sup>i</sup>	0.91	2.427	3.045(6)	125.3
N9—H9A…O18 <sup>i</sup>	0.91	2.349	3.020(6)	130.6

Symmetry: I = [-1+x, y, z]

Hydrogen-bond and close contact geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II) The Erdmann's Salt of Methamphetamine

D—H…A	D—H	H…A	D…A	D— H…A
N13—H13B…O1	0.91	1.983	2.887(8)	171.4
N14 <sup>ii</sup> —H14A <sup>ii</sup> …O13	0.91	1.957	2.848(8)	165.2
O1…O12			2.915(7)	
O7…O13			3.025(8)	

Symmetry: ii = [-x, 1/2+y, -z]

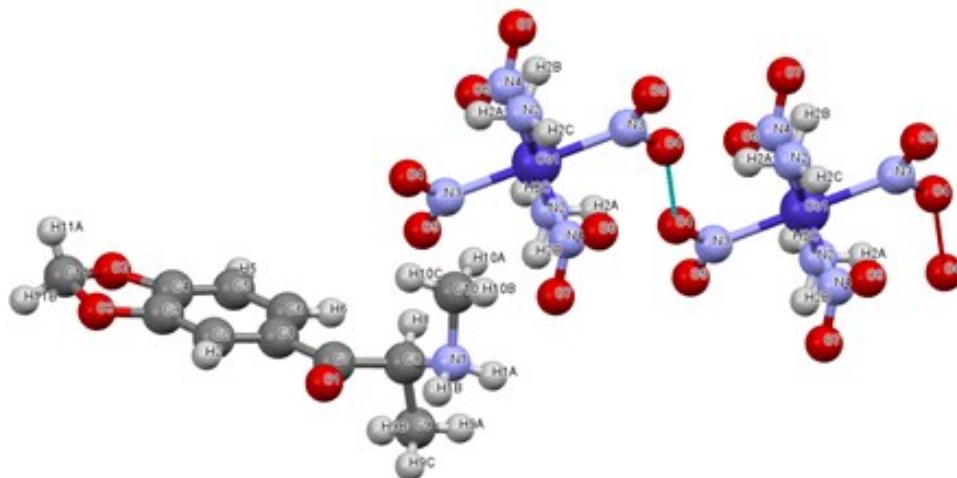
Hydrogen-bond and close contact geometry ( $\text{\AA}$ ,  $^\circ$ ) for (III) The Erdmann's Salt of Methylone

D—H…A	D—H	H…A	D…A	D— H…A
N2—H2A…O4 <sup>iii</sup>	0.91	2.334	3.15(1)	148.9
O4…O4 <sup>iii</sup>			3.015	

Symmetry: iii = [-x, -y, -z]

Methylone crystallized with Erdmann's anion in the P $\bar{1}$ , triclinic space group. A pair of symmetry related anions are joined across the inversion center of the unit cell by a hydrogen bond from N2-H2A to O4. Additionally, the O4 atoms of the symmetric pair are joined by close contacts. See Table 4-2 above

for bond distances and angles. Figure 4-5 shows the asymmetric unit with an additional symmetry-related [-x, -y, -z] anion present to show the close contact and to demonstrate the infinite propagation of anions this close contact allows. Interestingly, all of the H bonds in this crystal structure exclusively involve the anions. None involves the methylone cation.



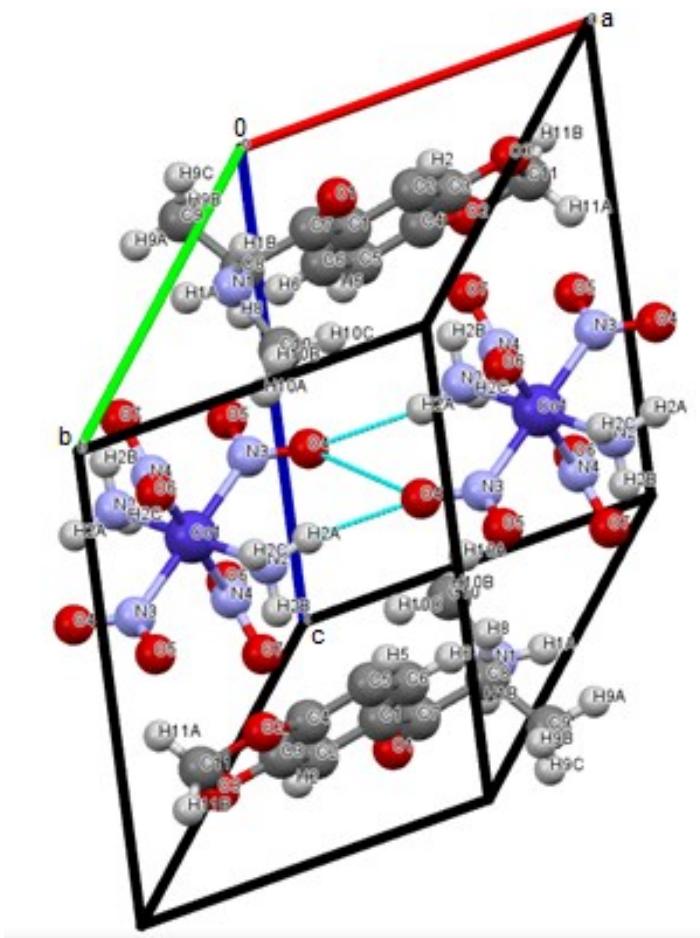


Figure 4-6. The packing diagram of (III) demonstrating the 'zig-zag' pattern of close contacts and the single H bond across the inversion center of the unit cell.

The powder diffraction pattern of the precipitation product of the potassium Erdmann's salt with each compound (Figure 4-7) will provide the necessary analytical confirmation to any forensic lab that is using powder X-ray diffraction in conjunction with crystal tests. X-ray diffraction is considered a "Category A" technique by the Scientific Working Group for the Analysis of Seized Drugs (SWGDrug) due to its high discrimination capabilities.<sup>9</sup>

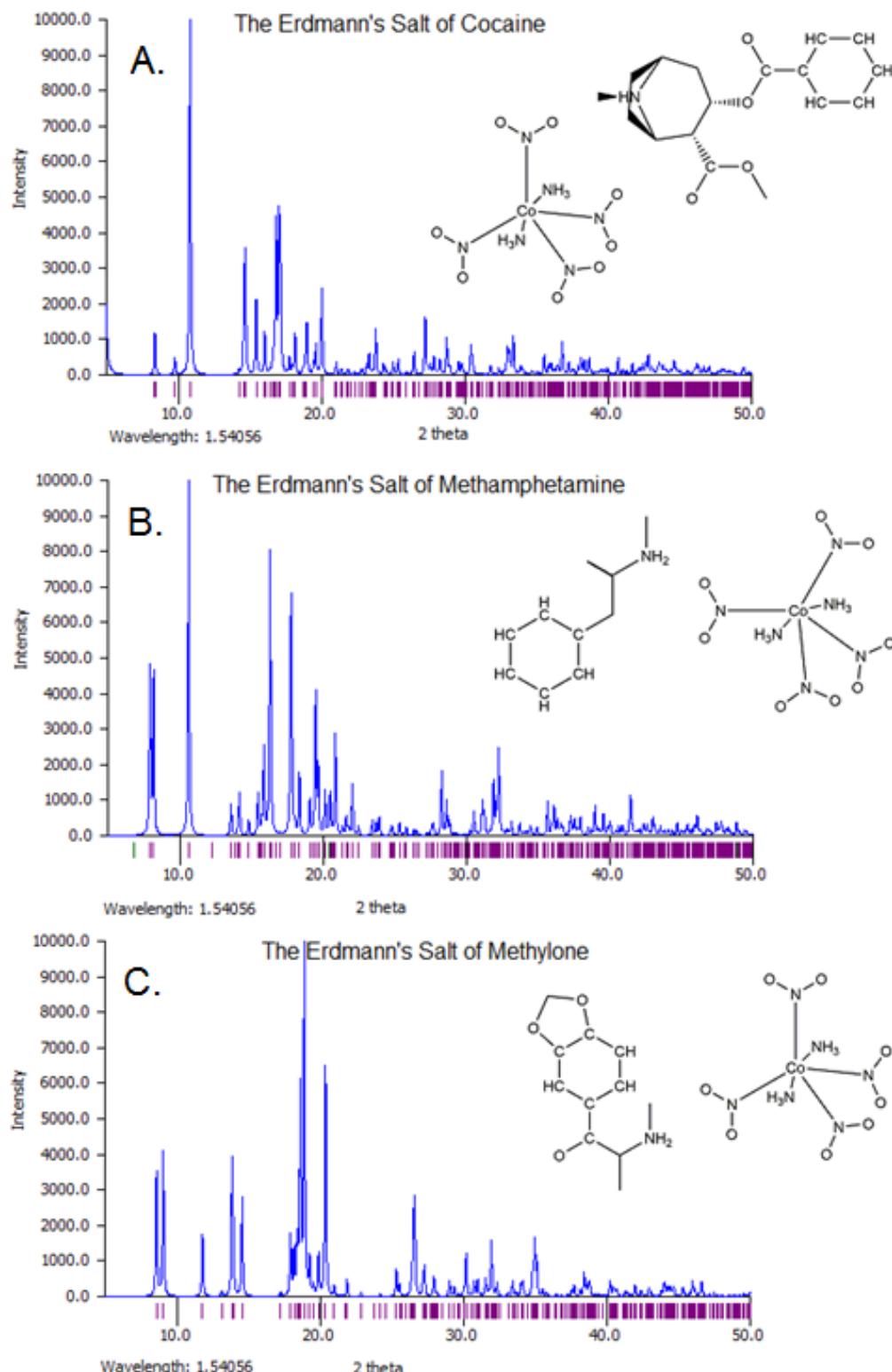


Figure 4-7. The X-ray powder diffraction patterns of (A.) the Erdmann's salt of cocaine, (B.) the Erdmann's salt of methamphetamine, (C.) the Erdmann's salt of methylone.

## CONCLUSION

Microcrystal tests is useful in the forensic science lab for their ability to quickly screen and presumptively identify a large number of drug substances. The Erdmann's salts have been shown to be a viable and inexpensive alternative to gold(III) chloride ( $\text{HAuCl}_4$ ) as a crystallizing reagent for forensic microcrystal tests. When a 10% solution of potassium Erdmann's salt is applied to a few milligrams of a suspected nitrogen-bearing drug compound, small crystals quickly form. The resulting crystal precipitates are suitable for single crystal X-ray diffraction analysis or comparison to the powder X-ray diffraction patterns calculated from previously solved structures, as examples, those presented here.

Using single crystal X-ray diffraction, the absolute structures of the Erdmann's salts of cocaine, methamphetamine, and methylone have been determined. Each structure demonstrates the unique atomic arrangement and bonding within the crystals.

The adoption and continued investigation of the utility of Erdmann's salt in forensic analytical testing scheme will aid the analyst by reducing sample preparation time, reduced reagent cost, and easy transfer of sample to a confirmation technique such as infrared spectroscopy or X-ray powder diffraction. Finally, testing with Erdmann's salt is essentially a non-destructive testing technique, preserving the resulting precipitate for further analysis or courtroom presentation.

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## CONCLUSION

Single crystal X-ray diffraction has been used to elucidate the absolute structure of nineteen forensically important compounds.

The structures analyzed within this research project included the precipitation products of the gold(III) chloride microcrystal test that has been used in the forensic analysis of drugs for over 150 years. Within this project, different classes of illegal drug compounds were examined. The first two compounds studied were cocaine and the final metabolite of cocaine, ecgonine. Both compounds were chosen to highlight the differences in both their microcrystal morphologies and their crystal lattices despite the similarities in their chemical structures. The second class of structures analyzed consisted of two controlled substances, methamphetamine and amphetamine, and the precursor, ephedrine. All three of these compounds differ only by a hydroxyl function on the  $\beta$  carbon, or a methyl group on the amine. The gold(III) chloride microcrystal test results demonstrate significant differences in their appearance, and the single crystal X-ray diffraction confirmed that the internal arrangement of atoms and bonds are considerably different, regardless of the relatedness of their structures. The X-ray structural analysis reveals the unique arrangement of atoms, close contacts, and hydrogen bonds that contribute to the morphology and microscopic characteristics of the microcrystal precipitates.

Synthetic cathinones, or “bath salts” have recently flooded the illicit drug market in a variety of analogues and structural modifications. Due to the recent emergence of these recreational drug compounds, very little is known regarding

their analytical profile, pharmacology, or even their structure. Many current analytical techniques employed by forensic laboratories rely on the comparison of chromatographs or spectra to a data library or simultaneous analyzed certified reference materials. In the case of never-before-seen drug products synthesized by clandestine chemists, these compounds do not have readily available standards. Single crystal X-ray diffraction provides a tool to the forensic community that produces the absolute identification of novel compounds. Once confirmed, the structural analysis verifies the results of other structural elucidation techniques, such as nmr, mass spectrometry, and infrared spectrophotometry. Furthermore, single crystal X-ray diffraction can be used to generate a library of unique powder diffraction spectra that can be used to quickly confirm the identity of drugs in laboratories that are equipped with this instrumentation. During the course of this research project, a number of synthetic cathinones were collected from law enforcement seizures and analyzed by single crystal X-ray diffraction. The results of the X-ray experiments confirmed the identity and structure of six new cathinone derivatives. Additionally, the structure analysis can be correlated to the physiological effects of these compounds through the analysis of the structure-activity relationships of known sympathomimetic compounds having similar features. This will aid clinicians and medical personnel in the emergent response to cathinone intoxications, by both quickly identifying the compound and better understanding the drug effects.

Erdmann's salt provides a low-cost crystallizing reagent that can be used in conjunction with powder X-ray diffraction to quickly identify drug compounds. Erdmann's was used with a representative compound from each class of drugs studied: cocaine, methamphetamine, and methylone. With each compound, Erdmann's formed a crystal precipitate that was suitable for single crystal X-ray diffraction. The resulting structures demonstrated the capability of Erdmann's anion to readily bind with nitrogen containing drug compounds and which were then used to generate powder diffraction patterns. The use of Erdmann's salt will allow laboratories equipped with powder X-ray diffractometers to produce microcrystals and then determine the powder pattern to confirm the drug presence in a relatively fast and non-destructive manner.

The results of this research and thesis provide fundamental support for the crystallographic characterization of the gold(III) chloride microcrystal test and for the incorporation of Erdmann's salt into the battery of testing for forensic science laboratories. The field of forensic science would benefit greatly from the continued investigation into the crystallographic characterization of microcrystal test products and the further development of a database of powder X-ray diffraction patterns that include these precipitates.

APPENDIX 1 (A) – COCAINE GOLD(III) TETRACHLORIDE  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	1.48067 (3)	-0.08296 (2)	0.827908 (6)	0.04897 (9)
Cl1	1.4831 (3)	-0.26793 (18)	0.77877 (5)	0.0723 (4)
O1	0.4481 (8)	0.5175 (7)	0.89138 (15)	0.0864 (16)
N1	1.1201 (7)	0.4034 (5)	0.83739 (15)	0.0523 (10)
H1A	1.1616	0.4136	0.8657	0.063*
C1	0.9621 (9)	0.3070 (6)	0.83835 (19)	0.0570 (14)
H1	0.9962	0.2074	0.8401	0.068*
Cl2	1.18875 (19)	-0.0958 (2)	0.83312 (6)	0.0714 (4)
O2	0.7201 (6)	0.5528 (5)	0.91443 (13)	0.0617 (10)
C2	0.8493 (9)	0.3483 (7)	0.87798 (19)	0.0539 (14)
H2	0.7457	0.2887	0.8777	0.065*
Cl3	1.7706 (2)	-0.0551 (2)	0.81918 (6)	0.0739 (5)
C3	0.7920 (10)	0.5049 (7)	0.87294 (19)	0.0602 (16)
H3	0.7043	0.5118	0.8494	0.072*
O3	1.0932 (7)	0.3471 (7)	0.92750 (16)	0.0824 (16)
Cl4	1.4790 (3)	0.0911 (2)	0.88051 (6)	0.0821 (4)
O4	0.8372 (7)	0.2909 (5)	0.95482 (16)	0.0682 (13)
C4	0.9404 (9)	0.5985 (6)	0.86168 (18)	0.0603 (15)
H4A	1.0157	0.6069	0.8875	0.072*
H4B	0.8977	0.6922	0.8544	0.072*
C5	1.0429 (10)	0.5405 (6)	0.82234 (17)	0.0580 (14)
H5	1.1329	0.6072	0.8130	0.070*
C6	0.9317 (11)	0.4944 (9)	0.7824 (2)	0.074 (2)
H6A	0.9976	0.4989	0.7549	0.089*
H6B	0.8307	0.5545	0.7796	0.089*
C7	0.8782 (12)	0.3408 (10)	0.7928 (2)	0.079 (2)
H7A	0.7534	0.3326	0.7946	0.095*
H7B	0.9203	0.2769	0.7699	0.095*
C8	1.2631 (11)	0.3534 (9)	0.8075 (2)	0.0745 (19)
H8A	1.2221	0.3488	0.7772	0.112*
H8B	1.3004	0.2612	0.8168	0.112*
H8C	1.3585	0.4182	0.8092	0.112*

C9	0.5503 (9)	0.5465 (6)	0.92093 (18)	0.0567 (14)
C10	0.5017 (10)	0.5735 (6)	0.96792 (18)	0.0636 (15)
C11	0.3276 (12)	0.5805 (9)	0.9789 (2)	0.0789 (19)
H11	0.2428	0.5779	0.9569	0.095*
C12	0.2836 (13)	0.5915 (10)	1.0241 (3)	0.093 (3)
H12	0.1675	0.5976	1.0320	0.112*
C13	0.4045 (17)	0.5937 (12)	1.0569 (3)	0.105 (4)
H13	0.3716	0.5986	1.0867	0.126*
C14	0.5712 (15)	0.5886 (13)	1.0458 (2)	0.098 (3)
H14	0.6539	0.5902	1.0683	0.117*
C15	0.6257 (13)	0.5810 (10)	1.0012 (2)	0.080 (2)
H15	0.7428	0.5810	0.9941	0.096*
C16	0.9428 (9)	0.3258 (6)	0.92225 (19)	0.0543 (14)
C17	0.9164 (12)	0.2851 (10)	0.9998 (3)	0.088 (3)
H17A	1.0242	0.2350	0.9982	0.132*
H17B	0.8398	0.2369	1.0199	0.132*
H17C	0.9365	0.3795	1.0104	0.132*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Au1	0.03817 (12)	0.06238 (13)	0.04636 (12)	-0.00480 (9)	-0.00432 (8)	0.01037 (9)
Cl1	0.0674 (10)	0.0800 (9)	0.0696 (8)	-0.0057 (9)	0.0116 (8)	-0.0080 (7)
O1	0.074 (4)	0.133 (5)	0.053 (2)	0.001 (3)	0.002 (2)	-0.009 (3)
N1	0.058 (3)	0.059 (3)	0.039 (2)	0.001 (2)	0.0005 (17)	0.001 (2)
C1	0.066 (4)	0.050 (2)	0.056 (3)	-0.004 (3)	0.007 (3)	-0.012 (2)
Cl2	0.0421 (7)	0.0984 (11)	0.0736 (9)	-0.0079 (8)	0.0022 (6)	-0.0121 (10)
O2	0.067 (3)	0.076 (3)	0.0423 (18)	0.004 (2)	0.0038 (17)	-0.0078 (18)
C2	0.056 (4)	0.060 (3)	0.046 (3)	-0.013 (3)	0.002 (3)	-0.005 (2)
Cl3	0.0411 (7)	0.1031 (13)	0.0776 (10)	-0.0110 (8)	-0.0036 (6)	0.0147 (9)
C3	0.063 (4)	0.075 (4)	0.043 (3)	0.018 (3)	0.006 (3)	-0.005 (3)
O3	0.067 (3)	0.129 (5)	0.051 (2)	-0.005 (3)	0.001 (2)	0.028 (3)
Cl4	0.0770 (11)	0.0890 (10)	0.0803 (9)	-0.0171 (12)	-0.0051 (9)	-0.0206 (8)
O4	0.076 (3)	0.071 (3)	0.058 (2)	-0.013 (2)	0.014 (2)	0.014 (2)

C4	0.090 (4)	0.044 (2)	0.047 (3)	0.004 (3)	0.011 (3)	-0.002 (2)
C5	0.077 (4)	0.050 (2)	0.047 (3)	0.004 (3)	0.010 (3)	0.008 (2)
C6	0.080 (5)	0.102 (5)	0.039 (3)	0.028 (4)	0.001 (3)	0.003 (3)
C7	0.077 (5)	0.110 (6)	0.050 (3)	-0.006 (4)	-0.001 (3)	-0.036 (4)
C8	0.072 (5)	0.096 (5)	0.056 (3)	0.019 (4)	0.013 (3)	0.003 (3)
C9	0.068 (4)	0.055 (3)	0.047 (3)	0.005 (3)	0.006 (3)	0.002 (2)
C10	0.087 (5)	0.054 (3)	0.050 (3)	0.013 (4)	0.016 (3)	-0.001 (2)
C11	0.095 (5)	0.076 (4)	0.066 (4)	-0.001 (5)	0.018 (4)	-0.011 (4)
C12	0.103 (6)	0.092 (5)	0.085 (5)	-0.007 (6)	0.044 (5)	-0.032 (5)
C13	0.178 (11)	0.086 (5)	0.051 (4)	-0.022 (7)	0.038 (5)	-0.022 (4)
C14	0.134 (8)	0.112 (7)	0.047 (4)	-0.007 (7)	0.011 (4)	-0.018 (4)
C15	0.107 (6)	0.085 (5)	0.048 (3)	-0.003 (5)	0.007 (3)	-0.011 (4)
C16	0.062 (4)	0.051 (3)	0.050 (3)	-0.007 (3)	0.006 (3)	0.008 (2)
C17	0.088 (6)	0.107 (6)	0.068 (4)	0.004 (5)	0.016 (4)	0.038 (4)

GEOMETRIC PARAMETERS ( $\text{\AA}$ ,  $^\circ$ )

Au1—Cl2	2.2669 (15)	C5—C6	1.535 (10)
Au1—Cl3	2.2732 (15)	C5—H5	0.9800
Au1—Cl4	2.2766 (17)	C6—C7	1.542 (12)
Au1—Cl1	2.2843 (16)	C6—H6A	0.9700
O1—C9	1.217 (9)	C6—H6B	0.9700
N1—C5	1.497 (7)	C7—H7A	0.9700
N1—C8	1.500 (8)	C7—H7B	0.9700
N1—C1	1.525 (8)	C8—H8A	0.9600
N1—H1A	0.9100	C8—H8B	0.9600
C1—C2	1.523 (8)	C8—H8C	0.9600
C1—C7	1.541 (10)	C9—C10	1.477 (7)
C1—H1	0.9800	C10—C15	1.384 (11)
O2—C9	1.330 (9)	C10—C11	1.389 (12)
O2—C3	1.433 (7)	C11—C12	1.398 (10)
C2—C16	1.523 (9)	C11—H11	0.9300
C2—C3	1.552 (9)	C12—C13	1.354 (15)
C2—H2	0.9800	C12—H12	0.9300
C3—C4	1.488 (10)	C13—C14	1.333 (17)
C3—H3	0.9800	C13—H13	0.9300
O3—C16	1.192 (9)	C14—C15	1.399 (10)
O4—C16	1.314 (8)	C14—H14	0.9300

O4—C17	1.478 (10)	C15—H15	0.9300
C4—C5	1.521 (8)	C17—H17A	0.9600
C4—H4A	0.9700	C17—H17B	0.9600
C4—H4B	0.9700	C17—H17C	0.9600
Cl2—Au1—Cl3	175.52 (8)	C7—C6—H6A	110.7
Cl2—Au1—Cl4	89.17 (7)	C5—C6—H6B	110.7
Cl3—Au1—Cl4	90.08 (7)	C7—C6—H6B	110.7
Cl2—Au1—Cl1	90.66 (7)	H6A—C6—H6B	108.8
Cl3—Au1—Cl1	90.37 (7)	C1—C7—C6	105.1 (6)
Cl4—Au1—Cl1	176.33 (7)	C1—C7—H7A	110.7
C5—N1—C8	112.8 (5)	C6—C7—H7A	110.7
C5—N1—C1	101.7 (5)	C1—C7—H7B	110.7
C8—N1—C1	114.5 (5)	C6—C7—H7B	110.7
C5—N1—H1A	109.2	H7A—C7—H7B	108.8
C8—N1—H1A	109.2	N1—C8—H8A	109.5
C1—N1—H1A	109.2	N1—C8—H8B	109.5
C2—C1—N1	108.7 (4)	H8A—C8—H8B	109.5
C2—C1—C7	113.2 (6)	N1—C8—H8C	109.5
N1—C1—C7	101.4 (5)	H8A—C8—H8C	109.5
C2—C1—H1	111.1	H8B—C8—H8C	109.5
N1—C1—H1	111.1	O1—C9—O2	123.1 (6)
C7—C1—H1	111.1	O1—C9—C10	124.4 (7)
C9—O2—C3	119.7 (5)	O2—C9—C10	112.5 (6)
C1—C2—C16	111.7 (6)	C15—C10—C11	120.0 (6)
C1—C2—C3	109.4 (5)	C15—C10—C9	121.1 (7)
C16—C2—C3	110.7 (5)	C11—C10—C9	118.7 (7)
C1—C2—H2	108.3	C10—C11—C12	118.0 (8)
C16—C2—H2	108.3	C10—C11—H11	121.0
C3—C2—H2	108.3	C12—C11—H11	121.0
O2—C3—C4	107.9 (5)	C13—C12—C11	122.1 (9)
O2—C3—C2	109.2 (5)	C13—C12—H12	118.9
C4—C3—C2	111.7 (5)	C11—C12—H12	118.9
O2—C3—H3	109.4	C14—C13—C12	119.2 (7)
C4—C3—H3	109.4	C14—C13—H13	120.4
C2—C3—H3	109.4	C12—C13—H13	120.4
C16—O4—C17	115.2 (6)	C13—C14—C15	122.1 (10)
C3—C4—C5	111.3 (5)	C13—C14—H14	119.0

C3—C4—H4A	109.4	C15—C14—H14	119.0
C5—C4—H4A	109.4	C10—C15—C14	118.6 (9)
C3—C4—H4B	109.4	C10—C15—H15	120.7
C5—C4—H4B	109.4	C14—C15—H15	120.7
H4A—C4—H4B	108.0	O3—C16—O4	123.5 (6)
N1—C5—C4	106.7 (4)	O3—C16—C2	123.7 (6)
N1—C5—C6	102.2 (5)	O4—C16—C2	112.6 (6)
C4—C5—C6	114.3 (6)	O4—C17—H17A	109.5
N1—C5—H5	111.0	O4—C17—H17B	109.5
C4—C5—H5	111.0	H17A—C17—H17B	109.5
C6—C5—H5	111.0	O4—C17—H17C	109.5
C5—C6—C7	105.1 (5)	H17A—C17—H17C	109.5
C5—C6—H6A	110.7	H17B—C17—H17C	109.5
C5—N1—C1—C2	-72.3 (5)	C2—C1—C7—C6	87.9 (7)
C8—N1—C1—C2	165.7 (5)	N1—C1—C7—C6	-28.4 (7)
C5—N1—C1—C7	47.1 (5)	C5—C6—C7—C1	0.0 (8)
C8—N1—C1—C7	-74.8 (6)	C3—O2—C9—O1	-9.1 (9)
N1—C1—C2—C16	-63.0 (6)	C3—O2—C9—C10	168.9 (5)
C7—C1—C2—C16	-174.8 (6)	O1—C9—C10—C15	168.4 (7)
N1—C1—C2—C3	59.8 (6)	O2—C9—C10—C15	-9.6 (9)
C7—C1—C2—C3	-52.0 (7)	O1—C9—C10—C11	-6.7 (10)
C9—O2—C3—C4	144.1 (6)	O2—C9—C10—C11	175.3 (6)
C9—O2—C3—C2	-94.4 (6)	C15—C10—C11—C12	-1.6 (12)
C1—C2—C3—O2	-167.1 (6)	C9—C10—C11—C12	173.6 (7)
C16—C2—C3—O2	-43.6 (7)	C10—C11—C12—C13	-0.9 (14)
C1—C2—C3—C4	-47.9 (7)	C11—C12—C13—C14	1.7 (18)
C16—C2—C3—C4	75.6 (6)	C12—C13—C14—C15	0 (2)
O2—C3—C4—C5	170.4 (5)	C11—C10—C15—C14	3.1 (13)
C2—C3—C4—C5	50.5 (7)	C9—C10—C15—C14	-171.9 (9)
C8—N1—C5—C4	-164.0 (6)	C13—C14—C15—C10	-2 (2)
C1—N1—C5—C4	72.9 (5)	C17—O4—C16—O3	2.4 (11)
C8—N1—C5—C6	75.7 (7)	C17—O4—C16—C2	-172.7 (6)
C1—N1—C5—C6	-47.4 (6)	C1—C2—C16—O3	37.0 (9)
C3—C4—C5—N1	-64.8 (7)	C3—C2—C16—O3	-85.2 (9)
C3—C4—C5—C6	47.4 (7)	C1—C2—C16—O4	-148.0 (5)
N1—C5—C6—C7	29.1 (7)	C3—C2—C16—O4	89.9 (6)
C4—C5—C6—C7	-85.8 (6)		

APPENDIX 1 (B) – ECGONINE HYDROCHLORIDE  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	1.15082 (5)	0.03004 (3)	0.93490 (2)	0.01911 (12)
O1	1.11678 (16)	0.09863 (10)	0.66307 (8)	0.0223 (3)
N1	0.90975 (18)	0.22175 (10)	0.80625 (10)	0.0151 (3)
H1A	0.993 (3)	0.1724 (15)	0.7911 (13)	0.011 (4)*
C1	0.8277 (2)	0.27231 (12)	0.70884 (11)	0.0166 (3)
H1	0.9205	0.3299	0.6810	0.020*
O2	1.00257 (18)	0.10367 (10)	0.50203 (8)	0.0225 (2)
H2A	1.114 (4)	0.0701 (18)	0.4919 (16)	0.030 (6)*
C2	0.7936 (2)	0.17867 (12)	0.63060 (10)	0.0156 (3)
H2	0.7340	0.2120	0.5675	0.019*
O3	0.65419 (18)	-0.00835 (9)	0.61569 (9)	0.0209 (2)
H3A	0.581 (3)	-0.0049 (18)	0.5697 (17)	0.027 (6)*
C3	0.6447 (2)	0.09137 (11)	0.67333 (11)	0.0167 (3)
H3	0.5062	0.1221	0.6690	0.020*
C4	0.6902 (2)	0.06231 (11)	0.78466 (11)	0.0171 (3)
H4A	0.5763	0.0204	0.8136	0.021*
H4B	0.8093	0.0137	0.7871	0.021*
C5	0.7279 (2)	0.16482 (12)	0.85015 (10)	0.0160 (3)
H5	0.7488	0.1445	0.9236	0.019*
C6	0.5645 (2)	0.25347 (13)	0.83876 (12)	0.0199 (3)
H6A	0.5552	0.2995	0.9013	0.024*
H6B	0.4331	0.2186	0.8258	0.024*
C7	0.6311 (2)	0.32474 (12)	0.74556 (11)	0.0198 (3)
H7A	0.5292	0.3225	0.6907	0.024*
H7B	0.6523	0.4029	0.7662	0.024*
C8	0.9992 (3)	0.30568 (12)	0.87629 (12)	0.0208 (3)
H8A	0.8960	0.3583	0.8980	0.031*
H8B	1.1057	0.3457	0.8404	0.031*
H8C	1.0548	0.2683	0.9365	0.031*
C9	0.9887 (2)	0.12311 (12)	0.60124 (11)	0.0170 (3)

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.02045 (18)	0.02077 (18)	0.01611 (18)	0.00468 (14)	-0.00101 (13)	0.00132 (12)
O1	0.0185 (6)	0.0301 (6)	0.0183 (5)	0.0077 (5)	-0.0008 (4)	-0.0025 (4)
N1	0.0164 (6)	0.0132 (6)	0.0157 (6)	0.0007 (5)	0.0003 (5)	-0.0015 (5)
C1	0.0207 (7)	0.0145 (6)	0.0146 (7)	0.0008 (6)	0.0011 (6)	0.0021 (5)
O2	0.0237 (6)	0.0285 (6)	0.0153 (5)	0.0099 (5)	0.0032 (4)	-0.0007 (4)
C2	0.0178 (7)	0.0161 (7)	0.0130 (6)	0.0019 (6)	-0.0001 (6)	0.0018 (6)
O3	0.0223 (5)	0.0192 (5)	0.0212 (5)	0.0010 (4)	-0.0055 (5)	-0.0052 (4)
C3	0.0155 (6)	0.0160 (7)	0.0186 (7)	0.0013 (6)	-0.0009 (6)	-0.0031 (5)
C4	0.0190 (7)	0.0152 (7)	0.0171 (7)	-0.0021 (5)	-0.0001 (6)	0.0019 (5)
C5	0.0170 (7)	0.0168 (7)	0.0143 (6)	-0.0007 (6)	0.0015 (6)	0.0014 (5)
C6	0.0213 (8)	0.0215 (8)	0.0168 (7)	0.0036 (6)	0.0025 (6)	-0.0001 (6)
C7	0.0243 (8)	0.0182 (7)	0.0169 (7)	0.0065 (6)	0.0005 (6)	0.0022 (6)
C8	0.0258 (8)	0.0170 (7)	0.0198 (7)	-0.0018 (6)	-0.0034 (7)	-0.0034 (6)
C9	0.0196 (7)	0.0148 (6)	0.0165 (7)	-0.0013 (6)	0.0008 (6)	-0.0003 (5)

GEOMETRIC PARAMETERS ( $\text{\AA}$ ,  $^\circ$ )

O1—C9	1.214 (2)	C3—C4	1.5266 (19)
N1—C8	1.4897 (19)	C3—H3	1.0000
N1—C5	1.5106 (18)	C4—C5	1.524 (2)
N1—C1	1.5141 (19)	C4—H4A	0.9900
N1—H1A	0.84 (2)	C4—H4B	0.9900
C1—C7	1.537 (2)	C5—C6	1.536 (2)
C1—C2	1.5397 (19)	C5—H5	1.0000
C1—H1	1.0000	C6—C7	1.555 (2)
O2—C9	1.3202 (18)	C6—H6A	0.9900
O2—H2A	0.86 (3)	C6—H6B	0.9900
C2—C9	1.518 (2)	C7—H7A	0.9900
C2—C3	1.553 (2)	C7—H7B	0.9900
C2—H2	1.0000	C8—H8A	0.9800
O3—C3	1.4196 (17)	C8—H8B	0.9800
O3—H3A	0.78 (2)	C8—H8C	0.9800

C8—N1—C5	113.55 (12)	C3—C4—H4B	109.1
C8—N1—C1	112.88 (11)	H4A—C4—H4B	107.8
C5—N1—C1	102.09 (11)	N1—C5—C4	106.79 (11)
C8—N1—H1A	110.9 (12)	N1—C5—C6	102.78 (12)
C5—N1—H1A	107.8 (12)	C4—C5—C6	113.04 (12)
C1—N1—H1A	109.2 (11)	N1—C5—H5	111.3
N1—C1—C7	102.35 (11)	C4—C5—H5	111.3
N1—C1—C2	108.47 (11)	C6—C5—H5	111.3
C7—C1—C2	112.42 (12)	C5—C6—C7	104.81 (12)
N1—C1—H1	111.1	C5—C6—H6A	110.8
C7—C1—H1	111.1	C7—C6—H6A	110.8
C2—C1—H1	111.1	C5—C6—H6B	110.8
C9—O2—H2A	107.2 (14)	C7—C6—H6B	110.8
C9—C2—C1	111.31 (12)	H6A—C6—H6B	108.9
C9—C2—C3	110.15 (11)	C1—C7—C6	105.24 (12)
C1—C2—C3	110.69 (11)	C1—C7—H7A	110.7
C9—C2—H2	108.2	C6—C7—H7A	110.7
C1—C2—H2	108.2	C1—C7—H7B	110.7
C3—C2—H2	108.2	C6—C7—H7B	110.7
C3—O3—H3A	109.7 (16)	H7A—C7—H7B	108.8
O3—C3—C4	107.59 (11)	N1—C8—H8A	109.5
O3—C3—C2	110.75 (11)	N1—C8—H8B	109.5
C4—C3—C2	111.71 (12)	H8A—C8—H8B	109.5
O3—C3—H3	108.9	N1—C8—H8C	109.5
C4—C3—H3	108.9	H8A—C8—H8C	109.5
C2—C3—H3	108.9	H8B—C8—H8C	109.5
C5—C4—C3	112.45 (11)	O1—C9—O2	124.07 (15)
C5—C4—H4A	109.1	O1—C9—C2	123.17 (13)
C3—C4—H4A	109.1	O2—C9—C2	112.76 (13)
C5—C4—H4B	109.1		
C8—N1—C1—C7	-76.54 (14)	C1—N1—C5—C4	73.48 (13)
C5—N1—C1—C7	45.72 (13)	C8—N1—C5—C6	76.10 (14)
C8—N1—C1—C2	164.47 (12)	C1—N1—C5—C6	-45.70 (13)
C5—N1—C1—C2	-73.27 (13)	C3—C4—C5—N1	-62.00 (15)
N1—C1—C2—C9	-63.62 (15)	C3—C4—C5—C6	50.30 (16)
C7—C1—C2—C9	-176.06 (12)	N1—C5—C6—C7	27.58 (14)
N1—C1—C2—C3	59.24 (15)	C4—C5—C6—C7	-87.15 (14)
C7—C1—C2—C3	-53.20 (15)	N1—C1—C7—C6	-27.97 (14)

C9—C2—C3—O3	-40.45 (15)	C2—C1—C7—C6	88.20 (14)
C1—C2—C3—O3	-163.98 (12)	C5—C6—C7—C1	0.32 (16)
C9—C2—C3—C4	79.46 (14)	C1—C2—C9—O1	43.35 (19)
C1—C2—C3—C4	-44.07 (15)	C3—C2—C9—O1	-79.82 (17)
O3—C3—C4—C5	167.87 (12)	C1—C2—C9—O2	-137.22 (13)
C2—C3—C4—C5	46.12 (16)	C3—C2—C9—O2	99.61 (14)
C8—N1—C5—C4	-164.71 (12)		

APPENDIX 1 (C) – THE HYDRATED ECGONINE  
 GOLD(III) TETRACHLORIDE SALT  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.74862 (5)	0.93435 (3)	0.715499 (8)	0.02738 (10)
Cl1	0.5420 (3)	0.93399 (18)	0.691119 (6)	0.0428 (6)
Cl2	0.7528 (3)	0.78521 (14)	0.71406 (4)	0.0293 (5)
Cl3	0.7363 (3)	1.08209 (16)	0.71804 (5)	0.0379 (6)
Cl4	0.9628 (3)	0.93526 (17)	0.73783 (5)	0.0375 (5)
O1A	0.1554 (8)	0.8451 (5)	0.66339 (15)	0.0371 (17)
O2A	-0.0728 (9)	0.8215 (5)	0.64890 (16)	0.0420 (19)
O3A	0.0555 (8)	0.6494 (5)	0.63127 (13)	0.0322 (15)
N1A	0.2677 (9)	0.7238 (5)	0.69855 (16)	0.0246 (17)
H1NA	0.2816	0.7672	0.6862	0.030*
C1A	0.1077 (11)	0.7106 (6)	0.70197 (18)	0.027 (2)
H1A	0.0664	0.7570	0.7135	0.032*
C2A	0.0357 (11)	0.7137 (6)	0.67500 (19)	0.028 (2)
H2A	-0.0697	0.7008	0.6775	0.033*
C3A	0.0996 (11)	0.6393 (6)	0.65789 (19)	0.029 (2)
H3A	0.0604	0.5824	0.6644	0.035*
C4A	0.2634 (12)	0.6351 (7)	0.65901 (18)	0.030 (2)
H4A1	0.3049	0.6849	0.6492	0.037*
H4A2	0.2972	0.5804	0.6507	0.037*
C5A	0.3166 (12)	0.6382 (6)	0.6871 (2)	0.030 (2)
H5A	0.4245	0.6319	0.6880	0.036*
C6A	0.2402 (12)	0.5736 (7)	0.7054 (2)	0.033 (2)
H6A1	0.3041	0.5581	0.7201	0.040*
H6A2	0.2133	0.5195	0.6960	0.040*
C7A	0.1011 (12)	0.6228 (7)	0.7152 (2)	0.035 (2)
H7A1	0.0120	0.5908	0.7102	0.042*
H7A2	0.1030	0.6295	0.7343	0.042*
C8A	0.3460 (13)	0.7509 (8)	0.72283 (19)	0.039 (2)
H8A1	0.3037	0.8052	0.7295	0.059*
H8A2	0.4489	0.7601	0.7189	0.059*

H8A3	0.3363	0.7049	0.7359	0.059*
C9A	0.0463 (13)	0.8008 (6)	0.66226 (19)	0.034 (2)
Au2	0.30570 (5)	0.92904 (3)	0.794261 (8)	0.02713 (10)
Cl5	0.2768 (3)	0.78095 (16)	0.79691 (7)	0.0480 (7)
Cl6	0.4922 (3)	0.9113 (2)	0.76612 (6)	0.0509 (8)
Cl7	0.1160 (3)	0.94711 (16)	0.82213 (5)	0.0345 (5)
Cl8	0.3296 (3)	1.07667 (15)	0.79252 (5)	0.0379 (6)
O1B	0.9797 (9)	0.6876 (4)	0.84537 (15)	0.0383 (18)
O2B	1.0975 (9)	0.5593 (5)	0.84181 (16)	0.046 (2)
O3B	0.7546 (9)	0.5194 (4)	0.84790 (14)	0.0384 (17)
H3B1	0.7802	0.4671	0.8461	0.046*
N1B	0.8210 (10)	0.7324 (6)	0.80203 (17)	0.0336 (19)
H1NB	0.8530	0.7438	0.8188	0.040*
C1B	0.8963 (12)	0.6514 (7)	0.79179 (18)	0.034 (2)
H1B	0.9954	0.6659	0.7852	0.041*
C2B	0.9046 (12)	0.5830 (6)	0.8140 (2)	0.032 (2)
H2B	0.9489	0.5287	0.8067	0.038*
C3B	0.7496 (13)	0.5605 (7)	0.8233 (2)	0.038 (3)
H3B	0.7035	0.5198	0.8105	0.046*
C4B	0.6522 (13)	0.6426 (7)	0.8264 (2)	0.039 (3)
H4B1	0.5498	0.6242	0.8285	0.046*
H4B2	0.6811	0.6747	0.8423	0.046*
C5B	0.6655 (13)	0.7032 (7)	0.8029 (2)	0.036 (2)
H5B	0.5993	0.7546	0.8048	0.043*
C6B	0.6434 (12)	0.6602 (7)	0.7772 (2)	0.037 (2)
H6B1	0.6089	0.7029	0.7641	0.044*
H6B2	0.5719	0.6121	0.7785	0.044*
C7B	0.7974 (14)	0.6241 (7)	0.7698 (2)	0.039 (3)
H7B1	0.7952	0.5597	0.7681	0.046*
H7B2	0.8308	0.6496	0.7532	0.046*
C8B	0.8517 (14)	0.8102 (7)	0.7852 (2)	0.042 (3)
H8B1	0.9533	0.8276	0.7873	0.063*
H8B2	0.7884	0.8587	0.7904	0.063*
H8B3	0.8333	0.7951	0.7671	0.063*
C9B	0.9985 (14)	0.6135 (7)	0.8352 (2)	0.038 (2)
Au3	0.94049 (4)	0.25918 (2)	0.956030 (8)	0.02640 (9)
Cl9	1.1271 (3)	0.25901 (18)	0.92737 (6)	0.0430 (6)
Cl10	0.7501 (3)	0.26223 (16)	0.98452 (5)	0.0352 (5)

Cl11	0.9699 (3)	0.11302 (15)	0.96206 (5)	0.0345 (5)
Cl12	0.9157 (3)	0.40534 (14)	0.94945 (5)	0.0354 (5)
O1C	0.4233 (9)	0.3312 (5)	0.90561 (15)	0.0399 (18)
O2C	0.5840 (10)	0.3634 (5)	0.87540 (17)	0.049 (2)
O3C	0.5037 (9)	0.5453 (5)	0.87533 (16)	0.0441 (19)
N1C	0.3872 (10)	0.4437 (6)	0.94632 (17)	0.035 (2)
H1NC	0.3450	0.4089	0.9336	0.043*
C1C	0.5536 (13)	0.4461 (8)	0.9423 (2)	0.042 (3)
H1C	0.6022	0.3931	0.9496	0.050*
C2C	0.5787 (14)	0.4553 (7)	0.9126 (2)	0.038 (3)
H2C	0.6856	0.4596	0.9095	0.046*
C3C	0.5077 (13)	0.5403 (7)	0.9030 (2)	0.037 (2)
H3C	0.5678	0.5903	0.9094	0.044*
C4C	0.3571 (14)	0.5521 (7)	0.9133 (2)	0.041 (3)
H4C1	0.3234	0.6118	0.9090	0.049*
H4C2	0.2918	0.5102	0.9044	0.049*
C5C	0.3442 (14)	0.5391 (7)	0.9419 (2)	0.037 (3)
H5C	0.2435	0.5512	0.9482	0.044*
C6C	0.4548 (15)	0.5875 (8)	0.9574 (2)	0.049 (3)
H6C1	0.4201	0.5969	0.9753	0.059*
H6C2	0.4753	0.6451	0.9494	0.059*
C7C	0.5940 (18)	0.5290 (9)	0.9573 (3)	0.061 (4)
H7C1	0.6752	0.5597	0.9486	0.073*
H7C2	0.6235	0.5144	0.9752	0.073*
C8C	0.3478 (16)	0.4101 (9)	0.9723 (2)	0.050 (3)
H8C1	0.4046	0.3574	0.9760	0.075*
H8C2	0.2442	0.3957	0.9726	0.075*
H8C3	0.3685	0.4548	0.9854	0.075*
C9C	0.5216 (13)	0.3768 (6)	0.8975 (2)	0.035 (2)
Au4	0.63437 (4)	0.84234 (3)	0.877377 (7)	0.02490 (9)
Cl13	0.4588 (3)	0.79712 (17)	0.90533 (5)	0.0360 (5)
Cl14	0.7996 (3)	0.77375 (18)	0.90306 (6)	0.0435 (6)
Cl15	0.4669 (3)	0.9127 (2)	0.85256 (6)	0.0476 (7)
Cl16	0.8114 (3)	0.88644 (16)	0.84947 (5)	0.0324 (5)
O1D	0.7144 (8)	0.0187 (4)	0.90788 (13)	0.0307 (15)
O2D	0.7544 (8)	0.1642 (4)	0.90693 (13)	0.0309 (15)
H2D1	0.8146	0.1596	0.8948	0.037*
O3D	0.4181 (8)	0.1525 (4)	0.90101 (13)	0.0322 (15)

H3D1	0.4201	0.2073	0.9023	0.035*
N1D	0.5444 (9)	-0.0414 (5)	0.94958 (17)	0.0303 (19)
H1ND	0.5800	-0.0499	0.9329	0.036*
C1D	0.5945 (10)	0.0475 (6)	0.95921 (17)	0.0228 (19)
H1D	0.6959	0.0456	0.9661	0.027*
C2D	0.5793 (10)	0.1123 (6)	0.93647 (17)	0.0242 (19)
H2D	0.6015	0.1719	0.9434	0.029*
C3D	0.4233 (11)	0.1142 (6)	0.92633 (18)	0.027 (2)
H3D	0.3629	0.1503	0.9384	0.033*
C4D	0.3543 (12)	0.0244 (6)	0.9238 (2)	0.036 (2)
H4D1	0.3965	-0.0059	0.9086	0.043*
H4D2	0.2489	0.0312	0.9207	0.043*
C5D	0.3780 (11)	-0.0318 (6)	0.94815 (19)	0.027 (2)
H5D	0.3281	-0.0897	0.9469	0.033*
C6D	0.3439 (11)	0.0148 (7)	0.9733 (2)	0.033 (2)
H6D1	0.3182	-0.0281	0.9870	0.039*
H6D2	0.2612	0.0553	0.9710	0.039*
C7D	0.4810 (11)	0.0656 (7)	0.98107 (19)	0.031 (2)
H7D1	0.5180	0.0451	0.9980	0.037*
H7D2	0.4600	0.1289	0.9823	0.037*
C8D	0.5951 (12)	-0.1156 (7)	0.9664 (2)	0.035 (2)
H8D1	0.7008	-0.1211	0.9651	0.053*
H8D2	0.5493	-0.1701	0.9606	0.053*
H8D3	0.5681	-0.1041	0.9845	0.053*
C9D	0.6869 (11)	0.0931 (6)	0.91624 (18)	0.027 (2)
Au5	0.98656 (4)	0.75277 (2)	0.966586 (7)	0.02257 (9)
Cl17	0.9949 (3)	0.90185 (14)	0.96923 (5)	0.0340 (5)
Cl18	0.8147 (3)	0.74489 (16)	0.99822 (5)	0.0328 (5)
Cl19	1.1606 (3)	0.75605 (16)	0.93526 (4)	0.0318 (5)
Cl20	0.9784 (3)	0.60447 (14)	0.96329 (5)	0.0312 (5)
O4	0.2397 (9)	0.1265 (5)	0.86078 (15)	0.0400 (18)
O5	0.4390 (9)	0.2617 (5)	0.84436 (15)	0.0412 (18)
O6	0.3090 (10)	0.6638 (7)	0.85737 (18)	0.057 (2)
O7	0.1339 (8)	0.8204 (5)	0.87393 (15)	0.0373 (17)
O8	0.0181 (9)	0.9550 (5)	0.90505 (16)	0.0404 (18)
O9	-0.0546 (12)	0.9287 (6)	0.61145 (17)	0.058 (2)
O10	0.1013 (13)	1.0722 (7)	0.5986 (2)	0.075 (3)

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Au1	0.0269 (2)	0.02786 (18)	0.02739 (18)	0.00195 (16)	0.00045 (17)	-0.00023 (15)
Cl1	0.0370 (15)	0.0415 (12)	0.0501 (14)	0.0089 (12)	-0.0135 (13)	-0.0073 (12)
Cl2	0.0302 (12)	0.0264 (10)	0.0312 (10)	0.0020 (8)	0.0017 (11)	-0.0023 (8)
Cl3	0.0409 (15)	0.0310 (11)	0.0419 (13)	0.0035 (10)	0.0000 (12)	-0.0023 (10)
Cl4	0.0350 (15)	0.0379 (11)	0.0396 (12)	-0.0070 (11)	-0.0079 (11)	0.0079 (11)
O1A	0.035 (5)	0.033 (3)	0.043 (4)	-0.007 (3)	-0.003 (4)	0.000 (3)
O2A	0.038 (5)	0.036 (4)	0.052 (5)	0.007 (3)	-0.002 (4)	0.003 (3)
O3A	0.019 (4)	0.056 (4)	0.022 (3)	-0.001 (3)	0.003 (3)	-0.006 (3)
N1A	0.016 (4)	0.031 (4)	0.026 (4)	-0.005 (3)	-0.002 (3)	-0.003 (3)
C1A	0.026 (6)	0.033 (4)	0.021 (4)	-0.005 (4)	-0.002 (4)	-0.001 (4)
C2A	0.019 (5)	0.036 (5)	0.027 (5)	0.001 (4)	-0.003 (4)	-0.003 (4)
C3A	0.026 (6)	0.034 (5)	0.027 (5)	0.005 (4)	0.004 (4)	-0.003 (4)
C4A	0.031 (6)	0.041 (5)	0.020 (4)	-0.003 (4)	0.004 (4)	0.005 (4)
C5A	0.023 (5)	0.031 (5)	0.037 (5)	0.000 (4)	-0.004 (5)	0.001 (4)
C6A	0.036 (6)	0.037 (5)	0.028 (5)	0.002 (5)	-0.004 (5)	0.012 (4)
C7A	0.028 (6)	0.042 (5)	0.034 (5)	-0.003 (4)	-0.002 (5)	0.003 (4)
C8A	0.036 (6)	0.052 (6)	0.029 (5)	-0.013 (5)	-0.001 (5)	-0.006 (5)
C9A	0.049 (7)	0.032 (5)	0.022 (4)	0.010 (5)	-0.003 (5)	0.000 (4)
Au2	0.0236 (2)	0.02822 (18)	0.02958 (18)	-0.00388 (15)	0.00276 (17)	-0.00384 (15)
Cl5	0.0339 (16)	0.0272 (11)	0.083 (2)	-0.0020 (10)	0.0071 (16)	-0.0114 (12)
Cl6	0.0366 (16)	0.0685 (18)	0.0478 (15)	-0.0171 (14)	0.0170 (14)	-0.0243 (14)
Cl7	0.0276 (13)	0.0403 (12)	0.0355 (11)	0.0082 (10)	0.0062 (11)	0.0021 (10)
Cl8	0.0351 (15)	0.0291 (11)	0.0495 (14)	-0.0051 (10)	-0.0124 (12)	0.0086 (10)
O1B	0.045 (5)	0.033 (4)	0.037 (4)	-0.001 (3)	-0.009 (4)	0.000 (3)
O2B	0.044 (5)	0.054 (5)	0.042 (4)	0.011 (4)	-0.005 (4)	-0.004 (4)
O3B	0.051 (5)	0.029 (3)	0.035 (4)	0.001 (3)	0.006 (4)	0.002 (3)

N1B	0.030 (5)	0.040 (5)	0.031 (4)	-0.002 (4)	-0.002 (4)	0.007 (4)
C1B	0.029 (6)	0.051 (6)	0.022 (4)	-0.004 (5)	0.014 (4)	0.000 (4)
C2B	0.028 (6)	0.036 (5)	0.032 (5)	-0.003 (4)	0.003 (5)	-0.003 (4)
C3B	0.049 (7)	0.030 (5)	0.036 (5)	-0.011 (5)	0.010 (5)	-0.008 (4)
C4B	0.032 (6)	0.043 (6)	0.041 (6)	0.000 (5)	-0.005 (5)	0.002 (5)
C5B	0.032 (6)	0.038 (5)	0.038 (6)	-0.004 (4)	0.013 (5)	0.002 (4)
C6B	0.020 (5)	0.036 (5)	0.054 (6)	0.001 (4)	0.003 (5)	0.001 (5)
C7B	0.049 (7)	0.038 (5)	0.029 (5)	-0.003 (5)	0.005 (5)	0.000 (4)
C8B	0.046 (7)	0.037 (5)	0.042 (6)	-0.007 (5)	-0.003 (6)	0.007 (5)
C9B	0.042 (7)	0.039 (5)	0.034 (5)	-0.006 (5)	0.007 (5)	0.001 (4)
Au3	0.0233 (2)	0.02463 (17)	0.03130 (18)	0.00021 (15)	-0.00206 (17)	0.00141 (15)
Cl9	0.0322 (14)	0.0440 (13)	0.0529 (15)	0.0072 (12)	0.0148 (13)	0.0114 (12)
Cl10	0.0346 (13)	0.0380 (12)	0.0329 (11)	-0.0004 (11)	0.0031 (11)	-0.0028 (10)
Cl11	0.0305 (14)	0.0279 (10)	0.0452 (13)	0.0052 (9)	-0.0019 (11)	0.0059 (10)
Cl12	0.0414 (15)	0.0242 (10)	0.0406 (12)	0.0022 (9)	-0.0001 (12)	0.0022 (9)
O1C	0.044 (5)	0.032 (3)	0.044 (4)	-0.008 (3)	0.019 (4)	-0.002 (3)
O2C	0.060 (6)	0.038 (4)	0.050 (5)	0.000 (4)	0.027 (5)	-0.002 (4)
O3C	0.044 (5)	0.044 (4)	0.044 (4)	0.014 (4)	0.008 (4)	0.007 (4)
N1C	0.030 (5)	0.044 (5)	0.033 (4)	0.012 (4)	0.007 (4)	0.004 (4)
C1C	0.025 (6)	0.050 (6)	0.051 (7)	0.005 (5)	-0.014 (6)	0.000 (5)
C2C	0.037 (7)	0.035 (5)	0.043 (6)	0.001 (4)	0.009 (5)	-0.005 (4)
C3C	0.035 (6)	0.037 (5)	0.038 (6)	0.009 (4)	-0.001 (5)	-0.006 (4)
C4C	0.044 (7)	0.038 (5)	0.041 (6)	0.011 (5)	0.008 (6)	-0.005 (5)
C5C	0.042 (7)	0.040 (5)	0.029 (5)	0.008 (5)	0.011 (5)	0.003 (4)
C6C	0.055 (8)	0.059 (7)	0.034 (5)	0.000 (6)	0.005 (6)	-0.014 (5)
C7C	0.067 (10)	0.067 (8)	0.048 (7)	0.001 (7)	0.006 (7)	-0.016 (7)
C8C	0.053 (8)	0.064 (8)	0.034 (6)	0.000 (6)	0.009 (6)	0.004 (5)
C9C	0.044 (7)	0.032 (5)	0.029 (5)	0.001 (5)	0.005 (5)	0.011 (4)
Au4	0.0206 (2)	0.02911 (17)	0.02497 (17)	-0.00038 (15)	0.00067 (16)	-0.00093 (14)
Cl13	0.0272 (14)	0.0452 (13)	0.0356 (12)	-0.0038 (10)	0.0057 (11)	0.0046 (10)
Cl14	0.0282 (14)	0.0545 (15)	0.0478 (14)	0.0042 (11)	-0.0037 (12)	0.0211 (12)
Cl15	0.0293	0.0736	0.0398 (13)	0.0037 (13)	-0.0048 (12)	0.0156 (13)

	(15)	(19)				
Cl16	0.0260 (12)	0.0385 (11)	0.0327 (11)	0.0013 (10)	0.0050 (10)	0.0054 (9)
O1D	0.026 (4)	0.035 (4)	0.030 (3)	-0.002 (3)	0.005 (3)	-0.001 (3)
O2D	0.029 (4)	0.032 (3)	0.031 (3)	-0.007 (3)	0.002 (3)	0.002 (3)
O3D	0.033 (4)	0.029 (3)	0.034 (4)	-0.001 (3)	-0.002 (3)	0.002 (3)
N1D	0.021 (5)	0.037 (4)	0.034 (4)	0.003 (3)	0.005 (4)	0.007 (4)
C1D	0.012 (5)	0.031 (4)	0.025 (4)	-0.004 (3)	-0.002 (4)	0.005 (4)
C2D	0.020 (5)	0.029 (4)	0.023 (4)	-0.003 (4)	-0.004 (4)	0.003 (4)
C3D	0.019 (5)	0.038 (5)	0.025 (4)	0.005 (4)	-0.005 (4)	0.003 (4)
C4D	0.024 (6)	0.030 (5)	0.052 (6)	0.001 (4)	-0.011 (5)	0.005 (5)
C5D	0.014 (5)	0.034 (4)	0.034 (5)	0.001 (4)	-0.008 (4)	-0.001 (4)
C6D	0.018 (5)	0.043 (5)	0.038 (5)	-0.002 (4)	0.006 (4)	0.013 (4)
C7D	0.021 (5)	0.039 (5)	0.033 (5)	-0.006 (4)	0.008 (4)	-0.006 (4)
C8D	0.030 (6)	0.036 (5)	0.039 (5)	0.005 (4)	-0.006 (5)	0.010 (4)
C9D	0.023 (5)	0.033 (5)	0.025 (4)	-0.007 (4)	-0.012 (4)	0.001 (4)
Au5	0.01943 (19)	0.02306 (17)	0.02521 (17)	0.00042 (14)	0.00062 (15)	0.00180 (14)
Cl17	0.0395 (15)	0.0225 (9)	0.0400 (12)	-0.0008 (9)	0.0031 (12)	0.0012 (9)
Cl18	0.0315 (12)	0.0333 (10)	0.0335 (10)	0.0051 (10)	0.0100 (10)	0.0062 (9)
Cl19	0.0266 (13)	0.0368 (11)	0.0318 (10)	0.0013 (10)	0.0077 (10)	0.0037 (10)
Cl20	0.0354 (14)	0.0234 (9)	0.0347 (11)	-0.0003 (9)	0.0030 (11)	-0.0020 (9)
O4	0.032 (4)	0.049 (4)	0.040 (4)	0.007 (3)	-0.008 (4)	-0.007 (3)
O5	0.047 (5)	0.039 (4)	0.038 (4)	0.006 (4)	-0.002 (4)	0.000 (3)
O6	0.037 (5)	0.080 (6)	0.053 (5)	0.011 (5)	-0.008 (4)	-0.002 (5)
O7	0.025 (4)	0.047 (4)	0.041 (4)	0.006 (3)	-0.004 (4)	0.003 (3)
O8	0.032 (4)	0.042 (4)	0.047 (4)	0.001 (3)	-0.004 (4)	-0.001 (3)
O9	0.084 (7)	0.049 (5)	0.042 (4)	0.004 (5)	-0.003 (5)	0.000 (4)
O10	0.083 (8)	0.080 (7)	0.062 (6)	-0.023 (6)	0.001 (6)	0.004 (6)

## GEOMETRIC PARAMETERS (Å, °)

Au1—Cl3	2.267 (2)	Au3—Cl10	2.289 (3)
Au1—Cl1	2.279 (3)	O1C—C9C	1.218 (13)
Au1—Cl2	2.283 (2)	O2C—C9C	1.295 (13)

Au1—Cl4	2.285 (3)	O3C—C3C	1.427 (13)
O1A—C9A	1.215 (14)	N1C—C8C	1.479 (13)
O2A—C9A	1.334 (14)	N1C—C5C	1.529 (13)
O3A—C3A	1.439 (11)	N1C—C1C	1.548 (15)
N1A—C1A	1.498 (13)	N1C—H1NC	0.9300
N1A—C8A	1.503 (12)	C1C—C7C	1.529 (17)
N1A—C5A	1.507 (12)	C1C—C2C	1.555 (15)
N1A—H1NA	0.9300	C1C—H1C	1.0000
C1A—C7A	1.508 (13)	C2C—C9C	1.523 (15)
C1A—C2A	1.541 (13)	C2C—C3C	1.539 (15)
C1A—H1A	1.0000	C2C—H2C	1.0000
C2A—C9A	1.489 (13)	C3C—C4C	1.498 (16)
C2A—C3A	1.554 (12)	C3C—H3C	1.0000
C2A—H2A	1.0000	C4C—C5C	1.494 (14)
C3A—C4A	1.513 (15)	C4C—H4C1	0.9900
C3A—H3A	1.0000	C4C—H4C2	0.9900
C4A—C5A	1.527 (13)	C5C—C6C	1.491 (17)
C4A—H4A1	0.9900	C5C—H5C	1.0000
C4A—H4A2	0.9900	C6C—C7C	1.56 (2)
C5A—C6A	1.537 (13)	C6C—H6C1	0.9900
C5A—H5A	1.0000	C6C—H6C2	0.9900
C6A—C7A	1.570 (15)	C7C—H7C1	0.9900
C6A—H6A1	0.9900	C7C—H7C2	0.9900
C6A—H6A2	0.9900	C8C—H8C1	0.9800
C7A—H7A1	0.9900	C8C—H8C2	0.9800
C7A—H7A2	0.9900	C8C—H8C3	0.9800
C8A—H8A1	0.9800	Au4—Cl13	2.274 (3)
C8A—H8A2	0.9800	Au4—Cl14	2.274 (3)
C8A—H8A3	0.9800	Au4—Cl15	2.276 (3)
Au2—Cl6	2.265 (3)	Au4—Cl16	2.277 (3)
Au2—Cl8	2.271 (2)	O1D—C9D	1.243 (12)
Au2—Cl7	2.279 (3)	O2D—C9D	1.342 (11)
Au2—Cl5	2.285 (3)	O2D—H2D1	0.8387
O1B—C9B	1.261 (13)	O3D—C3D	1.431 (11)
O2B—C9B	1.280 (15)	O3D—H3D1	0.8400
O3B—C3B	1.417 (12)	N1D—C8D	1.504 (12)
O3B—H3B1	0.8400	N1D—C1D	1.519 (12)
N1B—C8B	1.498 (12)	N1D—C5D	1.542 (13)

N1B—C5B	1.502 (14)	N1D—H1ND	0.9301
N1B—C1B	1.515 (13)	C1D—C2D	1.541 (12)
N1B—H1NB	0.9301	C1D—C7D	1.562 (13)
C1B—C7B	1.514 (15)	C1D—H1D	1.0000
C1B—C2B	1.552 (13)	C2D—C9D	1.468 (14)
C1B—H1B	1.0000	C2D—C3D	1.530 (13)
C2B—C9B	1.468 (15)	C2D—H2D	1.0000
C2B—C3B	1.546 (16)	C3D—C4D	1.520 (14)
C2B—H2B	1.0010	C3D—H3D	1.0000
C3B—C4B	1.552 (15)	C4D—C5D	1.538 (13)
C3B—H3B	1.0000	C4D—H4D1	0.9900
C4B—C5B	1.533 (14)	C4D—H4D2	0.9900
C4B—H4B1	0.9900	C5D—C6D	1.514 (14)
C4B—H4B2	0.9900	C5D—H5D	1.0000
C5B—C6B	1.491 (15)	C6D—C7D	1.537 (14)
C5B—H5B	1.0000	C6D—H6D1	0.9900
C6B—C7B	1.570 (16)	C6D—H6D2	0.9900
C6B—H6B1	0.9900	C7D—H7D1	0.9900
C6B—H6B2	0.9900	C7D—H7D2	0.9900
C7B—H7B1	0.9900	C8D—H8D1	0.9800
C7B—H7B2	0.9900	C8D—H8D2	0.9800
C8B—H8B1	0.9800	C8D—H8D3	0.9800
C8B—H8B2	0.9800	Au5—Cl19	2.276 (2)
C8B—H8B3	0.9800	Au5—Cl18	2.276 (2)
Au3—Cl9	2.267 (3)	Au5—Cl20	2.276 (2)
Au3—Cl12	2.273 (2)	Au5—Cl17	2.286 (2)
Au3—Cl11	2.274 (2)		
O10···Cl14 <sup>i</sup>	3.217 (11)	O2C···O5	2.600 (12)
O5···Cl1 <sup>ii</sup>	3.214 (8)	O3A···O4 <sup>iv</sup>	2.773 (11)
Cl9···O1C <sup>iii</sup>	3.150 (8)	O3D···O4	2.676 (11)
Cl15···Au2	3.361 (3)	O3C···O3B	2.739 (11)
O4···O5	2.893 (12)	O6···O2B <sup>v</sup>	2.646 (14)
O6···O7	3.012 (12)	O8···O1D <sup>vi</sup>	2.967 (11)
O7···O8	2.820 (11)	O7···O1B <sup>v</sup>	2.883 (11)
O9···O10	2.707 (15)	O6···O3C	2.713 (12)
O2A···O9	2.538 (12)		
Cl3—Au1—Cl1	89.55 (10)	Cl12—Au3—Cl10	89.92 (9)
Cl3—Au1—Cl2	177.60 (10)	Cl11—Au3—Cl10	91.37 (9)

Cl1—Au1—Cl2	89.65 (10)	C8C—N1C—C5C	113.7 (9)
Cl3—Au1—Cl4	90.47 (10)	C8C—N1C—C1C	111.8 (10)
Cl1—Au1—Cl4	176.90 (10)	C5C—N1C—C1C	102.3 (9)
Cl2—Au1—Cl4	90.45 (9)	C8C—N1C—H1NC	109.7
C1A—N1A—C8A	114.3 (8)	C5C—N1C—H1NC	109.5
C1A—N1A—C5A	102.9 (7)	C1C—N1C—H1NC	109.5
C8A—N1A—C5A	115.0 (8)	C7C—C1C—N1C	101.2 (10)
C1A—N1A—H1NA	108.2	C7C—C1C—C2C	112.6 (11)
C8A—N1A—H1NA	108.0	N1C—C1C—C2C	106.3 (9)
C5A—N1A—H1NA	108.0	C7C—C1C—H1C	112.0
N1A—C1A—C7A	102.3 (8)	N1C—C1C—H1C	112.0
N1A—C1A—C2A	108.3 (8)	C2C—C1C—H1C	112.0
C7A—C1A—C2A	114.7 (8)	C9C—C2C—C3C	110.8 (10)
N1A—C1A—H1A	110.4	C9C—C2C—C1C	112.3 (9)
C7A—C1A—H1A	110.4	C3C—C2C—C1C	109.3 (9)
C2A—C1A—H1A	110.4	C9C—C2C—H2C	108.1
C9A—C2A—C1A	113.4 (8)	C3C—C2C—H2C	108.1
C9A—C2A—C3A	112.3 (8)	C1C—C2C—H2C	108.1
C1A—C2A—C3A	109.1 (8)	O3C—C3C—C4C	108.9 (10)
C9A—C2A—H2A	107.2	O3C—C3C—C2C	112.3 (8)
C1A—C2A—H2A	107.2	C4C—C3C—C2C	112.4 (10)
C3A—C2A—H2A	107.2	O3C—C3C—H3C	107.7
O3A—C3A—C4A	108.8 (8)	C4C—C3C—H3C	107.7
O3A—C3A—C2A	110.8 (8)	C2C—C3C—H3C	107.7
C4A—C3A—C2A	112.8 (9)	C5C—C4C—C3C	114.1 (10)
O3A—C3A—H3A	108.1	C5C—C4C—H4C1	108.7
C4A—C3A—H3A	108.1	C3C—C4C—H4C1	108.7
C2A—C3A—H3A	108.1	C5C—C4C—H4C2	108.7
C3A—C4A—C5A	110.8 (9)	C3C—C4C—H4C2	108.7
C3A—C4A—H4A1	109.5	H4C1—C4C—H4C2	107.6
C5A—C4A—H4A1	109.5	C6C—C5C—C4C	114.0 (11)
C3A—C4A—H4A2	109.5	C6C—C5C—N1C	102.6 (10)
C5A—C4A—H4A2	109.5	C4C—C5C—N1C	104.6 (8)
H4A1—C4A—H4A2	108.1	C6C—C5C—H5C	111.7
N1A—C5A—C4A	107.6 (8)	C4C—C5C—H5C	111.7
N1A—C5A—C6A	100.4 (8)	N1C—C5C—H5C	111.7
C4A—C5A—C6A	114.5 (8)	C5C—C6C—C7C	105.9 (10)
N1A—C5A—H5A	111.3	C5C—C6C—H6C1	110.6

C4A—C5A—H5A	111.3	C7C—C6C—H6C1	110.6
C6A—C5A—H5A	111.3	C5C—C6C—H6C2	110.6
C5A—C6A—C7A	105.3 (8)	C7C—C6C—H6C2	110.6
C5A—C6A—H6A1	110.7	H6C1—C6C—H6C2	108.7
C7A—C6A—H6A1	110.7	C1C—C7C—C6C	106.1 (12)
C5A—C6A—H6A2	110.7	C1C—C7C—H7C1	110.5
C7A—C6A—H6A2	110.7	C6C—C7C—H7C1	110.5
H6A1—C6A—H6A2	108.8	C1C—C7C—H7C2	110.5
C1A—C7A—C6A	104.4 (8)	C6C—C7C—H7C2	110.5
C1A—C7A—H7A1	110.9	H7C1—C7C—H7C2	108.7
C6A—C7A—H7A1	110.9	N1C—C8C—H8C1	109.5
C1A—C7A—H7A2	110.9	N1C—C8C—H8C2	109.5
C6A—C7A—H7A2	110.9	H8C1—C8C—H8C2	109.5
H7A1—C7A—H7A2	108.9	N1C—C8C—H8C3	109.5
N1A—C8A—H8A1	109.5	H8C1—C8C—H8C3	109.5
N1A—C8A—H8A2	109.5	H8C2—C8C—H8C3	109.5
H8A1—C8A—H8A2	109.5	O1C—C9C—O2C	122.7 (11)
N1A—C8A—H8A3	109.5	O1C—C9C—C2C	122.4 (10)
H8A1—C8A—H8A3	109.5	O2C—C9C—C2C	114.9 (10)
H8A2—C8A—H8A3	109.5	Cl13—Au4—Cl14	88.12 (10)
O1A—C9A—O2A	124.9 (9)	Cl13—Au4—Cl15	91.01 (10)
O1A—C9A—C2A	122.2 (10)	Cl14—Au4—Cl15	178.58 (12)
O2A—C9A—C2A	112.8 (10)	Cl13—Au4—Cl16	179.46 (10)
Cl6—Au2—Cl8	91.17 (11)	Cl14—Au4—Cl16	91.41 (10)
Cl6—Au2—Cl7	179.25 (11)	Cl15—Au4—Cl16	89.46 (10)
Cl8—Au2—Cl7	88.78 (10)	C9D—O2D—H2D1	120.4
Cl6—Au2—Cl5	90.44 (11)	C3D—O3D—H3D1	109.5
Cl8—Au2—Cl5	178.38 (12)	C8D—N1D—C1D	113.1 (8)
Cl7—Au2—Cl5	89.61 (10)	C8D—N1D—C5D	114.1 (8)
C3B—O3B—H3B1	109.5	C1D—N1D—C5D	103.5 (7)
C8B—N1B—C5B	115.6 (9)	C8D—N1D—H1ND	108.6
C8B—N1B—C1B	111.3 (8)	C1D—N1D—H1ND	108.7
C5B—N1B—C1B	101.7 (8)	C5D—N1D—H1ND	108.6
C8B—N1B—H1NB	109.2	N1D—C1D—C2D	107.4 (7)
C5B—N1B—H1NB	109.4	N1D—C1D—C7D	101.0 (7)
C1B—N1B—H1NB	109.4	C2D—C1D—C7D	111.9 (8)
C7B—C1B—N1B	102.2 (9)	N1D—C1D—H1D	112.0
C7B—C1B—C2B	113.4 (9)	C2D—C1D—H1D	112.0

N1B—C1B—C2B	108.5 (7)	C7D—C1D—H1D	112.0
C7B—C1B—H1B	110.8	C9D—C2D—C3D	113.3 (8)
N1B—C1B—H1B	110.8	C9D—C2D—C1D	110.5 (8)
C2B—C1B—H1B	110.8	C3D—C2D—C1D	111.0 (8)
C9B—C2B—C3B	112.7 (9)	C9D—C2D—H2D	107.3
C9B—C2B—C1B	111.3 (9)	C3D—C2D—H2D	107.3
C3B—C2B—C1B	109.5 (9)	C1D—C2D—H2D	107.3
C9B—C2B—H2B	107.7	O3D—C3D—C4D	106.1 (8)
C3B—C2B—H2B	107.9	O3D—C3D—C2D	110.6 (8)
C1B—C2B—H2B	107.5	C4D—C3D—C2D	113.9 (8)
O3B—C3B—C2B	110.2 (10)	O3D—C3D—H3D	108.7
O3B—C3B—C4B	106.5 (8)	C4D—C3D—H3D	108.7
C2B—C3B—C4B	112.7 (9)	C2D—C3D—H3D	108.7
O3B—C3B—H3B	109.1	C3D—C4D—C5D	112.0 (9)
C2B—C3B—H3B	109.1	C3D—C4D—H4D1	109.2
C4B—C3B—H3B	109.1	C5D—C4D—H4D1	109.2
C5B—C4B—C3B	111.1 (9)	C3D—C4D—H4D2	109.2
C5B—C4B—H4B1	109.4	C5D—C4D—H4D2	109.2
C3B—C4B—H4B1	109.4	H4D1—C4D—H4D2	107.9
C5B—C4B—H4B2	109.4	C6D—C5D—C4D	114.1 (8)
C3B—C4B—H4B2	109.4	C6D—C5D—N1D	102.1 (8)
H4B1—C4B—H4B2	108.0	C4D—C5D—N1D	103.5 (8)
C6B—C5B—N1B	103.7 (9)	C6D—C5D—H5D	112.1
C6B—C5B—C4B	115.2 (9)	C4D—C5D—H5D	112.1
N1B—C5B—C4B	106.2 (9)	N1D—C5D—H5D	112.1
C6B—C5B—H5B	110.5	C5D—C6D—C7D	106.8 (8)
N1B—C5B—H5B	110.5	C5D—C6D—H6D1	110.4
C4B—C5B—H5B	110.5	C7D—C6D—H6D1	110.4
C5B—C6B—C7B	104.3 (9)	C5D—C6D—H6D2	110.4
C5B—C6B—H6B1	110.9	C7D—C6D—H6D2	110.4
C7B—C6B—H6B1	110.9	H6D1—C6D—H6D2	108.6
C5B—C6B—H6B2	110.9	C6D—C7D—C1D	105.9 (8)
C7B—C6B—H6B2	110.9	C6D—C7D—H7D1	110.6
H6B1—C6B—H6B2	108.9	C1D—C7D—H7D1	110.6
C1B—C7B—C6B	105.3 (8)	C6D—C7D—H7D2	110.6
C1B—C7B—H7B1	110.7	C1D—C7D—H7D2	110.6
C6B—C7B—H7B1	110.7	H7D1—C7D—H7D2	108.7
C1B—C7B—H7B2	110.7	N1D—C8D—H8D1	109.5

C6B—C7B—H7B2	110.7	N1D—C8D—H8D2	109.5
H7B1—C7B—H7B2	108.8	H8D1—C8D—H8D2	109.5
N1B—C8B—H8B1	109.5	N1D—C8D—H8D3	109.5
N1B—C8B—H8B2	109.5	H8D1—C8D—H8D3	109.5
H8B1—C8B—H8B2	109.5	H8D2—C8D—H8D3	109.5
N1B—C8B—H8B3	109.5	O1D—C9D—O2D	121.6 (9)
H8B1—C8B—H8B3	109.5	O1D—C9D—C2D	124.5 (9)
H8B2—C8B—H8B3	109.5	O2D—C9D—C2D	113.9 (8)
O1B—C9B—O2B	124.7 (11)	Cl19—Au5—Cl18	178.12 (9)
O1B—C9B—C2B	120.9 (11)	Cl19—Au5—Cl20	89.55 (9)
O2B—C9B—C2B	114.4 (10)	Cl18—Au5—Cl20	88.73 (9)
Cl9—Au3—Cl12	88.87 (10)	Cl19—Au5—Cl17	89.81 (9)
Cl9—Au3—Cl11	89.85 (10)	Cl18—Au5—Cl17	91.92 (9)
Cl12—Au3—Cl11	178.71 (10)	Cl20—Au5—Cl17	179.13 (9)
Cl9—Au3—Cl10	178.67 (10)		
C8A—N1A—C1A— C7A	-77.0 (10)	C8C—N1C—C1C— C7C	-78.6 (12)
C5A—N1A—C1A— C7A	48.4 (9)	C5C—N1C—C1C— C7C	43.5 (11)
C8A—N1A—C1A— C2A	161.5 (8)	C8C—N1C—C1C— C2C	163.6 (9)
C5A—N1A—C1A— C2A	-73.1 (9)	C5C—N1C—C1C— C2C	-74.3 (10)
N1A—C1A—C2A— C9A	-65.5 (11)	C7C—C1C—C2C— C9C	-173.2 (11)
C7A—C1A—C2A— C9A	-179.0 (9)	N1C—C1C—C2C— C9C	-63.2 (12)
N1A—C1A—C2A— C3A	60.5 (10)	C7C—C1C—C2C— C3C	-49.8 (14)
C7A—C1A—C2A— C3A	-53.0 (11)	N1C—C1C—C2C— C3C	60.2 (12)
C9A—C2A—C3A— O3A	-42.9 (12)	C9C—C2C—C3C— O3C	-45.1 (14)
C1A—C2A—C3A— O3A	-169.5 (8)	C1C—C2C—C3C— O3C	-169.4 (10)
C9A—C2A—C3A— C4A	79.4 (11)	C9C—C2C—C3C— C4C	78.0 (12)
C1A—C2A—C3A— C4A	-47.2 (11)	C1C—C2C—C3C— C4C	-46.3 (13)
O3A—C3A—C4A—	171.5 (7)	O3C—C3C—C4C—	174.0 (9)

C5A		C5C	
C2A—C3A—C4A— C5A	48.1 (11)	C2C—C3C—C4C— C5C	49.0 (13)
C1A—N1A—C5A— C4A	72.7 (9)	C3C—C4C—C5C— C6C	48.7 (13)
C8A—N1A—C5A— C4A	-162.3 (8)	C3C—C4C—C5C— N1C	-62.7 (13)
C1A—N1A—C5A— C6A	-47.3 (9)	C8C—N1C—C5C— C6C	75.0 (12)
C8A—N1A—C5A— C6A	77.6 (10)	C1C—N1C—C5C— C6C	-45.8 (10)
C3A—C4A—C5A— N1A	-61.2 (10)	C8C—N1C—C5C— C4C	-165.6 (11)
C3A—C4A—C5A— C6A	49.4 (12)	C1C—N1C—C5C— C4C	73.6 (11)
N1A—C5A—C6A— C7A	28.3 (10)	C4C—C5C—C6C— C7C	-83.2 (12)
C4A—C5A—C6A— C7A	-86.6 (10)	N1C—C5C—C6C— C7C	29.4 (12)
N1A—C1A—C7A— C6A	-28.8 (9)	N1C—C1C—C7C— C6C	-25.2 (13)
C2A—C1A—C7A— C6A	88.1 (10)	C2C—C1C—C7C— C6C	87.9 (13)
C5A—C6A—C7A— C1A	0.1 (11)	C5C—C6C—C7C— C1C	-2.3 (14)
C1A—C2A—C9A— O1A	40.1 (14)	C3C—C2C—C9C— O1C	-96.5 (13)
C3A—C2A—C9A— O1A	-84.1 (12)	C1C—C2C—C9C— O1C	26.1 (16)
C1A—C2A—C9A— O2A	-142.7 (9)	C3C—C2C—C9C— O2C	82.5 (13)
C3A—C2A—C9A— O2A	93.1 (11)	C1C—C2C—C9C— O2C	-155.0 (10)
C8B—N1B—C1B— C7B	-78.8 (10)	C8D—N1D—C1D— C2D	162.2 (8)
C5B—N1B—C1B— C7B	44.9 (9)	C5D—N1D—C1D— C2D	-73.9 (9)
C8B—N1B—C1B— C2B	161.2 (9)	C8D—N1D—C1D— C7D	-80.5 (9)
C5B—N1B—C1B— C2B	-75.1 (10)	C5D—N1D—C1D— C7D	43.5 (9)
C7B—C1B—C2B—	-178.5 (9)	N1D—C1D—C2D—	-69.7 (9)

C9B		C9D	
N1B—C1B—C2B— C9B	-65.7 (12)	C7D—C1D—C2D— C9D	-179.7 (8)
C7B—C1B—C2B— C3B	-53.2 (11)	N1D—C1D—C2D— C3D	56.8 (10)
N1B—C1B—C2B— C3B	59.5 (11)	C7D—C1D—C2D— C3D	-53.1 (10)
C9B—C2B—C3B— O3B	-38.5 (12)	C9D—C2D—C3D— O3D	-37.6 (11)
C1B—C2B—C3B— O3B	-162.9 (8)	C1D—C2D—C3D— O3D	-162.5 (7)
C9B—C2B—C3B— C4B	80.3 (12)	C9D—C2D—C3D— C4D	81.8 (10)
C1B—C2B—C3B— C4B	-44.1 (12)	C1D—C2D—C3D— C4D	-43.2 (11)
O3B—C3B—C4B— C5B	167.4 (9)	O3D—C3D—C4D— C5D	169.1 (8)
C2B—C3B—C4B— C5B	46.4 (13)	C2D—C3D—C4D— C5D	47.2 (12)
C8B—N1B—C5B— C6B	74.2 (11)	C3D—C4D—C5D— C6D	48.0 (12)
C1B—N1B—C5B— C6B	-46.5 (10)	C3D—C4D—C5D— N1D	-62.1 (11)
C8B—N1B—C5B— C4B	-164.1 (9)	C8D—N1D—C5D— C6D	79.6 (10)
C1B—N1B—C5B— C4B	75.3 (10)	C1D—N1D—C5D— C6D	-43.7 (9)
C3B—C4B—C5B— C6B	51.6 (13)	C8D—N1D—C5D— C4D	-161.6 (8)
C3B—C4B—C5B— N1B	-62.5 (11)	C1D—N1D—C5D— C4D	75.0 (9)
N1B—C5B—C6B— C7B	29.0 (10)	C4D—C5D—C6D— C7D	-85.2 (10)
C4B—C5B—C6B— C7B	-86.5 (11)	N1D—C5D—C6D— C7D	25.7 (10)
N1B—C1B—C7B— C6B	-26.7 (10)	C5D—C6D—C7D— C1D	0.7 (10)
C2B—C1B—C7B— C6B	89.8 (10)	N1D—C1D—C7D— C6D	-27.1 (9)
C5B—C6B—C7B— C1B	-1.2 (11)	C2D—C1D—C7D— C6D	86.9 (9)
C3B—C2B—C9B—	-71.3 (13)	C3D—C2D—C9D—	-79.9 (12)

O1B		O1D	
C1B—C2B—C9B—	52.1 (14)	C1D—C2D—C9D—	45.4 (13)
O1B		O1D	
C3B—C2B—C9B—	108.9 (11)	C3D—C2D—C9D—	99.4 (10)
O2B		O2D	
C1B—C2B—C9B—	-127.7 (10)	C1D—C2D—C9D—	-135.4 (8)
O2B		O2D	

Symmetry codes: (i)  $-x+1, y+1/2, -z+3/2$ ; (ii)  $-x+1, y-1/2, -z+3/2$ ; (iii)  $x+1, y, z$ ;  
 (iv)  $-x, y+1/2, -z+3/2$ ; (v)  $x-1, y, z$ ; (vi)  $x-1, y+1, z$ .

APPENDIX 1 (D) – THE ANHYDROUS ECGONINE  
 GOLD(III) TETRACHLORIDE SALT  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.187321 (15)	0.505994 (11)	0.090196 (8)	0.01499 (6)
Cl1	0.34843 (9)	0.50710 (7)	0.00321 (4)	0.01889 (19)
Cl2	0.19401 (10)	0.36001 (6)	0.09469 (6)	0.0236 (2)
Cl3	0.02630 (9)	0.50577 (8)	0.17652 (5)	0.0244 (2)
Cl4	0.18470 (11)	0.65024 (6)	0.08728 (6)	0.0228 (2)
O1	0.4912 (3)	0.75884 (19)	0.33650 (15)	0.0215 (7)
O2	0.4994 (3)	0.8345 (2)	0.43767 (16)	0.0272 (7)
H2	0.5809	0.8370	0.4277	0.041*
O3	0.2823 (3)	0.92123 (18)	0.34524 (16)	0.0223 (7)
H3	0.2952	0.9412	0.3865	0.033*
N1	0.2625 (3)	0.6623 (2)	0.32007 (17)	0.0147 (7)
H1	0.3475	0.6796	0.3064	0.018*
C1	0.2355 (4)	0.6914 (3)	0.3961 (2)	0.0159 (9)
H1B	0.2779	0.6525	0.4318	0.019*
C2	0.2891 (4)	0.7822 (3)	0.4035 (2)	0.0160 (9)
H2B	0.2720	0.8022	0.4536	0.019*
C3	0.2151 (4)	0.8422 (3)	0.3508 (2)	0.0166 (8)
H3B	0.1228	0.8524	0.3692	0.020*
C4	0.2061 (4)	0.8043 (3)	0.2760 (2)	0.0171 (8)
H4A	0.2948	0.8072	0.2528	0.021*
H4B	0.1432	0.8383	0.2468	0.021*
C5	0.1593 (4)	0.7119 (3)	0.2776 (2)	0.0157 (9)
H5A	0.1490	0.6885	0.2280	0.019*
C6	0.0330 (4)	0.6984 (3)	0.3219 (2)	0.0163 (9)
H6A	-0.0156	0.6472	0.3055	0.020*
H6B	-0.0269	0.7482	0.3180	0.020*
C7	0.0820 (4)	0.6870 (3)	0.4003 (2)	0.0169 (8)
H7A	0.0467	0.7328	0.4313	0.020*
H7B	0.0528	0.6315	0.4197	0.020*
C8	0.2514 (4)	0.5682 (3)	0.3122 (3)	0.0234 (10)

H8A	0.3174	0.5404	0.3431	0.035*
H8B	0.2679	0.5524	0.2621	0.035*
H8C	0.1616	0.5499	0.3261	0.035*
C9	0.4370 (4)	0.7886 (3)	0.3887 (2)	0.0173 (9)
Au2	0.792368 (15)	0.510510 (11)	-0.096686 (8)	0.01529 (6)
Cl5	0.58515 (10)	0.53140 (7)	-0.14391 (6)	0.0281 (2)
Cl6	0.76093 (11)	0.36699 (6)	-0.09842 (6)	0.0257 (2)
Cl7	0.99890 (10)	0.49006 (8)	-0.04920 (6)	0.0310 (2)
Cl8	0.82924 (10)	0.65411 (6)	-0.09756 (6)	0.0217 (2)
O1A	0.4689 (3)	0.64723 (18)	0.20930 (15)	0.0193 (6)
O2A	0.5411 (3)	0.51678 (18)	0.22023 (17)	0.0284 (7)
H2A	0.6078	0.4880	0.2079	0.043*
O3A	0.6462 (3)	0.54127 (17)	0.06095 (15)	0.0192 (6)
H3A	0.5632	0.5437	0.0552	0.029*
N1A	0.6350 (4)	0.7758 (2)	0.16987 (18)	0.0169 (8)
H1A	0.5495	0.7540	0.1758	0.020*
C1A	0.7366 (4)	0.7113 (3)	0.1973 (2)	0.0158 (9)
H1C	0.7436	0.7134	0.2508	0.019*
C2A	0.6950 (4)	0.6225 (3)	0.1715 (2)	0.0156 (8)
H2C	0.7631	0.5807	0.1886	0.019*
C3A	0.6934 (4)	0.6208 (2)	0.0877 (2)	0.0147 (8)
H3C	0.7881	0.6267	0.0715	0.018*
C4A	0.6174 (4)	0.6958 (3)	0.0570 (2)	0.0154 (8)
H4A1	0.5211	0.6893	0.0673	0.018*
H4A2	0.6290	0.6973	0.0043	0.018*
C5A	0.6683 (4)	0.7793 (3)	0.0898 (2)	0.0170 (9)
H5B	0.6266	0.8298	0.0662	0.020*
C6A	0.8205 (4)	0.7862 (3)	0.0909 (2)	0.0207 (9)
H6A1	0.8486	0.8465	0.0901	0.025*
H6A2	0.8597	0.7570	0.0488	0.025*
C7A	0.8658 (5)	0.7426 (3)	0.1619 (2)	0.0200 (10)
H7A1	0.9263	0.6944	0.1517	0.024*
H7A2	0.9126	0.7836	0.1933	0.024*
C8A	0.6444 (5)	0.8597 (3)	0.2061 (2)	0.0219 (9)
H8A1	0.6286	0.8525	0.2577	0.033*
H8A2	0.5772	0.8982	0.1861	0.033*
H8A3	0.7335	0.8836	0.1985	0.033*
C9A	0.5599 (4)	0.5970 (3)	0.2022 (2)	0.0180 (9)

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Au1	0.01423 (9)	0.01405 (9)	0.01670 (8)	-0.00097 (6)	-0.00022 (5)	0.00066 (7)
Cl1	0.0183 (4)	0.0180 (5)	0.0204 (4)	0.0005 (4)	0.0034 (3)	0.0013 (4)
Cl2	0.0219 (5)	0.0138 (5)	0.0351 (6)	0.0001 (4)	0.0027 (5)	0.0044 (5)
Cl3	0.0223 (5)	0.0249 (6)	0.0261 (4)	-0.0035 (5)	0.0072 (4)	-0.0020 (5)
Cl4	0.0323 (6)	0.0146 (5)	0.0214 (5)	-0.0012 (4)	0.0051 (5)	-0.0023 (4)
O1	0.0161 (15)	0.0243 (18)	0.0241 (16)	-0.0009 (12)	0.0010 (13)	-0.0065 (13)
O2	0.0215 (16)	0.036 (2)	0.0239 (15)	-0.0103 (14)	-0.0002 (13)	-0.0042 (14)
O3	0.0287 (17)	0.0103 (15)	0.0278 (16)	-0.0041 (13)	0.0007 (14)	0.0014 (12)
N1	0.0142 (17)	0.0122 (17)	0.0176 (16)	-0.0025 (13)	0.0007 (14)	0.0005 (14)
C1	0.020 (2)	0.014 (2)	0.0138 (19)	0.0007 (16)	-0.0026 (17)	0.0016 (17)
C2	0.019 (2)	0.0124 (19)	0.017 (2)	-0.0042 (16)	-0.0017 (18)	0.0007 (17)
C3	0.014 (2)	0.014 (2)	0.022 (2)	-0.0005 (18)	-0.0019 (17)	0.0026 (17)
C4	0.013 (2)	0.021 (2)	0.0173 (19)	0.0002 (18)	-0.0028 (17)	0.0007 (17)
C5	0.017 (2)	0.018 (2)	0.0125 (18)	0.0024 (17)	-0.0019 (17)	0.0006 (16)
C6	0.015 (2)	0.012 (2)	0.022 (2)	-0.0016 (17)	-0.0008 (16)	-0.0019 (17)
C7	0.020 (2)	0.016 (2)	0.0150 (19)	-0.0036 (16)	0.0035 (18)	0.0010 (18)
C8	0.023 (2)	0.012 (2)	0.035 (2)	0.0007 (17)	0.0045 (19)	-0.0042 (19)
C9	0.021 (2)	0.014 (2)	0.017 (2)	-0.0021 (17)	-0.0038 (17)	0.0040 (17)
Au2	0.01305 (9)	0.01716 (9)	0.01567 (8)	-0.00069 (6)	-0.00083 (6)	-0.00075 (7)
Cl5	0.0175 (5)	0.0231 (6)	0.0438 (6)	-0.0053 (4)	-0.0106 (4)	0.0110 (5)
Cl6	0.0267 (5)	0.0168 (5)	0.0337 (5)	-0.0003 (4)	-0.0055 (5)	0.0013 (5)
Cl7	0.0207 (5)	0.0338 (7)	0.0386 (5)	0.0027 (5)	-0.0126 (4)	-0.0025 (6)
Cl8	0.0214 (5)	0.0186 (5)	0.0250 (5)	-0.0039 (4)	0.0006 (5)	-0.0026 (5)
O1A	0.0209 (15)	0.0143 (15)	0.0228 (15)	0.0028 (13)	0.0048 (12)	0.0007 (12)
O2A	0.0314 (17)	0.0112 (15)	0.0426 (17)	0.0021 (13)	0.0172 (14)	0.0081 (15)
O3A	0.0201 (15)	0.0119 (15)	0.0256 (14)	0.0002 (12)	-0.0030 (12)	-0.0022 (12)
N1A	0.021 (2)	0.0099 (18)	0.0193 (18)	-0.0019 (15)	0.0020 (15)	0.0002 (14)
C1A	0.016 (2)	0.015 (2)	0.0163 (19)	-0.0005 (17)	-0.0038 (17)	0.0017 (17)
C2A	0.015 (2)	0.014 (2)	0.0187 (19)	0.0012 (16)	0.0000 (16)	0.0031 (16)
C3A	0.016 (2)	0.0102 (19)	0.0172 (19)	0.0000 (15)	0.0007 (16)	-0.0015 (16)
C4A	0.016 (2)	0.013 (2)	0.0176 (19)	0.0012 (16)	-0.0013 (16)	0.0017 (17)
C5A	0.023 (2)	0.013 (2)	0.015 (2)	0.0005 (16)	0.0019 (18)	0.0040 (17)
C6A	0.021 (2)	0.015 (2)	0.026 (2)	-0.0039 (16)	0.001 (2)	0.0044 (19)
C7A	0.017 (2)	0.013 (2)	0.030 (2)	-0.0030 (17)	-0.0013 (19)	-0.0009 (19)
C8A	0.030 (2)	0.015 (2)	0.021 (2)	-0.0008 (19)	0.0007 (18)	-0.0024 (18)

C9A 0.019 (2) 0.015 (2) 0.0195 (19) -0.0030 (18) 0.0031 (16) 0.0002 (17)

GEOMETRIC PARAMETERS ( $\text{\AA}$ ,  $^{\circ}$ )

Au1—Cl4	2.2704 (10)	C4—C5	1.528 (6)
Au1—Cl3	2.2796 (9)	C4—H4A	0.9900
Au1—Cl1	2.2890 (8)	C4—H4B	0.9900
Au1—Cl2	2.2994 (10)	C5—C6	1.526 (6)
Au2—Cl7	2.2752 (9)	C5—H5A	1.0000
Au2—Cl6	2.2803 (10)	C6—C7	1.552 (5)
Au2—Cl5	2.2805 (10)	C6—H6A	0.9900
Au2—Cl8	2.2895 (10)	C6—H6B	0.9900
O1—C9	1.209 (5)	C7—H7A	0.9900
O2—C9	1.322 (5)	C7—H7B	0.9900
O2—H2	0.8400	C8—H8A	0.9800
O3—C3	1.419 (5)	C8—H8B	0.9800
O3—H3	0.8400	C8—H8C	0.9800
O1A—C9A	1.214 (5)	C1A—C2A	1.535 (5)
O2A—C9A	1.320 (5)	C1A—C7A	1.535 (6)
O2A—H2A	0.8400	C1A—H1C	1.0000
O3A—C3A	1.428 (4)	C2A—C9A	1.525 (5)
O3A—H3A	0.8400	C2A—C3A	1.563 (5)
N1—C8	1.492 (5)	C2A—H2C	1.0000
N1—C1	1.514 (5)	C3A—C4A	1.518 (5)
N1—C5	1.518 (5)	C3A—H3C	1.0000
N1—H1	0.9300	C4A—C5A	1.536 (5)
N1A—C8A	1.486 (5)	C4A—H4A1	0.9900
N1A—C1A	1.526 (5)	C4A—H4A2	0.9900
N1A—C5A	1.531 (5)	C5A—C6A	1.530 (6)
N1A—H1A	0.9300	C5A—H5B	1.0000
C1—C2	1.532 (6)	C6A—C7A	1.559 (6)
C1—C7	1.543 (6)	C6A—H6A1	0.9900
C1—H1B	1.0000	C6A—H6A2	0.9900
C2—C9	1.512 (6)	C7A—H7A1	0.9900
C2—C3	1.552 (5)	C7A—H7A2	0.9900
C2—H2B	1.0000	C8A—H8A1	0.9800
C3—C4	1.519 (5)	C8A—H8A2	0.9800
C3—H3B	1.0000	C8A—H8A3	0.9800

Cl4—Au1—Cl3	90.59 (4)	C1—C7—H7A	110.7
Cl4—Au1—Cl1	89.06 (4)	C6—C7—H7A	110.7
Cl3—Au1—Cl1	179.60 (4)	C1—C7—H7B	110.7
Cl4—Au1—Cl2	178.76 (4)	C6—C7—H7B	110.7
Cl3—Au1—Cl2	89.62 (4)	H7A—C7—H7B	108.8
Cl1—Au1—Cl2	90.73 (4)	N1—C8—H8A	109.5
Cl7—Au2—Cl6	89.50 (4)	N1—C8—H8B	109.5
Cl7—Au2—Cl5	179.76 (5)	H8A—C8—H8B	109.5
Cl6—Au2—Cl5	90.65 (4)	N1—C8—H8C	109.5
Cl7—Au2—Cl8	89.73 (4)	H8A—C8—H8C	109.5
Cl6—Au2—Cl8	178.18 (4)	H8B—C8—H8C	109.5
Cl5—Au2—Cl8	90.12 (4)	O1—C9—O2	123.7 (4)
C9—O2—H2	109.5	O1—C9—C2	124.2 (4)
C3—O3—H3	109.5	O2—C9—C2	112.0 (4)
C9A—O2A—H2A	109.5	N1A—C1A—C2A	108.6 (3)
C3A—O3A—H3A	109.5	N1A—C1A—C7A	101.9 (3)
C8—N1—C1	112.3 (3)	C2A—C1A—C7A	112.7 (3)
C8—N1—C5	114.0 (3)	N1A—C1A—H1C	111.1
C1—N1—C5	102.2 (3)	C2A—C1A—H1C	111.1
C8—N1—H1	109.4	C7A—C1A—H1C	111.1
C1—N1—H1	109.4	C9A—C2A—C1A	111.3 (3)
C5—N1—H1	109.4	C9A—C2A—C3A	111.2 (3)
C8A—N1A—C1A	113.3 (3)	C1A—C2A—C3A	109.4 (3)
C8A—N1A—C5A	113.4 (3)	C9A—C2A—H2C	108.3
C1A—N1A—C5A	101.8 (3)	C1A—C2A—H2C	108.3
C8A—N1A—H1A	109.3	C3A—C2A—H2C	108.3
C1A—N1A—H1A	109.3	O3A—C3A—C4A	112.5 (3)
C5A—N1A—H1A	109.3	O3A—C3A—C2A	111.6 (3)
N1—C1—C2	107.7 (3)	C4A—C3A—C2A	111.6 (3)
N1—C1—C7	102.3 (3)	O3A—C3A—H3C	106.9
C2—C1—C7	112.8 (3)	C4A—C3A—H3C	106.9
N1—C1—H1B	111.2	C2A—C3A—H3C	106.9
C2—C1—H1B	111.2	C3A—C4A—C5A	110.4 (3)
C7—C1—H1B	111.2	C3A—C4A—H4A1	109.6
C9—C2—C1	112.9 (3)	C5A—C4A—H4A1	109.6
C9—C2—C3	108.3 (3)	C3A—C4A—H4A2	109.6
C1—C2—C3	110.0 (3)	C5A—C4A—H4A2	109.6
C9—C2—H2B	108.5	H4A1—C4A—H4A2	108.1

C1—C2—H2B	108.5	N1A—C5A—C6A	102.0 (3)
C3—C2—H2B	108.5	N1A—C5A—C4A	106.5 (3)
O3—C3—C4	107.8 (3)	C6A—C5A—C4A	113.4 (4)
O3—C3—C2	110.6 (3)	N1A—C5A—H5B	111.5
C4—C3—C2	111.8 (3)	C6A—C5A—H5B	111.5
O3—C3—H3B	108.9	C4A—C5A—H5B	111.5
C4—C3—H3B	108.9	C5A—C6A—C7A	105.7 (3)
C2—C3—H3B	108.9	C5A—C6A—H6A1	110.6
C3—C4—C5	111.9 (3)	C7A—C6A—H6A1	110.6
C3—C4—H4A	109.2	C5A—C6A—H6A2	110.6
C5—C4—H4A	109.2	C7A—C6A—H6A2	110.6
C3—C4—H4B	109.2	H6A1—C6A—H6A2	108.7
C5—C4—H4B	109.2	C1A—C7A—C6A	105.1 (3)
H4A—C4—H4B	107.9	C1A—C7A—H7A1	110.7
N1—C5—C6	102.2 (3)	C6A—C7A—H7A1	110.7
N1—C5—C4	106.8 (3)	C1A—C7A—H7A2	110.7
C6—C5—C4	113.4 (3)	C6A—C7A—H7A2	110.7
N1—C5—H5A	111.3	H7A1—C7A—H7A2	108.8
C6—C5—H5A	111.3	N1A—C8A—H8A1	109.5
C4—C5—H5A	111.3	N1A—C8A—H8A2	109.5
C5—C6—C7	105.2 (3)	H8A1—C8A—H8A2	109.5
C5—C6—H6A	110.7	N1A—C8A—H8A3	109.5
C7—C6—H6A	110.7	H8A1—C8A—H8A3	109.5
C5—C6—H6B	110.7	H8A2—C8A—H8A3	109.5
C7—C6—H6B	110.7	O1A—C9A—O2A	119.2 (4)
H6A—C6—H6B	108.8	O1A—C9A—C2A	122.5 (4)
C1—C7—C6	105.2 (3)	O2A—C9A—C2A	118.3 (4)
C8—N1—C1—C2	163.4 (3)	C8A—N1A—C1A— C2A	165.3 (3)
C5—N1—C1—C2	-74.0 (4)	C5A—N1A—C1A— C2A	-72.6 (4)
C8—N1—C1—C7	-77.6 (4)	C8A—N1A—C1A— C7A	-75.6 (4)
C5—N1—C1—C7	45.0 (4)	C5A—N1A—C1A— C7A	46.6 (4)
N1—C1—C2—C9	-59.5 (4)	N1A—C1A—C2A— C9A	-62.4 (4)
C7—C1—C2—C9	-171.6 (4)	C7A—C1A—C2A— C9A	-174.6 (3)

N1—C1—C2—C3	61.5 (4)	N1A—C1A—C2A—C3A	60.8 (4)
C7—C1—C2—C3	-50.6 (4)	C7A—C1A—C2A—C3A	-51.3 (4)
C9—C2—C3—O3	-43.2 (5)	C9A—C2A—C3A—O3A	-52.5 (4)
C1—C2—C3—O3	-167.0 (3)	C1A—C2A—C3A—O3A	-175.9 (3)
C9—C2—C3—C4	76.9 (4)	C9A—C2A—C3A—C4A	74.4 (4)
C1—C2—C3—C4	-46.9 (4)	C1A—C2A—C3A—C4A	-49.0 (4)
O3—C3—C4—C5	169.2 (3)	O3A—C3A—C4A—C5A	177.7 (3)
C2—C3—C4—C5	47.4 (5)	C2A—C3A—C4A—C5A	51.3 (4)
C8—N1—C5—C6	74.9 (4)	C8A—N1A—C5A—C6A	76.1 (4)
C1—N1—C5—C6	-46.5 (4)	C1A—N1A—C5A—C6A	-45.9 (4)
C8—N1—C5—C4	-165.7 (3)	C8A—N1A—C5A—C4A	-164.7 (3)
C1—N1—C5—C4	72.9 (4)	C1A—N1A—C5A—C4A	73.2 (4)
C3—C4—C5—N1	-61.4 (4)	C3A—C4A—C5A—N1A	-64.6 (4)
C3—C4—C5—C6	50.5 (5)	C3A—C4A—C5A—C6A	46.8 (5)
N1—C5—C6—C7	29.4 (4)	N1A—C5A—C6A—C7A	27.3 (4)
C4—C5—C6—C7	-85.3 (4)	C4A—C5A—C6A—C7A	-86.8 (4)
N1—C1—C7—C6	-26.3 (4)	N1A—C1A—C7A—C6A	-29.1 (4)
C2—C1—C7—C6	89.1 (4)	C2A—C1A—C7A—C6A	87.1 (4)
C5—C6—C7—C1	-2.0 (4)	C5A—C6A—C7A—C1A	1.0 (4)
C1—C2—C9—O1	49.5 (5)	C1A—C2A—C9A—O1A	38.2 (5)
C3—C2—C9—O1	-72.5 (5)	C3A—C2A—C9A—O1A	-84.1 (5)

C1—C2—C9—O2	-134.0 (4)	C1A—C2A—C9A— O2A	-143.3 (4)
C3—C2—C9—O2	104.1 (4)	C3A—C2A—C9A— O2A	94.5 (4)

APPENDIX 2 (A) – THE AMPHETAMINE GOLD(III) DICHLORIDE ADDUCT  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	1.07844 (4)	0.01245 (4)	0.407089 (12)	0.01872 (18)
Cl1	1.1273 (3)	-0.2166 (3)	0.37581 (10)	0.0393 (6)
Cl2	1.2031 (2)	-0.0494 (3)	0.48269 (7)	0.0314 (5)
N1	1.0337 (9)	0.2134 (8)	0.4411 (3)	0.0245 (15)
H1A	1.0066	0.1920	0.4730	0.029*
H1B	1.1207	0.2649	0.4429	0.029*
C1	0.9702 (10)	0.0730 (10)	0.3438 (3)	0.0244 (18)
C2	1.0233 (12)	0.0245 (11)	0.2987 (3)	0.032 (2)
H2	1.1069	-0.0382	0.2966	0.038*
C3	0.9492 (13)	0.0714 (14)	0.2564 (4)	0.046 (3)
H3	0.9831	0.0401	0.2250	0.055*
C4	0.8291 (12)	0.1614 (14)	0.2595 (4)	0.045 (3)
H4	0.7797	0.1916	0.2304	0.054*
C5	0.7785 (11)	0.2094 (12)	0.3057 (3)	0.035 (2)
H5	0.6951	0.2723	0.3076	0.042*
C6	0.8494 (10)	0.1656 (10)	0.3485 (3)	0.0269 (19)
C7	0.7994 (11)	0.2290 (11)	0.3965 (3)	0.033 (2)
H7A	0.7686	0.1471	0.4185	0.040*
H7B	0.7138	0.2944	0.3909	0.040*
C8	0.9221 (11)	0.3185 (11)	0.4211 (3)	0.033 (2)
H8	0.8784	0.3738	0.4494	0.040*
C9	0.9934 (14)	0.4297 (11)	0.3881 (4)	0.046 (3)
H9A	1.0425	0.3778	0.3610	0.069*
H9B	1.0655	0.4871	0.4069	0.069*
H9C	0.9189	0.4971	0.3748	0.069*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Au1	0.0216 (3)	0.0200 (2)	0.0146 (2)	-0.00106	0.00058	0.00607

			(12)	(12)	(12)
Cl1	0.0445 (14)	0.0272 (11)	0.0462 (14)	0.0075 (10)	-0.0041 (11)
Cl2	0.0375 (12)	0.0409 (12)	0.0159 (10)	0.0136 (10)	0.0023 (8)
N1	0.038 (4)	0.024 (4)	0.012 (3)	0.004 (3)	-0.004 (3)
C1	0.026 (4)	0.030 (5)	0.017 (4)	-0.008 (4)	0.000 (3)
C2	0.038 (5)	0.043 (6)	0.015 (4)	-0.018 (4)	0.005 (4)
C3	0.054 (7)	0.066 (7)	0.017 (5)	-0.029 (6)	0.009 (4)
C4	0.040 (6)	0.072 (8)	0.023 (5)	-0.017 (6)	-0.013 (4)
C5	0.030 (5)	0.049 (6)	0.027 (5)	-0.005 (4)	-0.007 (4)
C6	0.024 (4)	0.032 (5)	0.025 (4)	-0.008 (4)	-0.006 (3)
C7	0.036 (5)	0.037 (5)	0.026 (5)	0.008 (4)	-0.003 (4)
C8	0.050 (6)	0.029 (5)	0.020 (5)	0.011 (4)	-0.005 (4)
C9	0.068 (8)	0.022 (5)	0.048 (6)	0.001 (5)	-0.018 (6)
					0.008 (5)

## GEOMETRIC PARAMETERS (Å, °)

Au1—C1	2.057 (8)	C4—C5	1.406 (15)
Au1—N1	2.069 (7)	C4—H4	0.9500
Au1—Cl1	2.270 (2)	C5—C6	1.388 (12)
Au1—Cl2	2.414 (2)	C5—H5	0.9500
N1—C8	1.492 (11)	C6—C7	1.495 (13)
N1—H1A	0.9200	C7—C8	1.533 (14)
N1—H1B	0.9200	C7—H7A	0.9900
C1—C6	1.387 (13)	C7—H7B	0.9900
C1—C2	1.389 (13)	C8—C9	1.491 (15)
C2—C3	1.398 (15)	C8—H8	1.0000
C2—H2	0.9500	C9—H9A	0.9800
C3—C4	1.365 (17)	C9—H9B	0.9800
C3—H3	0.9500	C9—H9C	0.9800
C1—Au1—N1	92.8 (3)	C6—C5—C4	120.5 (10)
C1—Au1—Cl1	91.2 (3)	C6—C5—H5	119.7
N1—Au1—Cl1	175.4 (2)	C4—C5—H5	119.7
C1—Au1—Cl2	177.8 (3)	C1—C6—C5	117.7 (9)
N1—Au1—Cl2	85.0 (2)	C1—C6—C7	123.4 (8)
Cl1—Au1—Cl2	91.01 (9)	C5—C6—C7	118.7 (9)

C8—N1—Au1	121.6 (6)	C6—C7—C8	111.0 (8)
C8—N1—H1A	106.9	C6—C7—H7A	109.4
Au1—N1—H1A	106.9	C8—C7—H7A	109.4
C8—N1—H1B	106.9	C6—C7—H7B	109.4
Au1—N1—H1B	106.9	C8—C7—H7B	109.4
H1A—N1—H1B	106.7	H7A—C7—H7B	108.0
C6—C1—C2	123.1 (8)	C9—C8—N1	110.2 (9)
C6—C1—Au1	117.7 (6)	C9—C8—C7	114.1 (8)
C2—C1—Au1	119.2 (7)	N1—C8—C7	109.1 (8)
C1—C2—C3	117.5 (10)	C9—C8—H8	107.8
C1—C2—H2	121.2	N1—C8—H8	107.8
C3—C2—H2	121.2	C7—C8—H8	107.8
C4—C3—C2	121.2 (9)	C8—C9—H9A	109.5
C4—C3—H3	119.4	C8—C9—H9B	109.5
C2—C3—H3	119.4	H9A—C9—H9B	109.5
C3—C4—C5	120.0 (9)	C8—C9—H9C	109.5
C3—C4—H4	120.0	H9A—C9—H9C	109.5
C5—C4—H4	120.0	H9B—C9—H9C	109.5
C1—Au1—N1—C8	13.9 (7)	Au1—C1—C6—C5	178.5 (7)
C1—Au1—N1—C8	-166.1 (7)	C2—C1—C6—C7	-174.5 (9)
N1—Au1—C1—C6	-32.9 (7)	Au1—C1—C6—C7	3.2 (12)
C1—Au1—C1—C6	144.8 (7)	C4—C5—C6—C1	-0.4 (14)
N1—Au1—C1—C2	145.0 (7)	C4—C5—C6—C7	175.1 (9)
C1—Au1—C1—C2	-37.4 (7)	C1—C6—C7—C8	57.1 (12)
C6—C1—C2—C3	-0.6 (14)	C5—C6—C7—C8	-118.1 (9)
Au1—C1—C2—C3	-178.2 (7)	Au1—N1—C8—C9	-93.5 (9)
C1—C2—C3—C4	-0.1 (15)	Au1—N1—C8—C7	32.4 (10)
C2—C3—C4—C5	0.5 (16)	C6—C7—C8—C9	49.9 (11)
C3—C4—C5—C6	-0.2 (16)	C6—C7—C8—N1	-73.7 (10)
C2—C1—C6—C5	0.8 (13)		

APPENDIX 2 (B) – THE METHAMPHETAMINE  
GOLD(III) TETRACHLORIDE SALT  
FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.15523 (4)	0.16892 (2)	0.01409 (2)	0.01989 (11)
Cl1	0.1062 (3)	0.01049 (17)	-0.00062 (17)	0.0273 (5)
Cl2	0.1138 (3)	0.15942 (18)	0.17638 (12)	0.0284 (4)
Cl3	0.1893 (4)	0.32667 (19)	0.03219 (19)	0.0319 (5)
Cl4	0.1973 (3)	0.18108 (17)	-0.14766 (14)	0.0295 (5)
Au2	0.83880 (4)	0.14929 (2)	0.50634 (2)	0.01973 (11)
Cl5	0.9084 (3)	0.13179 (17)	0.66462 (14)	0.0282 (5)
Cl6	0.8617 (3)	-0.00867 (19)	0.48325 (19)	0.0286 (5)
Cl7	0.7724 (3)	0.17100 (18)	0.34684 (13)	0.0298 (5)
Cl8	0.8221 (3)	0.30781 (18)	0.5297 (2)	0.0300 (5)
N1	0.1540 (10)	-0.0642 (5)	0.6705 (5)	0.0251 (16)
H1C	0.1085	-0.0145	0.6359	0.030*
H1D	0.1739	-0.1128	0.6281	0.030*
C1	0.4644 (11)	-0.0100 (7)	0.6330 (6)	0.028 (2)
H1A	0.5810	0.0107	0.6617	0.033*
H1B	0.4894	-0.0677	0.5957	0.033*
C2	0.3362 (12)	-0.0352 (7)	0.7141 (6)	0.0246 (19)
H2A	0.3168	0.0218	0.7548	0.030*
C3	0.4094 (14)	-0.1125 (7)	0.7767 (7)	0.030 (2)
H3A	0.4235	-0.1698	0.7384	0.044*
H3B	0.3247	-0.1243	0.8296	0.044*
H3C	0.5278	-0.0938	0.8028	0.044*
C4	0.4020 (12)	0.0647 (7)	0.5642 (7)	0.027 (2)
C5	0.3966 (11)	0.1578 (8)	0.5933 (6)	0.031 (2)
H5	0.4348	0.1741	0.6564	0.037*
C6	0.3344 (13)	0.2291 (8)	0.5298 (9)	0.033 (2)
H6	0.3292	0.2928	0.5499	0.039*
C7	0.2828 (12)	0.2042 (7)	0.4399 (7)	0.030 (2)
H7	0.2405	0.2518	0.3975	0.035*
C8	0.2886 (13)	0.1133 (7)	0.4070 (7)	0.026 (2)

H8	0.2527	0.0980	0.3432	0.032*
C9	0.3493 (12)	0.0443 (8)	0.4708 (7)	0.028 (2)
H9	0.3547	-0.0190	0.4494	0.034*
C10	0.0133 (13)	-0.0947 (9)	0.7418 (7)	0.029 (2)
H10A	0.0379	-0.1594	0.7619	0.043*
H10B	-0.1074	-0.0914	0.7120	0.043*
H10C	0.0172	-0.0533	0.7980	0.043*
N1A	0.8383 (10)	-0.0172 (6)	0.1992 (6)	0.0317 (18)
H1G	0.8299	0.0276	0.2467	0.038*
H1H	0.8791	0.0124	0.1445	0.038*
C1A	0.5255 (12)	0.0273 (7)	0.1505 (6)	0.029 (2)
H1E	0.4035	0.0020	0.1352	0.035*
H1F	0.5122	0.0697	0.2065	0.035*
C2A	0.6496 (12)	-0.0548 (6)	0.1794 (7)	0.0241 (19)
H2B	0.6563	-0.1001	0.1246	0.029*
C3A	0.5806 (13)	-0.1055 (8)	0.2660 (7)	0.031 (2)
H3D	0.5862	-0.0637	0.3220	0.046*
H3E	0.6559	-0.1611	0.2779	0.046*
H3F	0.4544	-0.1249	0.2551	0.046*
C4A	0.5913 (12)	0.0846 (7)	0.0653 (7)	0.026 (2)
C5A	0.6010 (13)	0.0448 (8)	-0.0249 (7)	0.031 (2)
H5A	0.5675	-0.0190	-0.0343	0.038*
C6A	0.6597 (14)	0.0984 (8)	-0.1013 (9)	0.033 (2)
H6A	0.6656	0.0705	-0.1632	0.040*
C7A	0.7093 (13)	0.1895 (8)	-0.0909 (7)	0.033 (2)
H7A	0.7506	0.2243	-0.1448	0.039*
C8A	0.6993 (14)	0.2321 (8)	0.0002 (8)	0.037 (3)
H8A	0.7302	0.2964	0.0088	0.045*
C9A	0.6427 (13)	0.1774 (8)	0.0772 (7)	0.033 (2)
H9A	0.6392	0.2043	0.1396	0.040*
C10A	0.9776 (14)	-0.0880 (9)	0.2292 (8)	0.031 (2)
H10F	1.0978	-0.0583	0.2308	0.047*
H11E	0.9787	-0.1400	0.1832	0.047*
H12D	0.9477	-0.1119	0.2933	0.047*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Au1	0.01938 (16)	0.0224 (2)	0.01785 (16)	0.00090 (14)	-0.00045 (11)	0.00078 (14)
Cl1	0.0270 (10)	0.0229 (12)	0.0320 (12)	-0.0032 (10)	-0.0005 (9)	0.0003 (10)
Cl2	0.0312 (10)	0.0355 (12)	0.0186 (8)	-0.0013 (11)	0.0029 (7)	-0.0012 (11)
Cl3	0.0397 (13)	0.0226 (13)	0.0333 (13)	-0.0015 (10)	0.0029 (11)	-0.0019 (11)
Cl4	0.0336 (11)	0.0373 (13)	0.0177 (9)	0.0028 (10)	0.0016 (7)	0.0022 (10)
Au2	0.01885 (16)	0.0224 (2)	0.01797 (16)	-0.00004 (14)	0.00050 (10)	0.00034 (14)
Cl5	0.0307 (10)	0.0347 (12)	0.0193 (9)	-0.0005 (9)	-0.0051 (7)	0.0036 (9)
Cl6	0.0255 (11)	0.0252 (13)	0.0350 (13)	0.0032 (9)	-0.0004 (9)	-0.0008 (11)
Cl7	0.0322 (10)	0.0396 (13)	0.0177 (9)	0.0010 (10)	-0.0015 (7)	0.0013 (11)
Cl8	0.0387 (13)	0.0205 (12)	0.0307 (13)	-0.0007 (10)	-0.0024 (10)	0.0012 (11)
N1	0.024 (4)	0.030 (4)	0.022 (4)	-0.002 (3)	0.002 (3)	0.001 (3)
C1	0.018 (4)	0.043 (6)	0.022 (5)	0.000 (4)	-0.002 (3)	0.000 (4)
C2	0.025 (4)	0.031 (5)	0.018 (5)	-0.006 (4)	0.000 (4)	0.000 (4)
C3	0.037 (5)	0.034 (6)	0.018 (5)	0.002 (4)	-0.001 (4)	0.001 (4)
C4	0.012 (4)	0.041 (6)	0.028 (5)	-0.003 (4)	-0.007 (4)	0.002 (4)
C5	0.032 (4)	0.030 (6)	0.031 (5)	0.005 (5)	-0.006 (3)	-0.001 (5)
C6	0.025 (5)	0.032 (6)	0.041 (6)	0.009 (4)	0.008 (4)	0.008 (5)
C7	0.022 (4)	0.039 (6)	0.027 (6)	-0.002 (4)	-0.008 (4)	0.010 (4)
C8	0.025 (5)	0.048 (6)	0.006 (4)	-0.010 (4)	0.000 (3)	0.007 (4)
C9	0.028 (5)	0.043 (6)	0.014 (5)	-0.005 (4)	-0.006 (4)	-0.002 (4)
C10	0.031 (6)	0.032 (6)	0.024 (6)	-0.004 (4)	0.008 (4)	0.004 (4)
N1A	0.025 (4)	0.036 (5)	0.033 (5)	0.000 (3)	-0.005 (3)	0.006 (4)
C1A	0.024 (4)	0.043 (6)	0.021 (5)	0.005 (4)	-0.004 (3)	-0.005 (4)
C2A	0.025 (5)	0.028 (5)	0.019 (5)	-0.002 (4)	0.003 (4)	-0.008 (4)
C3A	0.030 (5)	0.045 (6)	0.018 (5)	0.002 (4)	0.003 (4)	-0.003 (4)
C4A	0.016 (4)	0.038 (6)	0.024 (5)	0.005 (4)	0.000 (4)	0.000 (4)

C5A	0.026 (5)	0.033 (6)	0.035 (6)	0.009 (4)	-0.004 (4)	-0.001 (5)
C6A	0.028 (5)	0.037 (6)	0.034 (6)	0.003 (4)	0.008 (4)	0.009 (5)
C7A	0.022 (5)	0.048 (6)	0.028 (5)	0.002 (4)	0.013 (4)	0.002 (5)
C8A	0.027 (5)	0.032 (6)	0.054 (7)	-0.010 (5)	0.007 (5)	-0.004 (5)
C9A	0.032 (5)	0.031 (6)	0.036 (5)	0.006 (5)	-0.017 (4)	-0.008 (5)
C10A	0.027 (5)	0.036 (6)	0.029 (6)	0.000 (4)	-0.008 (4)	-0.004 (5)

## GEOMETRIC PARAMETERS (Å, °)

Au1—Cl3	2.274 (3)	C9—H9	0.9500
Au1—Cl4	2.2782 (19)	C10—H10A	0.9800
Au1—Cl2	2.2825 (18)	C10—H10B	0.9800
Au1—Cl1	2.294 (2)	C10—H10C	0.9800
Au2—Cl5	2.2736 (19)	N1A—C10A	1.497 (13)
Au2—Cl6	2.278 (3)	N1A—C2A	1.513 (11)
Au2—Cl8	2.284 (3)	N1A—H1G	0.9200
Au2—Cl7	2.2921 (18)	N1A—H1H	0.9201
N1—C10	1.498 (12)	C1A—C4A	1.520 (13)
N1—C2	1.528 (11)	C1A—C2A	1.537 (13)
N1—H1C	0.9199	C1A—H1E	0.9900
N1—H1D	0.9200	C1A—H1F	0.9900
C1—C4	1.502 (13)	C2A—C3A	1.494 (13)
C1—C2	1.514 (12)	C2A—H2B	1.0000
C1—H1A	0.9900	C3A—H3D	0.9800
C1—H1B	0.9900	C3A—H3E	0.9800
C2—C3	1.503 (13)	C3A—H3F	0.9800
C2—H2A	1.0000	C4A—C5A	1.379 (14)
C3—H3A	0.9800	C4A—C9A	1.384 (15)
C3—H3B	0.9800	C5A—C6A	1.377 (15)
C3—H3C	0.9800	C5A—H5A	0.9500
C4—C9	1.386 (13)	C6A—C7A	1.355 (15)
C4—C5	1.387 (15)	C6A—H6A	0.9500
C5—C6	1.421 (14)	C7A—C8A	1.407 (15)
C5—H5	0.9500	C7A—H7A	0.9500
C6—C7	1.354 (15)	C8A—C9A	1.389 (15)
C6—H6	0.9500	C8A—H8A	0.9500
C7—C8	1.373 (14)	C9A—H9A	0.9500

C7—H7	0.9500	C10A—H10F	0.9800
C8—C9	1.397 (14)	C10A—H11E	0.9800
C8—H8	0.9500	C10A—H12D	0.9800
Cl3—Au1—Cl4	91.09 (9)	N1—C10—H10A	109.5
Cl3—Au1—Cl2	87.93 (9)	N1—C10—H10B	109.5
Cl4—Au1—Cl2	179.02 (10)	H10A—C10—H10B	109.5
Cl3—Au1—Cl1	177.03 (9)	N1—C10—H10C	109.5
Cl4—Au1—Cl1	90.48 (9)	H10A—C10—H10C	109.5
Cl2—Au1—Cl1	90.50 (9)	H10B—C10—H10C	109.5
Cl5—Au2—Cl6	90.67 (9)	C10A—N1A—C2A	116.1 (8)
Cl5—Au2—Cl8	88.99 (9)	C10A—N1A—H1G	108.2
Cl6—Au2—Cl8	178.83 (9)	C2A—N1A—H1G	108.3
Cl5—Au2—Cl7	178.39 (9)	C10A—N1A—H1H	108.3
Cl6—Au2—Cl7	90.71 (9)	C2A—N1A—H1H	108.2
Cl8—Au2—Cl7	89.61 (9)	H1G—N1A—H1H	107.4
C10—N1—C2	115.0 (7)	C4A—C1A—C2A	115.0 (8)
C10—N1—H1C	108.6	C4A—C1A—H1E	108.5
C2—N1—H1C	108.5	C2A—C1A—H1E	108.5
C10—N1—H1D	108.5	C4A—C1A—H1F	108.5
C2—N1—H1D	108.5	C2A—C1A—H1F	108.5
H1C—N1—H1D	107.5	H1E—C1A—H1F	107.5
C4—C1—C2	116.9 (8)	C3A—C2A—N1A	109.7 (8)
C4—C1—H1A	108.1	C3A—C2A—C1A	112.1 (8)
C2—C1—H1A	108.1	N1A—C2A—C1A	108.8 (7)
C4—C1—H1B	108.1	C3A—C2A—H2B	108.7
C2—C1—H1B	108.1	N1A—C2A—H2B	108.7
H1A—C1—H1B	107.3	C1A—C2A—H2B	108.7
C3—C2—C1	112.5 (8)	C2A—C3A—H3D	109.5
C3—C2—N1	110.2 (8)	C2A—C3A—H3E	109.5
C1—C2—N1	108.4 (7)	H3D—C3A—H3E	109.5
C3—C2—H2A	108.6	C2A—C3A—H3F	109.5
C1—C2—H2A	108.6	H3D—C3A—H3F	109.5
N1—C2—H2A	108.6	H3E—C3A—H3F	109.5
C2—C3—H3A	109.5	C5A—C4A—C9A	119.1 (10)
C2—C3—H3B	109.5	C5A—C4A—C1A	120.4 (9)
H3A—C3—H3B	109.5	C9A—C4A—C1A	120.5 (9)
C2—C3—H3C	109.5	C6A—C5A—C4A	119.4 (11)
H3A—C3—H3C	109.5	C6A—C5A—H5A	120.3

H3B—C3—H3C	109.5	C4A—C5A—H5A	120.3
C9—C4—C5	117.7 (9)	C7A—C6A—C5A	122.2 (12)
C9—C4—C1	122.3 (9)	C7A—C6A—H6A	118.9
C5—C4—C1	120.0 (8)	C5A—C6A—H6A	118.9
C4—C5—C6	120.7 (9)	C6A—C7A—C8A	119.7 (11)
C4—C5—H5	119.6	C6A—C7A—H7A	120.2
C6—C5—H5	119.6	C8A—C7A—H7A	120.2
C7—C6—C5	118.5 (10)	C9A—C8A—C7A	117.9 (10)
C7—C6—H6	120.8	C9A—C8A—H8A	121.1
C5—C6—H6	120.8	C7A—C8A—H8A	121.1
C6—C7—C8	123.1 (9)	C4A—C9A—C8A	121.7 (10)
C6—C7—H7	118.5	C4A—C9A—H9A	119.1
C8—C7—H7	118.5	C8A—C9A—H9A	119.1
C7—C8—C9	117.5 (9)	N1A—C10A—H10F	109.5
C7—C8—H8	121.3	N1A—C10A—H11E	109.5
C9—C8—H8	121.3	H10F—C10A—H11E	109.5
C4—C9—C8	122.5 (10)	N1A—C10A—H12D	109.5
C4—C9—H9	118.8	H10F—C10A—H12D	109.5
C8—C9—H9	118.8	H11E—C10A—H12D	109.5
C4—C1—C2—C3	178.2 (8)	C10A—N1A—C2A— C3A	56.7 (10)
C4—C1—C2—N1	56.1 (11)	C10A—N1A—C2A— C1A	179.6 (8)
C10—N1—C2—C3	54.5 (11)	C4A—C1A—C2A— C3A	177.6 (8)
C10—N1—C2—C1	178.0 (9)	C4A—C1A—C2A— N1A	56.1 (10)
C2—C1—C4—C9	-108.0 (11)	C2A—C1A—C4A— C5A	65.8 (11)
C2—C1—C4—C5	72.3 (11)	C2A—C1A—C4A— C9A	-114.0 (10)
C9—C4—C5—C6	1.6 (13)	C9A—C4A—C5A— C6A	-0.7 (14)
C1—C4—C5—C6	-178.7 (8)	C1A—C4A—C5A— C6A	179.5 (9)
C4—C5—C6—C7	-0.8 (14)	C4A—C5A—C6A— C7A	0.2 (16)
C5—C6—C7—C8	-0.4 (15)	C5A—C6A—C7A— C8A	-0.8 (16)
C6—C7—C8—C9	0.7 (15)	C6A—C7A—C8A—	1.7 (15)

C5—C4—C9—C8	-1.3 (14)	C9A C5A—C4A—C9A— C8A	1.7 (14)
C1—C4—C9—C8	179.0 (9)	C1A—C4A—C9A— C8A	-178.5 (9)
C7—C8—C9—C4	0.2 (14)	C7A—C8A—C9A— C4A	-2.2 (15)

APPENDIX 2 (C) – THE EPHEDRINE  
GOLD(III) TETRACHLORIDE SALT  
FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Au1	0.51006 (4)	0.076623 (12)	0.056401 (19)	0.02202 (11)
Cl1	0.2212 (2)	0.09400 (9)	0.05762 (13)	0.0325 (4)
Cl2	0.4833 (2)	0.06536 (8)	-0.09056 (12)	0.0290 (4)
Cl3	0.8006 (2)	0.06545 (8)	0.05363 (13)	0.0303 (4)
Cl4	0.5373 (3)	0.08461 (9)	0.20336 (13)	0.0366 (5)
Au2	0.48945 (4)	0.012413 (13)	0.62846 (2)	0.02478 (11)
Cl5	0.5179 (2)	-0.07059 (7)	0.56997 (12)	0.0276 (4)
Cl6	0.1954 (3)	0.00565 (9)	0.61780 (16)	0.0412 (5)
Cl7	0.4660 (3)	0.09502 (8)	0.68776 (14)	0.0361 (5)
Cl8	0.7820 (2)	0.02260 (8)	0.63758 (13)	0.0330 (4)
O1	0.0588 (7)	0.3790 (2)	0.2068 (4)	0.0324 (13)
H1	0.1164	0.4055	0.1919	0.049*
N1	-0.1352 (8)	0.4183 (3)	0.3320 (4)	0.0269 (14)
H1B	-0.1719	0.4217	0.2744	0.032*
H1C	-0.2318	0.4189	0.3634	0.032*
C1	0.1119 (10)	0.3647 (3)	0.2937 (5)	0.0292 (18)
H1D	0.1934	0.3926	0.3183	0.035*
C2	-0.0498 (10)	0.3651 (3)	0.3448 (5)	0.0254 (17)
H2A	-0.0147	0.3603	0.4078	0.030*
C3	-0.1829 (11)	0.3225 (3)	0.3169 (7)	0.040 (2)
H3A	-0.2860	0.3271	0.3494	0.060*
H3B	-0.1335	0.2870	0.3287	0.060*
H3C	-0.2145	0.3260	0.2547	0.060*
C4	0.2038 (10)	0.3109 (3)	0.2987 (5)	0.0283 (18)
C5	0.2999 (11)	0.2966 (4)	0.3742 (6)	0.0345 (19)
H5	0.3056	0.3199	0.4228	0.041*
C6	0.3883 (12)	0.2478 (4)	0.3791 (6)	0.042 (2)
H6	0.4517	0.2379	0.4314	0.051*
C7	0.3840 (12)	0.2144 (4)	0.3092 (6)	0.040 (2)
H7	0.4469	0.1818	0.3122	0.048*

C8	0.2872 (12)	0.2283 (3)	0.2339 (6)	0.038 (2)
H8	0.2825	0.2049	0.1854	0.045*
C9	0.1974 (11)	0.2762 (3)	0.2289 (6)	0.0332 (19)
H9	0.1309	0.2853	0.1772	0.040*
C10	-0.0258 (11)	0.4658 (3)	0.3574 (6)	0.0327 (19)
H10D	0.0403	0.4585	0.4124	0.049*
H10E	-0.1001	0.4970	0.3641	0.049*
H10F	0.0540	0.4729	0.3123	0.049*
O1A	1.1608 (12)	0.1516 (4)	0.5115 (6)	0.083 (3)
H2	1.1821	0.1451	0.5645	0.124*
N1A	1.0668 (9)	0.1027 (3)	0.3631 (4)	0.0312 (15)
H1E	1.1788	0.1047	0.3868	0.037*
H1F	1.0189	0.0721	0.3843	0.037*
C1A	0.9824 (12)	0.1485 (4)	0.4914 (6)	0.041 (2)
H1A	0.9367	0.1137	0.5120	0.049*
C2A	0.9778 (16)	0.1493 (6)	0.3966 (7)	0.080 (5)
H2A1	1.0607	0.1788	0.3858	0.095*
C3A	0.8167 (17)	0.1673 (6)	0.3433 (8)	0.108 (7)
H3A1	0.7355	0.1374	0.3361	0.162*
H3A2	0.8484	0.1794	0.2863	0.162*
H3A3	0.7622	0.1967	0.3732	0.162*
C4A	0.8854 (12)	0.1950 (4)	0.5298 (6)	0.038 (2)
C5A	0.7302 (13)	0.1846 (4)	0.5637 (6)	0.046 (2)
H5A	0.6847	0.1493	0.5625	0.055*
C6A	0.6381 (15)	0.2266 (5)	0.6005 (6)	0.057 (3)
H6A	0.5310	0.2195	0.6246	0.069*
C7A	0.7027 (17)	0.2772 (5)	0.6012 (7)	0.058 (3)
H7A	0.6402	0.3056	0.6253	0.070*
C8A	0.8593 (16)	0.2870 (4)	0.5670 (6)	0.055 (3)
H8A	0.9042	0.3224	0.5678	0.066*
C9A	0.9511 (14)	0.2465 (4)	0.5317 (6)	0.049 (3)
H9A	1.0592	0.2537	0.5087	0.059*
C10A	1.0723 (14)	0.0971 (4)	0.2677 (6)	0.046 (2)
H10A	0.9615	0.0831	0.2432	0.069*
H10B	1.1653	0.0724	0.2548	0.069*
H10C	1.0938	0.1321	0.2422	0.069*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Au1	0.02034 (18)	0.02480 (18)	0.02078 (18)	-0.00058 (11)	0.00045 (11)	0.00126 (12)
Cl1	0.0216 (10)	0.0474 (12)	0.0285 (10)	0.0007 (8)	0.0026 (7)	0.0019 (9)
Cl2	0.0229 (10)	0.0443 (11)	0.0196 (9)	-0.0003 (7)	-0.0001 (7)	-0.0013 (8)
Cl3	0.0212 (10)	0.0377 (11)	0.0317 (10)	0.0037 (7)	-0.0012 (7)	0.0019 (8)
Cl4	0.0351 (12)	0.0518 (13)	0.0227 (10)	0.0027 (9)	-0.0001 (8)	-0.0020 (9)
Au2	0.02086 (18)	0.03138 (19)	0.02224 (18)	-0.00393 (12)	0.00258 (12)	-0.00216 (13)
Cl5	0.0284 (10)	0.0288 (9)	0.0252 (9)	-0.0024 (7)	-0.0015 (7)	-0.0014 (8)
Cl6	0.0224 (11)	0.0422 (12)	0.0601 (15)	-0.0045 (8)	0.0111 (9)	-0.0105 (11)
Cl7	0.0334 (11)	0.0370 (11)	0.0387 (12)	-0.0062 (8)	0.0087 (8)	-0.0130 (9)
Cl8	0.0199 (10)	0.0439 (12)	0.0348 (11)	-0.0044 (8)	-0.0012 (7)	-0.0055 (9)
O1	0.033 (3)	0.035 (3)	0.029 (3)	0.003 (2)	-0.001 (2)	0.005 (3)
N1	0.024 (4)	0.031 (4)	0.025 (4)	0.001 (3)	0.000 (3)	-0.005 (3)
C1	0.029 (5)	0.032 (4)	0.025 (4)	-0.002 (3)	-0.004 (3)	-0.001 (4)
C2	0.025 (4)	0.025 (4)	0.025 (4)	0.002 (3)	-0.007 (3)	0.001 (3)
C3	0.027 (5)	0.034 (5)	0.059 (6)	0.000 (4)	-0.002 (4)	-0.001 (4)
C4	0.020 (4)	0.036 (5)	0.029 (4)	0.002 (3)	0.005 (3)	0.001 (4)
C5	0.035 (5)	0.035 (5)	0.034 (5)	-0.001 (4)	-0.001 (4)	-0.006 (4)
C6	0.041 (6)	0.042 (5)	0.043 (6)	0.006 (4)	-0.006 (4)	0.005 (5)
C7	0.035 (5)	0.030 (5)	0.057 (6)	0.002 (4)	0.017 (4)	0.006 (4)
C8	0.046 (6)	0.031 (5)	0.038 (5)	0.002 (4)	0.018 (4)	0.000 (4)
C9	0.031 (5)	0.035 (5)	0.034 (5)	-0.003 (3)	0.006 (3)	0.005 (4)
C10	0.035 (5)	0.029 (4)	0.035 (5)	0.001 (3)	0.000 (4)	-0.001 (4)
O1A	0.076 (6)	0.086 (7)	0.084 (7)	0.011 (5)	-0.012 (5)	-0.034 (5)
N1A	0.030 (4)	0.036 (4)	0.027 (4)	0.001 (3)	-0.001 (3)	-0.005 (3)
C1A	0.039 (6)	0.053 (6)	0.031 (5)	0.011 (4)	-0.002 (4)	-0.004 (4)
C2A	0.096 (10)	0.103 (11)	0.036 (6)	0.067 (8)	-0.019 (6)	-0.019 (7)
C3A	0.166 (17)	0.112 (13)	0.046 (8)	0.097 (12)	-0.003 (9)	0.000 (8)
C4A	0.045 (6)	0.040 (5)	0.029 (5)	0.008 (4)	-0.001 (4)	-0.006 (4)
C5A	0.050 (6)	0.058 (6)	0.030 (5)	0.008 (5)	-0.003 (4)	-0.005 (5)
C6A	0.063 (7)	0.080 (9)	0.030 (5)	0.030 (6)	0.011 (5)	-0.002 (5)
C7A	0.086 (9)	0.057 (7)	0.032 (6)	0.035 (6)	-0.003 (5)	-0.006 (5)
C8A	0.091 (9)	0.038 (6)	0.034 (6)	0.016 (5)	-0.011 (5)	0.004 (5)
C9A	0.058 (7)	0.057 (7)	0.033 (5)	0.015 (5)	0.003 (4)	0.003 (5)

C10A	0.064 (7)	0.050 (6)	0.025 (5)	0.003 (5)	0.008 (4)	-0.002 (4)
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GEOMETRIC PARAMETERS ( $\text{\AA}$ ,  $^\circ$ )

Au1—Cl3	2.2734 (18)	C9—H9	0.9500
Au1—Cl4	2.276 (2)	C10—H10D	0.9800
Au1—Cl1	2.2831 (19)	C10—H10E	0.9800
Au1—Cl2	2.2846 (18)	C10—H10F	0.9800
Au2—Cl7	2.274 (2)	O1A—C1A	1.399 (12)
Au2—Cl8	2.2776 (19)	O1A—H2	0.8399
Au2—Cl6	2.281 (2)	N1A—C2A	1.468 (12)
Au2—Cl5	2.2823 (19)	N1A—C10A	1.485 (11)
O1—C1	1.423 (9)	N1A—H1E	0.9200
O1—H1	0.8399	N1A—H1F	0.9199
N1—C2	1.495 (10)	C1A—C2A	1.463 (14)
N1—C10	1.495 (10)	C1A—C4A	1.527 (12)
N1—H1B	0.9200	C1A—H1A	1.0000
N1—H1C	0.9200	C2A—C3A	1.517 (2)
C1—C4	1.522 (11)	C2A—H2A1	1.0000
C1—C2	1.528 (11)	C3A—H3A1	0.9800
C1—H1D	1.0000	C3A—H3A2	0.9800
C2—C3	1.525 (11)	C3A—H3A3	0.9800
C2—H2A	1.0000	C4A—C5A	1.370 (14)
C3—H3A	0.9800	C4A—C9A	1.385 (15)
C3—H3B	0.9800	C5A—C6A	1.411 (14)
C3—H3C	0.9800	C5A—H5A	0.9500
C4—C9	1.383 (12)	C6A—C7A	1.362 (17)
C4—C5	1.388 (12)	C6A—H6A	0.9500
C5—C6	1.399 (13)	C7A—C8A	1.379 (17)
C5—H5	0.9500	C7A—H7A	0.9500
C6—C7	1.364 (13)	C8A—C9A	1.374 (14)
C6—H6	0.9500	C8A—H8A	0.9500
C7—C8	1.386 (13)	C9A—H9A	0.9500
C7—H7	0.9500	C10A—H10A	0.9800
C8—C9	1.386 (12)	C10A—H10B	0.9800
C8—H8	0.9500	C10A—H10C	0.9800
Cl5···Au2 <sup>i</sup>	3.3924 (19)		

Cl3—Au1—Cl4	90.29 (7)	N1—C10—H10D	109.5
Cl3—Au1—Cl1	176.04 (7)	N1—C10—H10E	109.5
Cl4—Au1—Cl1	89.96 (7)	H10D—C10—H10E	109.5
Cl3—Au1—Cl2	89.36 (7)	N1—C10—H10F	109.5
Cl4—Au1—Cl2	177.95 (8)	H10D—C10—H10F	109.5
Cl1—Au1—Cl2	90.53 (7)	H10E—C10—H10F	109.5
Cl7—Au2—Cl8	88.86 (7)	C1A—O1A—H2	109.4
Cl7—Au2—Cl6	89.39 (8)	C2A—N1A—C10A	118.1 (8)
Cl8—Au2—Cl6	177.75 (8)	C2A—N1A—H1E	105.6
Cl7—Au2—Cl5	178.99 (7)	C10A—N1A—H1E	108.1
Cl8—Au2—Cl5	90.21 (7)	C2A—N1A—H1F	108.9
Cl6—Au2—Cl5	91.55 (7)	C10A—N1A—H1F	108.4
C1—O1—H1	109.4	H1E—N1A—H1F	107.3
C2—N1—C10	115.8 (6)	O1A—C1A—C2A	100.2 (9)
C2—N1—H1B	108.3	O1A—C1A—C4A	112.1 (8)
C10—N1—H1B	108.3	C2A—C1A—C4A	113.6 (8)
C2—N1—H1C	108.3	O1A—C1A—H1A	110.2
C10—N1—H1C	108.4	C2A—C1A—H1A	110.2
H1B—N1—H1C	107.4	C4A—C1A—H1A	110.2
O1—C1—C4	112.0 (7)	C1A—C2A—N1A	111.3 (9)
O1—C1—C2	107.0 (6)	C1A—C2A—C3A	120.7 (10)
C4—C1—C2	112.1 (7)	N1A—C2A—C3A	115.7 (9)
O1—C1—H1D	108.5	C1A—C2A—H2A1	101.8
C4—C1—H1D	108.5	N1A—C2A—H2A1	101.8
C2—C1—H1D	108.5	C3A—C2A—H2A1	101.8
N1—C2—C3	107.5 (6)	C2A—C3A—H3A1	109.5
N1—C2—C1	108.0 (6)	C2A—C3A—H3A2	109.5
C3—C2—C1	114.3 (7)	H3A1—C3A—H3A2	109.5
N1—C2—H2A	109.0	C2A—C3A—H3A3	109.5
C3—C2—H2A	109.0	H3A1—C3A—H3A3	109.5
C1—C2—H2A	109.0	H3A2—C3A—H3A3	109.5
C2—C3—H3A	109.5	C5A—C4A—C9A	120.0 (9)
C2—C3—H3B	109.5	C5A—C4A—C1A	118.2 (9)
H3A—C3—H3B	109.5	C9A—C4A—C1A	121.8 (9)
C2—C3—H3C	109.5	C4A—C5A—C6A	119.7 (11)
H3A—C3—H3C	109.5	C4A—C5A—H5A	120.2
H3B—C3—H3C	109.5	C6A—C5A—H5A	120.2
C9—C4—C5	118.8 (8)	C7A—C6A—C5A	120.0 (11)

C9—C4—C1	121.6 (7)	C7A—C6A—H6A	120.0
C5—C4—C1	119.6 (7)	C5A—C6A—H6A	120.0
C4—C5—C6	120.2 (8)	C6A—C7A—C8A	119.8 (10)
C4—C5—H5	119.9	C6A—C7A—H7A	120.1
C6—C5—H5	119.9	C8A—C7A—H7A	120.1
C7—C6—C5	120.4 (9)	C9A—C8A—C7A	120.9 (11)
C7—C6—H6	119.8	C9A—C8A—H8A	119.6
C5—C6—H6	119.8	C7A—C8A—H8A	119.6
C6—C7—C8	119.6 (9)	C8A—C9A—C4A	119.7 (11)
C6—C7—H7	120.2	C8A—C9A—H9A	120.1
C8—C7—H7	120.2	C4A—C9A—H9A	120.1
C7—C8—C9	120.3 (9)	N1A—C10A—H10A	109.5
C7—C8—H8	119.9	N1A—C10A—H10B	109.5
C9—C8—H8	119.9	H10A—C10A—H10B	109.5
C4—C9—C8	120.6 (9)	N1A—C10A—H10C	109.5
C4—C9—H9	119.7	H10A—C10A—H10C	109.5
C8—C9—H9	119.7	H10B—C10A—H10C	109.5
C10—N1—C2—C3	179.0 (7)	O1A—C1A—C2A— N1A	62.5 (13)
C10—N1—C2—C1	-57.2 (8)	C4A—C1A—C2A— N1A	-177.7 (9)
O1—C1—C2—N1	-53.9 (8)	O1A—C1A—C2A— C3A	-156.8 (14)
C4—C1—C2—N1	-177.1 (6)	C4A—C1A—C2A— C3A	-37.1 (19)
O1—C1—C2—C3	65.8 (9)	C10A—N1A—C2A— C1A	179.4 (9)
C4—C1—C2—C3	-57.4 (9)	C10A—N1A—C2A— C3A	36.6 (18)
O1—C1—C4—C9	-13.8 (11)	O1A—C1A—C4A— C5A	-140.4 (9)
C2—C1—C4—C9	106.5 (9)	C2A—C1A—C4A— C5A	106.9 (12)
O1—C1—C4—C5	164.6 (7)	O1A—C1A—C4A— C9A	39.0 (13)
C2—C1—C4—C5	-75.1 (9)	C2A—C1A—C4A— C9A	-73.7 (13)
C9—C4—C5—C6	0.0 (13)	C9A—C4A—C5A— C6A	0.0 (14)
C1—C4—C5—C6	-178.5 (8)	C1A—C4A—C5A—	179.4 (9)

	C6A	
C4—C5—C6—C7	1.4 (14)	C4A—C5A—C6A— C7A
C5—C6—C7—C8	-1.8 (14)	C5A—C6A—C7A— C8A
C6—C7—C8—C9	1.0 (13)	C6A—C7A—C8A— C9A
C5—C4—C9—C8	-0.8 (12)	C7A—C8A—C9A— C4A
C1—C4—C9—C8	177.6 (8)	C5A—C4A—C9A— C8A
C7—C8—C9—C4	0.4 (13)	C1A—C4A—C9A— C8A

Symmetry code: (i)  $-x+1, -y, -z+1$ .

APPENDIX 3 (A) – THE MIXED SALT OF  
MDPV HYDROBROMIDE (0.34) / HYDROCHLORIDE(0.66)  
FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cl1	1.2980 (3)	0.17033 (17)	0.15215 (11)	0.0151 (9)	0.6568
Br1	1.2981 (4)	0.16938 (17)	0.15208 (12)	0.0306 (11)	0.3432
O1	0.90394 (13)	0.07940 (5)	0.05485 (4)	0.0235 (2)	
O2	0.21449 (14)	-0.11780 (6)	0.08320 (4)	0.0320 (3)	
O3	0.34965 (14)	-0.19493 (5)	0.01853 (4)	0.0256 (2)	
N1	0.85333 (17)	0.15400 (6)	0.14626 (4)	0.0192 (2)	
H1	0.979 (3)	0.1464 (8)	0.1413 (6)	0.023*	
C1	0.66150 (18)	-0.01211 (7)	0.06467 (5)	0.0183 (3)	
C2	0.48103 (19)	-0.02830 (7)	0.08732 (5)	0.0207 (3)	
H2	0.4266	0.0023	0.1144	0.025*	
C3	0.38964 (18)	-0.09027 (7)	0.06808 (5)	0.0209 (3)	
C4	0.46855 (19)	-0.13593 (7)	0.02905 (5)	0.0203 (3)	
C5	0.6420 (2)	-0.12096 (7)	0.00609 (5)	0.0221 (3)	
H5	0.6944	-0.1521	-0.0210	0.027*	
C6	0.7374 (2)	-0.05753 (7)	0.02474 (5)	0.0210 (3)	
H6	0.8576	-0.0450	0.0098	0.025*	
C7	0.77859 (18)	0.05254 (7)	0.08261 (5)	0.0185 (3)	
C8	0.74521 (19)	0.08217 (7)	0.13902 (5)	0.0194 (3)	
H8	0.6061	0.0927	0.1436	0.023*	
C9	0.79433 (19)	0.21617 (7)	0.10770 (6)	0.0224 (3)	
H9A	0.8996	0.2281	0.0827	0.027*	
H9B	0.6813	0.2008	0.0866	0.027*	
C10	0.7478 (2)	0.28363 (8)	0.14276 (6)	0.0271 (3)	
H10A	0.6092	0.2865	0.1501	0.033*	
H10B	0.7894	0.3308	0.1255	0.033*	
C11	0.8599 (2)	0.26915 (8)	0.19427 (6)	0.0281 (3)	
H11A	0.9963	0.2820	0.1899	0.034*	
H11B	0.8067	0.2980	0.2246	0.034*	
C12	0.8329 (2)	0.18580 (8)	0.20211 (6)	0.0244 (3)	
H12A	0.7053	0.1747	0.2171	0.029*	

H12B	0.9314	0.1651	0.2263	0.029*
C13	0.80501 (19)	0.02272 (8)	0.18023 (5)	0.0234 (3)
H13A	0.7866	0.0437	0.2165	0.028*
H13B	0.7193	-0.0211	0.1767	0.028*
C14	1.0107 (2)	-0.00422 (8)	0.17520 (6)	0.0291 (3)
H14A	1.0355	-0.0193	0.1377	0.035*
H14B	1.0981	0.0375	0.1841	0.035*
C15	1.0513 (2)	-0.07005 (8)	0.21202 (7)	0.0345 (4)
H15A	1.0288	-0.0550	0.2492	0.052*
H15B	1.1845	-0.0857	0.2078	0.052*
H15C	0.9670	-0.1119	0.2028	0.052*
C16	0.1791 (2)	-0.18174 (8)	0.04995 (6)	0.0248 (3)
H16A	0.0690	-0.1721	0.0261	0.030*
H16B	0.1500	-0.2261	0.0723	0.030*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0017 (12)	0.0238 (17)	0.0198 (16)	-0.0012 (9)	0.0016 (8)	0.0049 (12)
Br1	0.0275 (17)	0.0298 (18)	0.0344 (19)	0.0013 (10)	0.0026 (10)	-0.0015 (12)
O1	0.0264 (5)	0.0213 (5)	0.0227 (5)	-0.0016 (4)	0.0077 (4)	-0.0013 (4)
O2	0.0241 (6)	0.0309 (6)	0.0409 (6)	-0.0083 (4)	0.0080 (4)	-0.0151 (5)
O3	0.0249 (5)	0.0230 (5)	0.0288 (5)	-0.0019 (4)	-0.0008 (4)	-0.0075 (4)
N1	0.0189 (6)	0.0195 (6)	0.0192 (6)	-0.0012 (5)	0.0020 (4)	-0.0030 (4)
C1	0.0225 (7)	0.0171 (6)	0.0154 (6)	0.0022 (5)	-0.0006 (5)	0.0006 (5)
C2	0.0222 (7)	0.0202 (6)	0.0197 (6)	0.0025 (5)	0.0009 (5)	-0.0027 (5)
C3	0.0192 (7)	0.0218 (7)	0.0217 (7)	0.0009 (5)	-0.0005 (5)	0.0005 (5)
C4	0.0253 (7)	0.0167 (6)	0.0190 (7)	0.0025 (5)	-0.0052 (5)	-0.0005 (5)
C5	0.0277 (7)	0.0198 (7)	0.0189 (7)	0.0040 (5)	0.0015 (5)	-0.0028 (5)
C6	0.0237 (7)	0.0203 (7)	0.0190 (7)	0.0022 (5)	0.0034 (5)	0.0011 (5)
C7	0.0193 (7)	0.0169 (6)	0.0192 (7)	0.0037 (5)	0.0012 (5)	0.0015 (5)
C8	0.0193 (6)	0.0193 (7)	0.0196 (7)	-0.0026 (5)	0.0025 (5)	-0.0021 (5)
C9	0.0262 (8)	0.0185 (7)	0.0225 (7)	0.0002 (5)	0.0019 (5)	0.0002 (6)
C10	0.0295 (7)	0.0204 (7)	0.0314 (8)	0.0005 (6)	0.0035 (6)	-0.0040 (6)
C11	0.0283 (8)	0.0248 (7)	0.0312 (8)	-0.0021 (6)	0.0018 (6)	-0.0118 (6)
C12	0.0268 (8)	0.0273 (7)	0.0190 (7)	-0.0010 (6)	0.0013 (5)	-0.0069 (6)
C13	0.0306 (8)	0.0221 (7)	0.0176 (7)	-0.0046 (5)	0.0016 (5)	0.0016 (5)
C14	0.0315 (8)	0.0259 (7)	0.0299 (8)	0.0018 (6)	-0.0005 (6)	0.0061 (6)

C15	0.0420 (9)	0.0245 (7)	0.0369 (9)	-0.0055 (6)	-0.0143 (7)	0.0048 (6)
C16	0.0242 (7)	0.0222 (7)	0.0279 (8)	-0.0030 (5)	-0.0015 (6)	-0.0046 (6)

## GEOMETRIC PARAMETERS (Å, °)

O1—C7	1.2183 (16)	C9—C10	1.5245 (19)
O2—C3	1.3759 (16)	C9—H9A	0.9900
O2—C16	1.4333 (17)	C9—H9B	0.9900
O3—C4	1.3683 (16)	C10—C11	1.531 (2)
O3—C16	1.4501 (17)	C10—H10A	0.9900
N1—C8	1.5000 (16)	C10—H10B	0.9900
N1—C12	1.5141 (17)	C11—C12	1.5116 (19)
N1—C9	1.5268 (17)	C11—H11A	0.9900
N1—H1	0.902 (18)	C11—H11B	0.9900
C1—C6	1.3915 (18)	C12—H12A	0.9900
C1—C2	1.4164 (19)	C12—H12B	0.9900
C1—C7	1.4851 (18)	C13—C14	1.525 (2)
C2—C3	1.3653 (18)	C13—H13A	0.9900
C2—H2	0.9500	C13—H13B	0.9900
C3—C4	1.3865 (18)	C14—C15	1.519 (2)
C4—C5	1.3716 (19)	C14—H14A	0.9900
C5—C6	1.3946 (19)	C14—H14B	0.9900
C5—H5	0.9500	C15—H15A	0.9800
C6—H6	0.9500	C15—H15B	0.9800
C7—C8	1.5245 (18)	C15—H15C	0.9800
C8—C13	1.5371 (18)	C16—H16A	0.9900
C8—H8	1.0000	C16—H16B	0.9900
C3—O2—C16	106.22 (10)	C9—C10—H10A	111.0
C4—O3—C16	105.89 (10)	C11—C10—H10A	111.0
C8—N1—C12	112.56 (10)	C9—C10—H10B	111.0
C8—N1—C9	114.04 (10)	C11—C10—H10B	111.0
C12—N1—C9	106.54 (10)	H10A—C10—H10B	109.0
C8—N1—H1	110.5 (10)	C12—C11—C10	102.16 (11)
C12—N1—H1	106.0 (10)	C12—C11—H11A	111.3
C9—N1—H1	106.7 (10)	C10—C11—H11A	111.3
C6—C1—C2	120.65 (12)	C12—C11—H11B	111.3
C6—C1—C7	117.23 (12)	C10—C11—H11B	111.3
C2—C1—C7	122.12 (11)	H11A—C11—H11B	109.2

C3—C2—C1	116.34 (12)	C11—C12—N1	103.72 (11)
C3—C2—H2	121.8	C11—C12—H12A	111.0
C1—C2—H2	121.8	N1—C12—H12A	111.0
C2—C3—O2	127.69 (12)	C11—C12—H12B	111.0
C2—C3—C4	122.43 (13)	N1—C12—H12B	111.0
O2—C3—C4	109.88 (11)	H12A—C12—H12B	109.0
O3—C4—C5	127.58 (12)	C14—C13—C8	114.84 (11)
O3—C4—C3	110.12 (12)	C14—C13—H13A	108.6
C5—C4—C3	122.29 (12)	C8—C13—H13A	108.6
C4—C5—C6	116.31 (12)	C14—C13—H13B	108.6
C4—C5—H5	121.8	C8—C13—H13B	108.6
C6—C5—H5	121.8	H13A—C13—H13B	107.5
C1—C6—C5	121.95 (13)	C15—C14—C13	111.79 (13)
C1—C6—H6	119.0	C15—C14—H14A	109.3
C5—C6—H6	119.0	C13—C14—H14A	109.3
O1—C7—C1	122.17 (12)	C15—C14—H14B	109.3
O1—C7—C8	120.10 (11)	C13—C14—H14B	109.3
C1—C7—C8	117.64 (11)	H14A—C14—H14B	107.9
N1—C8—C7	109.29 (10)	C14—C15—H15A	109.5
N1—C8—C13	111.75 (11)	C14—C15—H15B	109.5
C7—C8—C13	109.83 (10)	H15A—C15—H15B	109.5
N1—C8—H8	108.6	C14—C15—H15C	109.5
C7—C8—H8	108.6	H15A—C15—H15C	109.5
C13—C8—H8	108.6	H15B—C15—H15C	109.5
C10—C9—N1	105.56 (11)	O2—C16—O3	107.50 (10)
C10—C9—H9A	110.6	O2—C16—H16A	110.2
N1—C9—H9A	110.6	O3—C16—H16A	110.2
C10—C9—H9B	110.6	O2—C16—H16B	110.2
N1—C9—H9B	110.6	O3—C16—H16B	110.2
H9A—C9—H9B	108.8	H16A—C16—H16B	108.5
C9—C10—C11	103.92 (11)		
C6—C1—C2—C3	0.48 (19)	C12—N1—C8—C7	-178.05 (11)
C7—C1—C2—C3	-178.63 (12)	C9—N1—C8—C7	60.42 (14)
C1—C2—C3—O2	-179.89 (12)	C12—N1—C8—C13	-56.28 (14)
C1—C2—C3—C4	0.85 (19)	C9—N1—C8—C13	-177.80 (10)
C16—O2—C3—C2	177.78 (13)	O1—C7—C8—N1	12.32 (17)

C16—O2—C3—C4	-2.88 (15)	C1—C7—C8—N1	-171.13 (11)
C16—O3—C4—C5	-175.48 (13)	O1—C7—C8—C13	-110.60 (13)
C16—O3—C4—C3	4.77 (14)	C1—C7—C8—C13	65.94 (14)
C2—C3—C4—O3	178.12 (12)	C8—N1—C9—C10	126.74 (12)
O2—C3—C4—O3	-1.26 (15)	C12—N1—C9—C10	1.94 (14)
C2—C3—C4—C5	-1.6 (2)	N1—C9—C10—C11	23.49 (14)
O2—C3—C4—C5	178.98 (12)	C9—C10—C11—C12	-40.10 (14)
O3—C4—C5—C6	-178.75 (12)	C10—C11—C12—N1	41.25 (14)
C3—C4—C5—C6	0.97 (19)	C8—N1—C12—C11	-152.67 (11)
C2—C1—C6—C5	-1.1 (2)	C9—N1—C12—C11	-26.97 (14)
C7—C1—C6—C5	178.03 (12)	N1—C8—C13—C14	-65.13 (15)
C4—C5—C6—C1	0.4 (2)	C7—C8—C13—C14	56.33 (15)
C6—C1—C7—O1	21.76 (19)	C8—C13—C14—C15	-172.24 (12)
C2—C1—C7—O1	-159.10 (12)	C3—O2—C16—O3	5.72 (15)
C6—C1—C7—C8	-154.71 (12)	C4—O3—C16—O2	-6.45 (14)
C2—C1—C7—C8	24.43 (18)		

APPENDIX 3 (B) – THE MDPV HYDROBROMIDE SALT  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.24512 (4)	0.11423 (2)	0.51185 (3)	0.02080 (17)
O1	0.6359 (3)	0.16662 (10)	0.7789 (2)	0.0126 (4)
O2	1.0762 (3)	0.22853 (10)	1.1743 (2)	0.0133 (5)
O3	1.3764 (3)	0.19542 (10)	1.1351 (2)	0.0148 (5)
N1	0.6950 (4)	0.10850 (11)	0.5502 (2)	0.0078 (5)
H1	0.573 (3)	0.1110 (16)	0.549 (4)	0.009*
C1	0.9461 (4)	0.14754 (13)	0.8689 (3)	0.0084 (6)
C2	0.9151 (4)	0.18242 (13)	0.9796 (3)	0.0092 (6)
H2	0.7950	0.1954	0.9960	0.011*
C3	1.0692 (4)	0.19605 (13)	1.0611 (3)	0.0088 (6)
C4	1.2490 (4)	0.17612 (14)	1.0389 (3)	0.0101 (6)
C5	1.2829 (4)	0.14139 (14)	0.9337 (3)	0.0116 (6)
H5	1.4035	0.1278	0.9201	0.014*
C6	1.1270 (4)	0.12737 (14)	0.8474 (3)	0.0103 (6)
H6	1.1444	0.1042	0.7746	0.012*
C7	0.7821 (4)	0.13681 (13)	0.7753 (3)	0.0088 (6)
C8	0.7882 (4)	0.08502 (13)	0.6750 (3)	0.0081 (6)
H8	0.9188	0.0730	0.6654	0.010*
C9	0.7556 (4)	0.17352 (14)	0.5109 (3)	0.0120 (6)
H9A	0.8801	0.1834	0.5508	0.014*
H9B	0.6677	0.2050	0.5357	0.014*
C10	0.7572 (5)	0.17139 (15)	0.3656 (3)	0.0156 (6)
H10A	0.8850	0.1741	0.3412	0.019*
H10B	0.6844	0.2058	0.3262	0.019*
C11	0.6680 (5)	0.10822 (14)	0.3247 (3)	0.0129 (6)
H11A	0.5320	0.1115	0.3106	0.015*
H11B	0.7174	0.0926	0.2478	0.015*
C12	0.7266 (4)	0.06627 (14)	0.4390 (3)	0.0107 (6)
H12A	0.6485	0.0290	0.4390	0.013*
H12B	0.8577	0.0539	0.4400	0.013*
C13	0.6757 (4)	0.02809 (13)	0.7171 (3)	0.0109 (6)
H13A	0.5467	0.0411	0.7245	0.013*

H13B	0.6734	-0.0036	0.6509	0.013*
C14	0.7526 (4)	-0.00147 (14)	0.8432 (3)	0.0133 (6)
H14A	0.7680	0.0309	0.9080	0.016*
H14B	0.6617	-0.0315	0.8697	0.016*
C15	0.9409 (5)	-0.03448 (15)	0.8345 (3)	0.0183 (7)
H15A	0.9280	-0.0654	0.7681	0.027*
H15B	0.9788	-0.0545	0.9144	0.027*
H15C	1.0344	-0.0043	0.8157	0.027*
C16	1.2736 (4)	0.23485 (15)	1.2172 (3)	0.0152 (6)
H16A	1.2965	0.2215	1.3053	0.018*
H16B	1.3130	0.2782	1.2110	0.018*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.0163 (2)	0.0259 (3)	0.0200 (2)	0.00014 (12)	0.00035 (15)	-0.00320 (13)
O1	0.0092 (10)	0.0141 (10)	0.0141 (10)	0.0013 (8)	-0.0015 (8)	-0.0017 (8)
O2	0.0131 (11)	0.0171 (11)	0.0091 (10)	0.0002 (8)	-0.0019 (8)	-0.0055 (8)
O3	0.0119 (10)	0.0201 (11)	0.0111 (10)	0.0011 (8)	-0.0054 (8)	-0.0054 (9)
N1	0.0088 (12)	0.0066 (11)	0.0075 (12)	-0.0004 (9)	-0.0015 (10)	0.0016 (9)
C1	0.0105 (13)	0.0060 (12)	0.0083 (13)	-0.0012 (10)	-0.0010 (11)	0.0022 (10)
C2	0.0100 (13)	0.0072 (12)	0.0101 (14)	0.0013 (10)	0.0002 (11)	0.0008 (11)
C3	0.0137 (14)	0.0065 (13)	0.0061 (13)	-0.0010 (10)	-0.0001 (11)	-0.0001 (10)
C4	0.0113 (14)	0.0094 (13)	0.0087 (13)	-0.0023 (10)	-0.0041 (11)	0.0025 (11)
C5	0.0101 (14)	0.0141 (14)	0.0104 (14)	-0.0001 (11)	-0.0002 (11)	0.0003 (12)
C6	0.0117 (14)	0.0108 (13)	0.0083 (14)	-0.0010 (11)	0.0006 (11)	0.0006 (11)
C7	0.0096 (14)	0.0073 (13)	0.0093 (14)	-0.0024 (10)	-0.0003 (11)	0.0019 (11)
C8	0.0095	0.0083	0.0058	-0.0007	-0.0029	0.0017 (11)

	(13)	(13)	(13)	(10)	(10)	
C9	0.0175 (16)	0.0053 (14)	0.0128 (15)	-0.0034 (10)	-0.0012 (12)	0.0035 (10)
C10	0.0187 (16)	0.0165 (15)	0.0112 (15)	-0.0047 (12)	-0.0014 (12)	0.0051 (12)
C11	0.0149 (15)	0.0155 (15)	0.0078 (14)	0.0004 (11)	-0.0015 (12)	0.0021 (11)
C12	0.0132 (14)	0.0100 (13)	0.0085 (14)	0.0000 (11)	-0.0020 (11)	-0.0019 (11)
C13	0.0134 (14)	0.0086 (13)	0.0101 (14)	-0.0028 (11)	-0.0020 (11)	0.0017 (11)
C14	0.0197 (15)	0.0106 (14)	0.0090 (14)	-0.0024 (11)	-0.0021 (12)	0.0033 (11)
C15	0.0224 (17)	0.0124 (14)	0.0186 (16)	0.0010 (12)	-0.0065 (13)	0.0057 (12)
C16	0.0155 (15)	0.0178 (15)	0.0113 (14)	-0.0006 (12)	-0.0042 (12)	-0.0049 (12)

## GEOMETRIC PARAMETERS (Å, °)

O1—C7	1.225 (4)	C9—C10	1.531 (4)
O2—C3	1.375 (3)	C9—H9A	0.9700
O2—C16	1.445 (4)	C9—H9B	0.9700
O3—C4	1.362 (4)	C10—C11	1.535 (4)
O3—C16	1.451 (4)	C10—H10A	0.9700
N1—C8	1.504 (3)	C10—H10B	0.9700
N1—C12	1.510 (4)	C11—C12	1.527 (4)
N1—C9	1.521 (4)	C11—H11A	0.9700
N1—H1	0.868 (19)	C11—H11B	0.9700
C1—C6	1.397 (4)	C12—H12A	0.9700
C1—C2	1.417 (4)	C12—H12B	0.9700
C1—C7	1.477 (4)	C13—C14	1.526 (4)
C2—C3	1.364 (4)	C13—H13A	0.9700
C2—H2	0.9300	C13—H13B	0.9700
C3—C4	1.390 (4)	C14—C15	1.526 (4)
C4—C5	1.372 (4)	C14—H14A	0.9700
C5—C6	1.403 (4)	C14—H14B	0.9700
C5—H5	0.9300	C15—H15A	0.9600
C6—H6	0.9300	C15—H15B	0.9600

C7—C8	1.531 (4)	C15—H15C	0.9600
C8—C13	1.542 (4)	C16—H16A	0.9700
C8—H8	0.9800	C16—H16B	0.9700
C3—O2—C16	106.1 (2)	C9—C10—H10A	110.7
C4—O3—C16	106.2 (2)	C11—C10—H10A	110.7
C8—N1—C12	113.2 (2)	C9—C10—H10B	110.7
C8—N1—C9	115.3 (2)	C11—C10—H10B	110.7
C12—N1—C9	105.5 (2)	H10A—C10—H10B	108.8
C8—N1—H1	113 (3)	C12—C11—C10	102.5 (2)
C12—N1—H1	104 (2)	C12—C11—H11A	111.3
C9—N1—H1	104 (2)	C10—C11—H11A	111.3
C6—C1—C2	120.6 (3)	C12—C11—H11B	111.3
C6—C1—C7	122.1 (3)	C10—C11—H11B	111.3
C2—C1—C7	117.2 (3)	H11A—C11—H11B	109.2
C3—C2—C1	117.0 (3)	N1—C12—C11	102.2 (2)
C3—C2—H2	121.5	N1—C12—H12A	111.3
C1—C2—H2	121.5	C11—C12—H12A	111.3
C2—C3—O2	128.1 (3)	N1—C12—H12B	111.3
C2—C3—C4	122.2 (3)	C11—C12—H12B	111.3
O2—C3—C4	109.7 (2)	H12A—C12—H12B	109.2
O3—C4—C5	127.6 (3)	C14—C13—C8	114.8 (2)
O3—C4—C3	110.3 (3)	C14—C13—H13A	108.6
C5—C4—C3	122.2 (3)	C8—C13—H13A	108.6
C4—C5—C6	116.8 (3)	C14—C13—H13B	108.6
C4—C5—H5	121.6	C8—C13—H13B	108.6
C6—C5—H5	121.6	H13A—C13—H13B	107.5
C1—C6—C5	121.3 (3)	C15—C14—C13	112.9 (3)
C1—C6—H6	119.3	C15—C14—H14A	109.0
C5—C6—H6	119.3	C13—C14—H14A	109.0
O1—C7—C1	121.6 (3)	C15—C14—H14B	109.0
O1—C7—C8	118.2 (3)	C13—C14—H14B	109.0
C1—C7—C8	120.1 (2)	H14A—C14—H14B	107.8
N1—C8—C7	108.9 (2)	C14—C15—H15A	109.5
N1—C8—C13	108.2 (2)	C14—C15—H15B	109.5
C7—C8—C13	108.8 (2)	H15A—C15—H15B	109.5
N1—C8—H8	110.3	C14—C15—H15C	109.5
C7—C8—H8	110.3	H15A—C15—H15C	109.5
C13—C8—H8	110.3	H15B—C15—H15C	109.5

N1—C9—C10	105.8 (2)	O2—C16—O3	106.8 (2)
N1—C9—H9A	110.6	O2—C16—H16A	110.4
C10—C9—H9A	110.6	O3—C16—H16A	110.4
N1—C9—H9B	110.6	O2—C16—H16B	110.4
C10—C9—H9B	110.6	O3—C16—H16B	110.4
H9A—C9—H9B	108.7	H16A—C16—H16B	108.6
C9—C10—C11	105.4 (2)		
C6—C1—C2—C3	1.3 (4)	C12—N1—C8—C7	168.7 (2)
C7—C1—C2—C3	-175.4 (2)	C9—N1—C8—C7	47.0 (3)
C1—C2—C3—O2	-179.5 (3)	C12—N1—C8—C13	-73.1 (3)
C1—C2—C3—C4	-1.0 (4)	C9—N1—C8—C13	165.2 (2)
C16—O2—C3—C2	-174.9 (3)	O1—C7—C8—N1	43.0 (3)
C16—O2—C3—C4	6.4 (3)	C1—C7—C8—N1	-140.3 (3)
C16—O3—C4—C5	175.3 (3)	O1—C7—C8—C13	-74.8 (3)
C16—O3—C4—C3	-5.4 (3)	C1—C7—C8—C13	101.9 (3)
C2—C3—C4—O3	-179.4 (3)	C8—N1—C9—C10	144.1 (2)
O2—C3—C4—O3	-0.6 (3)	C12—N1—C9—C10	18.4 (3)
C2—C3—C4—C5	-0.1 (5)	N1—C9—C10—C11	8.5 (3)
O2—C3—C4—C5	178.7 (3)	C9—C10—C11—C12	-31.6 (3)
O3—C4—C5—C6	-180.0 (3)	C8—N1—C12—C11	-165.1 (2)
C3—C4—C5—C6	0.8 (4)	C9—N1—C12—C11	-38.1 (3)
C2—C1—C6—C5	-0.6 (4)	C10—C11—C12—N1	42.8 (3)
C7—C1—C6—C5	176.0 (3)	N1—C8—C13—C14	180.0 (2)
C4—C5—C6—C1	-0.5 (4)	C7—C8—C13—C14	-61.7 (3)
C6—C1—C7—O1	-162.3 (3)	C8—C13—C14—C15	-69.0 (3)
C2—C1—C7—O1	14.4 (4)	C3—O2—C16—O3	-9.6 (3)
C6—C1—C7—C8	21.1 (4)	C4—O3—C16—O2	9.2 (3)
C2—C1—C7—C8	-162.3 (3)		

APPENDIX 3 (C) – THE MDPV GOLD(III) TETRACHLORIDE SALT  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Au1	-0.25988 (5)	0.56871 (4)	0.73961 (3)	0.02131 (17)	
Cl1	-0.1087 (3)	0.4661 (3)	0.6703 (2)	0.0243 (8)	
Cl2	-0.4186 (3)	0.4495 (3)	0.68729 (18)	0.0165 (6)	
Cl3	-0.4104 (3)	0.6774 (3)	0.8065 (2)	0.0208 (7)	
Cl4	-0.1020 (3)	0.6797 (3)	0.7969 (2)	0.0238 (7)	
O1	0.1064 (9)	0.4066 (8)	0.8349 (6)	0.028 (2)	
O2	0.2999 (8)	0.0654 (9)	0.9967 (5)	0.030 (2)	
O3	0.5179 (10)	0.0964 (10)	0.9978 (6)	0.039 (3)	
N1	0.1920 (10)	0.5795 (9)	0.7451 (6)	0.026 (2)	
H1	0.114 (5)	0.581 (13)	0.769 (6)	0.031*	
C1	0.3050 (13)	0.3437 (11)	0.8823 (8)	0.021 (3)	
C2	0.2480 (18)	0.2434 (10)	0.9192 (6)	0.027 (3)	
H2	0.1587	0.2302	0.9191	0.032*	
C3	0.3314 (14)	0.1671 (12)	0.9549 (8)	0.026 (3)	
C4	0.4579 (13)	0.1849 (13)	0.9577 (8)	0.026 (3)	
C5	0.5162 (14)	0.2821 (14)	0.9232 (8)	0.032 (3)	
H5	0.6059	0.2928	0.9239	0.038*	
C6	0.4347 (15)	0.3633 (14)	0.8872 (8)	0.031 (3)	
H6	0.4695	0.4341	0.8655	0.037*	
C7	0.2178 (13)	0.4277 (12)	0.8428 (7)	0.026 (3)	
C8	0.2704 (16)	0.5474 (11)	0.8150 (7)	0.032 (3)	
H8A	0.3603	0.5456	0.8052	0.038*	0.5133
H8AA	0.3531	0.5284	0.7950	0.038*	0.4867
C9	0.2175 (14)	0.4997 (12)	0.6775 (7)	0.028 (3)	
H9A	0.1628	0.4275	0.6794	0.034*	
H9B	0.3077	0.4740	0.6768	0.034*	
C10	0.1869 (17)	0.5748 (19)	0.6073 (9)	0.052 (5)	
H10A	0.1162	0.5386	0.5779	0.062*	
H10B	0.2623	0.5819	0.5738	0.062*	
C11	0.1477 (15)	0.6995 (15)	0.6394 (11)	0.044 (4)	
H11A	0.1796	0.7649	0.6063	0.053*	
H11B	0.0540	0.7062	0.6437	0.053*	

C12	0.2085 (16)	0.7042 (13)	0.7159 (8)	0.039 (4)	
H12A	0.1653	0.7630	0.7494	0.047*	
H12B	0.2998	0.7255	0.7118	0.047*	
C13	0.231 (4)	0.651 (2)	0.8644 (10)	0.047 (9)	0.51 (4)
H13A	0.1721	0.6997	0.8330	0.51 (4)*	0.51 (4)
H13B	0.3084	0.7003	0.8716	0.51 (4)*	0.51 (4)
C13A	0.297 (3)	0.633 (2)	0.8819 (13)	0.011 (6)	0.49 (4)
H13C	0.3906	0.6428	0.8788	0.487*	0.49 (4)
H13D	0.2617	0.7094	0.8629	0.487*	0.49 (4)
C14	0.169 (3)	0.642 (2)	0.9432 (12)	0.044 (10)	0.51 (4)
H14A	0.1837	0.5604	0.9640	0.51 (4)*	0.51 (4)
H14B	0.0759	0.6531	0.9379	0.51 (4)*	0.51 (4)
C14A	0.279 (3)	0.640 (2)	0.9466 (12)	0.042 (10)	0.49 (4)
H14C	0.3638	0.6246	0.9692	0.487*	0.49 (4)
H14D	0.2284	0.5669	0.9580	0.487*	0.49 (4)
C15	0.221 (2)	0.7347 (14)	0.9993 (10)	0.065 (6)	
H15A	0.1593	0.7477	1.0403	0.097*	0.51 (4)
H15B	0.2366	0.8103	0.9724	0.097*	0.51 (4)
H15C	0.3013	0.7054	1.0212	0.097*	0.51 (4)
H15D	0.3055	0.7612	0.9823	0.097*	0.49 (4)
H15E	0.2282	0.6986	1.0501	0.097*	0.49 (4)
H15F	0.1635	0.8036	1.0014	0.097*	0.49 (4)
C16	0.4192 (15)	0.0127 (15)	1.0181 (9)	0.036 (4)	
H16A	0.4318	-0.0641	0.9909	0.043*	
H16B	0.4209	-0.0030	1.0737	0.043*	

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Au1	0.0199 (3)	0.0167 (2)	0.0274 (3)	-0.0004 (2)	0.0005 (2)	0.00284 (18)
Cl1	0.0191 (16)	0.0164 (15)	0.037 (2)	0.0031 (12)	0.0047 (13)	0.0007 (13)
Cl2	0.0132 (13)	0.0117 (13)	0.0247 (15)	-0.0056 (11)	0.0005 (11)	-0.0017 (12)
Cl3	0.0115 (14)	0.0198 (16)	0.0309 (18)	0.0015 (12)	0.0082 (13)	-0.0100 (14)
Cl4	0.0222 (17)	0.0199 (16)	0.0293 (18)	-0.0017 (13)	-0.0045 (14)	-0.0008 (14)

O1	0.027 (6)	0.025 (5)	0.031 (5)	-0.004 (4)	-0.007 (4)	0.000 (4)
O2	0.031 (5)	0.026 (5)	0.032 (5)	-0.006 (5)	-0.008 (4)	0.005 (4)
O3	0.032 (6)	0.051 (7)	0.034 (6)	-0.007 (5)	-0.007 (5)	0.017 (5)
N1	0.026 (5)	0.023 (5)	0.029 (6)	0.009 (5)	0.009 (5)	0.001 (5)
C1	0.026 (7)	0.013 (6)	0.025 (7)	-0.006 (5)	0.009 (5)	0.001 (5)
C2	0.036 (8)	0.024 (6)	0.021 (6)	0.004 (8)	0.000 (8)	-0.005 (4)
C3	0.040 (9)	0.021 (7)	0.017 (7)	0.000 (6)	0.000 (6)	0.000 (5)
C4	0.023 (7)	0.031 (8)	0.023 (7)	-0.007 (6)	0.000 (6)	-0.003 (6)
C5	0.022 (8)	0.044 (9)	0.028 (8)	-0.008 (7)	0.002 (6)	0.001 (7)
C6	0.034 (9)	0.039 (8)	0.020 (7)	-0.006 (7)	0.004 (6)	0.000 (6)
C7	0.031 (8)	0.021 (6)	0.025 (6)	-0.001 (7)	0.003 (5)	-0.005 (5)
C8	0.051 (10)	0.024 (6)	0.021 (6)	-0.006 (7)	-0.005 (7)	-0.001 (5)
C9	0.029 (9)	0.030 (7)	0.024 (7)	0.006 (6)	-0.001 (6)	-0.002 (5)
C10	0.047 (10)	0.073 (13)	0.034 (9)	-0.021 (11)	-0.003 (7)	0.016 (10)
C11	0.021 (8)	0.043 (9)	0.068 (12)	0.001 (7)	-0.004 (8)	0.029 (9)
C12	0.051 (10)	0.030 (7)	0.037 (8)	0.008 (7)	0.017 (7)	0.018 (6)
C13	0.052 (15)	0.040 (12)	0.050 (13)	0.001 (11)	0.004 (12)	-0.001 (10)
C13A	0.012 (7)	0.011 (7)	0.011 (7)	-0.001 (3)	-0.002 (3)	0.001 (3)
C14	0.038 (15)	0.038 (13)	0.055 (15)	-0.002 (10)	-0.008 (11)	-0.011 (11)
C14A	0.042 (15)	0.038 (13)	0.046 (14)	0.002 (10)	-0.016 (11)	-0.007 (10)
C15	0.091 (17)	0.042 (10)	0.060 (11)	-0.009 (11)	0.035 (12)	-0.014 (8)
C16	0.024 (8)	0.048 (9)	0.035 (9)	-0.005 (7)	-0.005 (7)	0.007 (7)

## GEOMETRIC PARAMETERS (Å, °)

Au1—Cl4	2.300 (3)	C9—H9B	0.9900
Au1—Cl1	2.304 (3)	C10—C11	1.56 (3)
Au1—Cl3	2.312 (3)	C10—H10A	0.9900
Au1—Cl2	2.321 (3)	C10—H10B	0.9900
O1—C7	1.201 (16)	C11—C12	1.48 (2)
O2—C3	1.389 (16)	C11—H11A	0.9900
O2—C16	1.434 (18)	C11—H11B	0.9900
O3—C4	1.366 (17)	C12—H12A	0.9900
O3—C16	1.439 (18)	C12—H12B	0.9900
N1—C12	1.492 (17)	C13—C14	1.529 (3)
N1—C9	1.505 (16)	C13—H13A	0.9900
N1—C8	1.519 (17)	C13—H13B	0.9900
N1—H1	0.920 (3)	C13A—C14A	1.15 (3)

C1—C6	1.38 (2)	C13A—H13C	0.9900
C1—C2	1.424 (18)	C13A—H13D	0.9900
C1—C7	1.482 (19)	C14—C15	1.530 (3)
C2—C3	1.37 (2)	C14—H14A	0.9900
C2—H2	0.9500	C14—H14B	0.9900
C3—C4	1.34 (2)	C14A—C15	1.531 (3)
C4—C5	1.38 (2)	C14A—H14C	0.9900
C5—C6	1.40 (2)	C14A—H14D	0.9900
C5—H5	0.9500	C15—H15A	0.9800
C6—H6	0.9500	C15—H15B	0.9800
C7—C8	1.525 (18)	C15—H15C	0.9800
C8—C13	1.50 (2)	C15—H15D	0.9800
C8—C13A	1.54 (2)	C15—H15E	0.9800
C8—H8A	0.9601	C15—H15F	0.9800
C8—H8AA	0.9603	C16—H16A	0.9900
C9—C10	1.52 (2)	C16—H16B	0.9900
C9—H9A	0.9900		
Cl4—Au1—Cl1	90.02 (12)	C10—C11—H11B	110.9
Cl4—Au1—Cl3	89.41 (10)	H11A—C11—H11B	109.0
Cl1—Au1—Cl3	178.02 (13)	C11—C12—N1	103.1 (13)
Cl4—Au1—Cl2	176.92 (12)	C11—C12—H12A	111.1
Cl1—Au1—Cl2	90.13 (10)	N1—C12—H12A	111.1
Cl3—Au1—Cl2	90.54 (11)	C11—C12—H12B	111.1
C3—O2—C16	105.3 (11)	N1—C12—H12B	111.1
C4—O3—C16	105.3 (11)	H12A—C12—H12B	109.1
C12—N1—C9	105.1 (10)	C8—C13—C14	126 (2)
C12—N1—C8	115.6 (11)	C8—C13—H13A	105.8
C9—N1—C8	113.5 (9)	C14—C13—H13A	105.8
C12—N1—H1	104 (9)	C8—C13—H13B	105.8
C9—N1—H1	122 (8)	C14—C13—H13B	105.8
C8—N1—H1	96 (7)	H13A—C13—H13B	106.2
C6—C1—C2	120.7 (14)	C14A—C13A—C8	140 (3)
C6—C1—C7	122.6 (12)	C14A—C13A—H13C	102.1
C2—C1—C7	116.6 (12)	C8—C13A—H13C	102.1
C3—C2—C1	115.2 (15)	C14A—C13A—H13D	102.1
C3—C2—H2	122.4	C8—C13A—H13D	102.1
C1—C2—H2	122.4	H13C—C13A—H13D	104.8
C4—C3—C2	123.7 (14)	C13—C14—C15	112.4 (15)

C4—C3—O2	109.7 (12)	C13—C14—H14A	109.1
C2—C3—O2	126.5 (14)	C15—C14—H14A	109.1
C3—C4—O3	111.6 (12)	C13—C14—H14B	109.1
C3—C4—C5	122.5 (14)	C15—C14—H14B	109.1
O3—C4—C5	125.9 (13)	H14A—C14—H14B	107.8
C4—C5—C6	115.7 (14)	C13A—C14A—C15	135 (2)
C4—C5—H5	122.1	C13A—C14A—H14C	103.5
C6—C5—H5	122.1	C15—C14A—H14C	103.5
C1—C6—C5	122.0 (14)	C13A—C14A—H14D	103.5
C1—C6—H6	119.0	C15—C14A—H14D	103.5
C5—C6—H6	119.0	H14C—C14A—H14D	105.3
O1—C7—C1	122.2 (12)	C14—C15—C14A	44.4 (18)
O1—C7—C8	119.2 (12)	C14—C15—H15A	109.5
C1—C7—C8	118.6 (12)	C14A—C15—H15A	143.9
C13—C8—N1	97.7 (14)	C14—C15—H15B	109.5
C13—C8—C7	112.9 (15)	C14A—C15—H15B	103.9
N1—C8—C7	105.5 (11)	H15A—C15—H15B	109.5
C13—C8—C13A	30.0 (13)	C14—C15—H15C	109.5
N1—C8—C13A	124.7 (14)	C14A—C15—H15C	70.4
C7—C8—C13A	111.4 (13)	H15A—C15—H15C	109.5
C13—C8—H8A	113.0	H15B—C15—H15C	109.5
N1—C8—H8A	113.3	C14—C15—H15D	109.5
C7—C8—H8A	113.3	C14A—C15—H15D	70.6
C13A—C8—H8A	88.3	H15A—C15—H15D	141.1
C13—C8—H8AA	129.0	H15B—C15—H15D	56.3
N1—C8—H8AA	104.4	H15C—C15—H15D	56.3
C7—C8—H8AA	104.5	C14—C15—H15E	109.5
C13A—C8—H8AA	104.5	C14A—C15—H15E	103.6
H8A—C8—H8AA	16.3	H15A—C15—H15E	56.3
N1—C9—C10	105.8 (12)	H15B—C15—H15E	141.1
N1—C9—H9A	110.6	H15C—C15—H15E	56.3
C10—C9—H9A	110.6	H15D—C15—H15E	109.5
N1—C9—H9B	110.6	C14—C15—H15F	109.5
C10—C9—H9B	110.6	C14A—C15—H15F	144.2
H9A—C9—H9B	108.7	H15A—C15—H15F	56.3
C9—C10—C11	104.9 (13)	H15B—C15—H15F	56.3
C9—C10—H10A	110.8	H15C—C15—H15F	141.1
C11—C10—H10A	110.8	H15D—C15—H15F	109.5

C9—C10—H10B	110.8	H15E—C15—H15F	109.5
C11—C10—H10B	110.8	O2—C16—O3	107.4 (12)
H10A—C10—H10B	108.9	O2—C16—H16A	110.2
C12—C11—C10	104.1 (13)	O3—C16—H16A	110.2
C12—C11—H11A	110.9	O2—C16—H16B	110.2
C10—C11—H11A	110.9	O3—C16—H16B	110.2
C12—C11—H11B	110.9	H16A—C16—H16B	108.5
C6—C1—C2—C3	-3.5 (18)	C9—N1—C8—C13A	159.7 (16)
C7—C1—C2—C3	179.7 (11)	O1—C7—C8—C13	73 (2)
C1—C2—C3—C4	1.7 (19)	C1—C7—C8—C13	-104.4 (19)
C1—C2—C3—O2	177.9 (11)	O1—C7—C8—N1	-33.0 (15)
C16—O2—C3—C4	-6.8 (15)	C1—C7—C8—N1	150.1 (11)
C16—O2—C3—C2	176.5 (13)	O1—C7—C8—C13A	104.9 (17)
C2—C3—C4—O3	179.0 (12)	C1—C7—C8—C13A	-72.0 (18)
O2—C3—C4—O3	2.3 (16)	C12—N1—C9—C10	-25.8 (14)
C2—C3—C4—C5	-1 (2)	C8—N1—C9—C10	-153.1 (12)
O2—C3—C4—C5	-177.8 (12)	N1—C9—C10—C11	1.7 (15)
C16—O3—C4—C3	3.3 (16)	C9—C10—C11—C12	23.1 (16)
C16—O3—C4—C5	-176.6 (15)	C10—C11—C12—N1	-39.0 (15)
C3—C4—C5—C6	2 (2)	C9—N1—C12—C11	40.7 (14)
O3—C4—C5—C6	-178.1 (13)	C8—N1—C12—C11	166.7 (12)
C2—C1—C6—C5	5 (2)	N1—C8—C13—C14	123 (3)
C7—C1—C6—C5	-178.5 (13)	C7—C8—C13—C14	12 (4)
C4—C5—C6—C1	-4 (2)	C13A—C8—C13—C14	-81 (3)
C6—C1—C7—O1	175.5 (13)	C13—C8—C13A—	
		C14A	89 (4)
C2—C1—C7—O1	-7.7 (18)	N1—C8—C13A—C14A	118 (3)
C6—C1—C7—C8	-7.7 (19)	C7—C8—C13A—C14A	-10 (4)
C2—C1—C7—C8	169.1 (10)	C8—C13—C14—C15	139 (3)
C12—N1—C8—C13	52.4 (18)	C8—C13A—C14A—	
		C15	-127 (4)
C9—N1—C8—C13	174.0 (16)	C13—C14—C15—	
		C14A	-52.5 (17)
C12—N1—C8—C7	168.8 (11)	C13A—C14A—C15—	
		C14	77 (4)
C9—N1—C8—C7	-69.6 (14)	C3—O2—C16—O3	8.7 (15)
C12—N1—C8—C13A	38 (2)	C4—O3—C16—O2	-7.4 (15)

APPENDIX 3 (D) – ETHYLONE HYDROCHLORIDE  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.15694 (5)	1.27762 (7)	0.29089 (3)	0.01916 (17)
O1	0.36322 (15)	0.8936 (2)	0.40504 (9)	0.0229 (4)
O2	0.29141 (16)	0.1995 (2)	0.58561 (9)	0.0261 (4)
O3	0.45735 (15)	0.3175 (2)	0.68818 (9)	0.0243 (4)
N1	0.13611 (18)	0.8424 (3)	0.29510 (10)	0.0165 (4)
H1A	0.157 (2)	0.964 (3)	0.3047 (14)	0.020*
H1B	0.0489 (17)	0.839 (4)	0.2697 (13)	0.020*
C1	0.3410 (2)	0.6464 (3)	0.49155 (12)	0.0167 (4)
C2	0.2827 (2)	0.4704 (3)	0.49730 (12)	0.0180 (5)
H2	0.2129	0.4231	0.4562	0.022*
C3	0.3320 (2)	0.3715 (3)	0.56527 (12)	0.0184 (5)
C4	0.4317 (2)	0.4407 (3)	0.62628 (12)	0.0196 (5)
C5	0.4909 (2)	0.6104 (3)	0.62154 (12)	0.0210 (5)
H5	0.5604	0.6558	0.6633	0.025*
C6	0.4440 (2)	0.7129 (3)	0.55232 (12)	0.0191 (5)
H6	0.4830	0.8305	0.5464	0.023*
C7	0.2959 (2)	0.7698 (3)	0.42134 (12)	0.0169 (4)
C8	0.1547 (2)	0.7454 (3)	0.37234 (12)	0.0179 (5)
H8	0.1346	0.6084	0.3635	0.022*
C9	0.0625 (2)	0.8330 (4)	0.41627 (13)	0.0259 (5)
H9A	0.0877	0.9641	0.4293	0.039*
H9B	0.0681	0.7622	0.4648	0.039*
H9C	-0.0273	0.8286	0.3829	0.039*
C10	0.2096 (2)	0.7604 (3)	0.24129 (13)	0.0225 (5)
H10A	0.2003	0.6217	0.2402	0.027*
H10B	0.3036	0.7909	0.2612	0.027*
C11	0.1584 (2)	0.8377 (4)	0.15924 (13)	0.0274 (5)
H11A	0.0665	0.8021	0.1386	0.041*
H11B	0.2095	0.7861	0.1252	0.041*
H11C	0.1659	0.9752	0.1606	0.041*
C12	0.3786 (2)	0.1531 (4)	0.66032 (13)	0.0242 (5)

H12A	0.4351	0.0459	0.6547	0.029*
H12B	0.3284	0.1172	0.6981	0.029*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C11	0.0170 (3)	0.0162 (3)	0.0223 (3)	-0.00033 (18)	0.0019 (2)	-0.00118 (19)
O1	0.0224 (8)	0.0231 (9)	0.0218 (8)	-0.0049 (7)	0.0034 (6)	0.0024 (7)
O2	0.0295 (9)	0.0240 (9)	0.0216 (8)	-0.0058 (7)	0.0009 (7)	0.0069 (7)
O3	0.0235 (8)	0.0306 (10)	0.0167 (7)	-0.0002 (7)	0.0014 (6)	0.0059 (7)
N1	0.0170 (9)	0.0149 (9)	0.0167 (9)	-0.0009 (7)	0.0030 (7)	0.0003 (7)
C1	0.0162 (10)	0.0189 (11)	0.0158 (10)	0.0017 (8)	0.0058 (8)	0.0001 (8)
C2	0.0169 (10)	0.0212 (12)	0.0153 (9)	0.0002 (9)	0.0031 (8)	-0.0022 (8)
C3	0.0195 (10)	0.0189 (12)	0.0184 (10)	0.0000 (9)	0.0077 (8)	-0.0001 (9)
C4	0.0159 (10)	0.0289 (13)	0.0142 (9)	0.0053 (9)	0.0044 (8)	0.0011 (9)
C5	0.0154 (10)	0.0295 (13)	0.0169 (10)	-0.0017 (9)	0.0021 (8)	-0.0039 (9)
C6	0.0166 (10)	0.0220 (12)	0.0195 (10)	-0.0003 (9)	0.0062 (8)	-0.0023 (9)
C7	0.0192 (10)	0.0156 (11)	0.0166 (10)	-0.0009 (9)	0.0060 (8)	-0.0028 (8)
C8	0.0185 (10)	0.0183 (11)	0.0158 (10)	-0.0009 (9)	0.0023 (8)	0.0018 (8)
C9	0.0224 (11)	0.0355 (14)	0.0205 (11)	0.0033 (10)	0.0069 (9)	0.0019 (10)
C10	0.0261 (11)	0.0218 (12)	0.0219 (11)	0.0049 (10)	0.0104 (9)	0.0011 (9)
C11	0.0245 (11)	0.0376 (15)	0.0214 (11)	-0.0024 (11)	0.0087 (9)	0.0007 (10)
C12	0.0255 (11)	0.0267 (13)	0.0203 (11)	0.0018 (10)	0.0055 (9)	0.0044 (9)

GEOMETRIC PARAMETERS ( $\text{\AA}$ ,  $^\circ$ )

O1—C7	1.215 (3)	C5—H5	0.9500
O2—C3	1.374 (3)	C6—H6	0.9500
O2—C12	1.434 (3)	C7—C8	1.529 (3)
O3—C4	1.370 (3)	C8—C9	1.532 (3)
O3—C12	1.445 (3)	C8—H8	1.0000
N1—C8	1.493 (3)	C9—H9A	0.9800
N1—C10	1.497 (3)	C9—H9B	0.9800
N1—H1A	0.896 (17)	C9—H9C	0.9800
N1—H1B	0.916 (16)	C10—C11	1.508 (3)
C1—C6	1.396 (3)	C10—H10A	0.9900
C1—C2	1.411 (3)	C10—H10B	0.9900
C1—C7	1.489 (3)	C11—H11A	0.9800

C2—C3	1.369 (3)	C11—H11B	0.9800
C2—H2	0.9500	C11—H11C	0.9800
C3—C4	1.385 (3)	C12—H12A	0.9900
C4—C5	1.372 (3)	C12—H12B	0.9900
C5—C6	1.396 (3)		
C3—O2—C12	105.89 (17)	N1—C8—C9	109.00 (18)
C4—O3—C12	105.72 (16)	C7—C8—C9	109.27 (17)
C8—N1—C10	115.66 (17)	N1—C8—H8	109.6
C8—N1—H1A	107.9 (16)	C7—C8—H8	109.6
C10—N1—H1A	110.2 (16)	C9—C8—H8	109.6
C8—N1—H1B	107.9 (16)	C8—C9—H9A	109.5
C10—N1—H1B	107.9 (16)	C8—C9—H9B	109.5
H1A—N1—H1B	107 (2)	H9A—C9—H9B	109.5
C6—C1—C2	120.99 (19)	C8—C9—H9C	109.5
C6—C1—C7	116.9 (2)	H9A—C9—H9C	109.5
C2—C1—C7	122.07 (18)	H9B—C9—H9C	109.5
C3—C2—C1	116.42 (19)	N1—C10—C11	110.50 (18)
C3—C2—H2	121.8	N1—C10—H10A	109.6
C1—C2—H2	121.8	C11—C10—H10A	109.6
C2—C3—O2	127.7 (2)	N1—C10—H10B	109.6
C2—C3—C4	122.3 (2)	C11—C10—H10B	109.6
O2—C3—C4	109.94 (19)	H10A—C10—H10B	108.1
O3—C4—C5	127.78 (19)	C10—C11—H11A	109.5
O3—C4—C3	110.0 (2)	C10—C11—H11B	109.5
C5—C4—C3	122.2 (2)	H11A—C11—H11B	109.5
C4—C5—C6	116.66 (19)	C10—C11—H11C	109.5
C4—C5—H5	121.7	H11A—C11—H11C	109.5
C6—C5—H5	121.7	H11B—C11—H11C	109.5
C5—C6—C1	121.4 (2)	O2—C12—O3	107.52 (18)
C5—C6—H6	119.3	O2—C12—H12A	110.2
C1—C6—H6	119.3	O3—C12—H12A	110.2
O1—C7—C1	122.90 (19)	O2—C12—H12B	110.2
O1—C7—C8	119.89 (19)	O3—C12—H12B	110.2
C1—C7—C8	117.05 (18)	H12A—C12—H12B	108.5
N1—C8—C7	109.69 (17)		
C6—C1—C2—C3	0.5 (3)	C2—C1—C6—C5	-1.6 (3)
C7—C1—C2—C3	-179.19 (19)	C7—C1—C6—C5	178.13 (19)
C1—C2—C3—O2	179.0 (2)	C6—C1—C7—O1	20.6 (3)

C1—C2—C3—C4	1.4 (3)	C2—C1—C7—O1	-159.7 (2)
C12—O2—C3—C2	176.9 (2)	C6—C1—C7—C8	-154.76 (19)
C12—O2—C3—C4	-5.2 (2)	C2—C1—C7—C8	24.9 (3)
C12—O3—C4—C5	-174.0 (2)	C10—N1—C8—C7	66.3 (2)
C12—O3—C4—C3	6.6 (2)	C10—N1—C8—C9	-174.07 (18)
C2—C3—C4—O3	177.09 (19)	O1—C7—C8—N1	18.5 (3)
O2—C3—C4—O3	-0.9 (2)	C1—C7—C8—N1	-165.97 (18)
C2—C3—C4—C5	-2.3 (3)	O1—C7—C8—C9	-100.9 (2)
O2—C3—C4—C5	179.69 (19)	C1—C7—C8—C9	74.6 (2)
O3—C4—C5—C6	-178.1 (2)	C8—N1—C10—C11	166.02 (19)
C3—C4—C5—C6	1.2 (3)	C3—O2—C12—O3	9.2 (2)
C4—C5—C6—C1	0.7 (3)	C4—O3—C12—O2	-9.7 (2)

APPENDIX 3 (E) – MDPV HYDROCHLORIDE HYDROXONIUM  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.81575 (4)	0.44395 (5)	-0.20852 (5)	0.0120 (2)
Cl2	0.86519 (4)	0.92061 (5)	-0.22051 (6)	0.0205 (2)
O1	0.63452 (13)	0.21312 (18)	-0.17429 (17)	0.0235 (5)
O2	0.44639 (14)	0.09337 (19)	0.19210 (19)	0.0262 (5)
O3	0.32086 (14)	0.06743 (19)	0.0303 (2)	0.0285 (5)
O4	0.81206 (16)	0.6990 (2)	-0.1030 (2)	0.0345 (5)
H4A	0.8110	0.6260	-0.1280	0.052*
H4B	0.8220	0.7550	-0.1490	0.052*
O5	0.94897 (16)	0.5593 (2)	-0.3237 (2)	0.0368 (6)
H5A	0.9110	0.5290	-0.2900	0.055*
H5B	1.0008	0.5250	-0.3130	0.055*
O6	0.91195 (16)	0.7670 (2)	-0.3960 (2)	0.0350 (6)
H6A	0.8950	0.8080	-0.3430	0.053*
H6B	0.9170	0.6930	-0.3720	0.053*
H6C	0.8790	0.7890	-0.4684	0.053*
N1	0.78492 (16)	0.2702 (2)	-0.0051 (2)	0.0202 (5)
H1	0.777 (2)	0.315 (3)	-0.077 (3)	0.024*
C1	0.54542 (19)	0.1745 (2)	-0.0466 (3)	0.0204 (6)
C2	0.54399 (19)	0.1547 (2)	0.0725 (3)	0.0207 (6)
H2	0.5955	0.1642	0.1395	0.025*
C3	0.4645 (2)	0.1209 (2)	0.0869 (3)	0.0214 (6)
C4	0.38886 (19)	0.1052 (2)	-0.0103 (3)	0.0232 (6)
C5	0.3889 (2)	0.1230 (3)	-0.1275 (3)	0.0248 (6)
H5	0.3371	0.1118	-0.1937	0.030*
C6	0.4689 (2)	0.1582 (2)	-0.1437 (3)	0.0223 (6)
H6	0.4716	0.1716	-0.2232	0.027*
C7	0.62697 (19)	0.2129 (2)	-0.0727 (2)	0.0198 (6)
C8	0.70189 (18)	0.2617 (2)	0.0320 (2)	0.0198 (6)
H8	0.7127	0.2066	0.1018	0.024*
C9	0.86129 (19)	0.3256 (3)	0.0893 (3)	0.0257 (6)
H9A	0.8621	0.3002	0.1710	0.031*
H9B	0.8569	0.4121	0.0849	0.031*

C10	0.9444 (2)	0.2836 (3)	0.0605 (3)	0.0391 (9)
H10A	0.9894	0.2563	0.1347	0.047*
H10B	0.9702	0.3478	0.0247	0.047*
C11	0.9149 (2)	0.1824 (3)	-0.0295 (3)	0.0268 (7)
H11A	0.9163	0.2065	-0.1107	0.032*
H11B	0.9542	0.1137	-0.0033	0.032*
C12	0.8210 (2)	0.1536 (3)	-0.0307 (3)	0.0249 (6)
H12A	0.7859	0.1226	-0.1102	0.030*
H12B	0.8207	0.0954	0.0323	0.030*
C13	0.67422 (19)	0.3815 (2)	0.0697 (3)	0.0218 (6)
H13A	0.6253	0.3694	0.1052	0.026*
H13B	0.7249	0.4149	0.1333	0.026*
C14	0.6443 (2)	0.4703 (3)	-0.0325 (3)	0.0271 (7)
H14A	0.6923	0.4820	-0.0700	0.033*
H14B	0.5918	0.4395	-0.0951	0.033*
C15	0.6212 (3)	0.5872 (3)	0.0133 (3)	0.0373 (8)
H15A	0.5724	0.5762	0.0480	0.056*
H15B	0.6032	0.6429	-0.0537	0.056*
H15C	0.6732	0.6178	0.0752	0.056*
C16	0.3524 (2)	0.0827 (3)	0.1598 (3)	0.0283 (7)
H16A	0.3262	0.1540	0.1836	0.034*
H16B	0.3358	0.0144	0.2008	0.034*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0159 (3)	0.0109 (3)	0.0112 (3)	-0.0004 (2)	0.0070 (2)	0.0028 (2)
Cl2	0.0241 (4)	0.0166 (3)	0.0204 (4)	0.0029 (2)	0.0063 (3)	0.0004 (2)
O1	0.0276 (11)	0.0239 (10)	0.0191 (10)	0.0010 (8)	0.0072 (8)	0.0006 (8)
O2	0.0273 (11)	0.0281 (11)	0.0257 (11)	-0.0019 (9)	0.0117 (9)	-0.0020 (9)
O3	0.0242 (11)	0.0303 (12)	0.0313 (12)	-0.0039 (9)	0.0090 (9)	-0.0029 (9)
O4	0.0399 (13)	0.0301 (12)	0.0340 (13)	-0.0010 (10)	0.0121 (10)	0.0019 (10)
O5	0.0386 (13)	0.0309 (13)	0.0456 (14)	0.0031 (10)	0.0199 (11)	0.0048 (10)
O6	0.0423 (13)	0.0322 (12)	0.0321 (12)	0.0062 (10)	0.0135 (10)	0.0002 (10)
N1	0.0235 (12)	0.0185 (12)	0.0183 (12)	0.0019 (9)	0.0057 (10)	0.0003 (9)
C1	0.0260 (14)	0.0127 (13)	0.0220 (14)	0.0031 (11)	0.0064 (11)	-0.0007 (10)
C2	0.0226 (14)	0.0172 (13)	0.0212 (14)	0.0017 (11)	0.0047 (11)	-0.0011 (11)
C3	0.0288 (15)	0.0140 (13)	0.0221 (14)	0.0013 (11)	0.0087 (12)	-0.0011 (10)
C4	0.0232 (15)	0.0162 (14)	0.0304 (16)	0.0011 (11)	0.0083 (12)	-0.0010 (11)

C5	0.0251 (15)	0.0198 (14)	0.0252 (15)	0.0009 (11)	0.0011 (12)	-0.0002 (11)
C6	0.0279 (15)	0.0166 (13)	0.0207 (14)	0.0020 (11)	0.0048 (12)	0.0003 (11)
C7	0.0262 (15)	0.0140 (13)	0.0191 (14)	0.0044 (10)	0.0064 (11)	0.0013 (10)
C8	0.0236 (14)	0.0178 (14)	0.0187 (13)	0.0005 (11)	0.0074 (11)	0.0012 (11)
C9	0.0235 (15)	0.0282 (16)	0.0231 (15)	-0.0014 (12)	0.0036 (12)	-0.0054 (12)
C10	0.0243 (17)	0.045 (2)	0.044 (2)	0.0035 (14)	0.0033 (14)	-0.0170 (16)
C11	0.0263 (15)	0.0268 (16)	0.0263 (15)	0.0045 (12)	0.0064 (12)	-0.0031 (12)
C12	0.0281 (15)	0.0199 (14)	0.0276 (15)	0.0040 (12)	0.0096 (12)	-0.0016 (12)
C13	0.0230 (14)	0.0214 (14)	0.0213 (14)	-0.0003 (11)	0.0069 (11)	-0.0034 (11)
C14	0.0339 (17)	0.0207 (15)	0.0271 (16)	0.0044 (12)	0.0098 (13)	0.0005 (12)
C15	0.048 (2)	0.0250 (17)	0.0351 (19)	0.0094 (15)	0.0062 (16)	-0.0026 (14)
C16	0.0282 (16)	0.0285 (16)	0.0311 (17)	-0.0027 (12)	0.0135 (13)	-0.0039 (13)

GEOMETRIC PARAMETERS ( $\text{\AA}$ ,  $^\circ$ )

O1—C7	1.222 (3)	C7—C8	1.528 (4)
O2—C3	1.374 (4)	C8—C13	1.539 (4)
O2—C16	1.424 (4)	C8—H8	1.0000
O3—C4	1.367 (4)	C9—C10	1.526 (4)
O3—C16	1.448 (4)	C9—H9A	0.9900
O4—H4A	0.8806	C9—H9B	0.9900
O4—H4B	0.8776	C10—C11	1.535 (4)
O5—H5A	0.8800	C10—H10A	0.9900
O5—H5B	0.8828	C10—H10B	0.9900
O6—H6A	0.8775	C11—C12	1.517 (4)
O6—H6B	0.8860	C11—H11A	0.9900
O6—H6C	0.8831	C11—H11B	0.9900
N1—C8	1.503 (4)	C12—H12A	0.9900
N1—C9	1.507 (4)	C12—H12B	0.9900
N1—C12	1.512 (4)	C13—C14	1.526 (4)
N1—H1	0.95 (4)	C13—H13A	0.9900
C1—C6	1.398 (4)	C13—H13B	0.9900
C1—C2	1.411 (4)	C14—C15	1.521 (4)
C1—C7	1.477 (4)	C14—H14A	0.9900
C2—C3	1.371 (4)	C14—H14B	0.9900
C2—H2	0.9500	C15—H15A	0.9800
C3—C4	1.389 (4)	C15—H15B	0.9800
C4—C5	1.379 (4)	C15—H15C	0.9800
C5—C6	1.393 (4)	C16—H16A	0.9900

C5—H5	0.9500	C16—H16B	0.9900
C6—H6	0.9500		
C3—O2—C16	105.3 (2)	C10—C9—H9B	110.7
C4—O3—C16	105.0 (2)	H9A—C9—H9B	108.8
H4A—O4—H4B	118.5	C9—C10—C11	106.3 (3)
H5A—O5—H5B	119.4	C9—C10—H10A	110.5
H6A—O6—H6B	107.7	C11—C10—H10A	110.5
H6A—O6—H6C	107.5	C9—C10—H10B	110.5
H6B—O6—H6C	122.9	C11—C10—H10B	110.5
C8—N1—C9	113.3 (2)	H10A—C10—H10B	108.7
C8—N1—C12	114.4 (2)	C12—C11—C10	105.4 (2)
C9—N1—C12	104.3 (2)	C12—C11—H11A	110.7
C8—N1—H1	113 (2)	C10—C11—H11A	110.7
C9—N1—H1	106 (2)	C12—C11—H11B	110.7
C12—N1—H1	105 (2)	C10—C11—H11B	110.7
C6—C1—C2	120.5 (3)	H11A—C11—H11B	108.8
C6—C1—C7	118.1 (3)	N1—C12—C11	103.5 (2)
C2—C1—C7	121.4 (3)	N1—C12—H12A	111.1
C3—C2—C1	116.7 (3)	C11—C12—H12A	111.1
C3—C2—H2	121.6	N1—C12—H12B	111.1
C1—C2—H2	121.6	C11—C12—H12B	111.1
C2—C3—O2	128.0 (3)	H12A—C12—H12B	109.0
C2—C3—C4	122.3 (3)	C14—C13—C8	114.6 (2)
O2—C3—C4	109.6 (3)	C14—C13—H13A	108.6
O3—C4—C5	128.4 (3)	C8—C13—H13A	108.6
O3—C4—C3	109.5 (3)	C14—C13—H13B	108.6
C5—C4—C3	122.0 (3)	C8—C13—H13B	108.6
C4—C5—C6	116.5 (3)	H13A—C13—H13B	107.6
C4—C5—H5	121.8	C15—C14—C13	111.1 (3)
C6—C5—H5	121.8	C15—C14—H14A	109.4
C5—C6—C1	122.0 (3)	C13—C14—H14A	109.4
C5—C6—H6	119.0	C15—C14—H14B	109.4
C1—C6—H6	119.0	C13—C14—H14B	109.4
O1—C7—C1	122.9 (3)	H14A—C14—H14B	108.0
O1—C7—C8	119.5 (3)	C14—C15—H15A	109.5
C1—C7—C8	117.4 (2)	C14—C15—H15B	109.5
N1—C8—C7	109.3 (2)	H15A—C15—H15B	109.5
N1—C8—C13	111.8 (2)	C14—C15—H15C	109.5

C7—C8—C13	109.4 (2)	H15A—C15—H15C	109.5
N1—C8—H8	108.7	H15B—C15—H15C	109.5
C7—C8—H8	108.7	O2—C16—O3	107.0 (2)
C13—C8—H8	108.7	O2—C16—H16A	110.3
N1—C9—C10	105.2 (2)	O3—C16—H16A	110.3
N1—C9—H9A	110.7	O2—C16—H16B	110.3
C10—C9—H9A	110.7	O3—C16—H16B	110.3
N1—C9—H9B	110.7	H16A—C16—H16B	108.6
C6—C1—C2—C3	-0.9 (4)	C9—N1—C8—C7	175.9 (2)
C7—C1—C2—C3	179.0 (2)	C12—N1—C8—C7	-64.8 (3)
C1—C2—C3—O2	178.0 (3)	C9—N1—C8—C13	54.6 (3)
C1—C2—C3—C4	0.8 (4)	C12—N1—C8—C13	173.9 (2)
C16—O2—C3—C2	171.0 (3)	O1—C7—C8—N1	-16.7 (3)
C16—O2—C3—C4	-11.5 (3)	C1—C7—C8—N1	167.4 (2)
C16—O3—C4—C5	-171.0 (3)	O1—C7—C8—C13	106.1 (3)
C16—O3—C4—C3	11.3 (3)	C1—C7—C8—C13	-69.9 (3)
C2—C3—C4—O3	177.7 (3)	C8—N1—C9—C10	158.0 (3)
O2—C3—C4—O3	0.0 (3)	C12—N1—C9—C10	33.0 (3)
C2—C3—C4—C5	-0.2 (4)	N1—C9—C10—C11	-13.5 (4)
O2—C3—C4—C5	-177.9 (3)	C9—C10—C11—C12	-10.9 (4)
O3—C4—C5—C6	-177.8 (3)	C8—N1—C12—C11	-164.1 (2)
C3—C4—C5—C6	-0.3 (4)	C9—N1—C12—C11	-39.8 (3)
C4—C5—C6—C1	0.2 (4)	C10—C11—C12—N1	31.0 (3)
C2—C1—C6—C5	0.4 (4)	N1—C8—C13—C14	67.1 (3)
C7—C1—C6—C5	-179.5 (3)	C7—C8—C13—C14	-54.1 (3)
C6—C1—C7—O1	-11.9 (4)	C8—C13—C14—C15	-178.1 (3)
C2—C1—C7—O1	168.2 (3)	C3—O2—C16—O3	18.2 (3)
C6—C1—C7—C8	163.9 (2)	C4—O3—C16—O2	-18.2 (3)
C2—C1—C7—C8	-16.0 (4)		

APPENDIX 3 (F) –  $\alpha$ -PVP HYDROCHLORIDE  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cl1	0.13431 (5)	0.13435 (7)	0.16898 (4)	0.03800 (19)	
O1	0.33489 (13)	0.05219 (16)	0.47174 (12)	0.0293 (4)	
O2	-0.10932 (18)	0.1425 (3)	-0.00914 (19)	0.0378 (8)	0.786 (7)
H2A	-0.041 (4)	0.139 (4)	0.038 (4)	0.057*	0.786 (7)
H2B	-0.116 (3)	0.075 (5)	-0.053 (4)	0.057*	0.786 (7)
N1	0.14861 (14)	0.1979 (2)	0.39803 (15)	0.0239 (4)	
H1	0.1652 (19)	0.175 (3)	0.341 (2)	0.029*	
C1	0.34224 (18)	0.1502 (2)	0.53401 (17)	0.0232 (5)	
C2	0.44313 (17)	0.1747 (2)	0.64323 (17)	0.0228 (4)	
C3	0.54176 (18)	0.1163 (2)	0.65872 (19)	0.0260 (5)	
H3	0.5430	0.0636	0.6000	0.031*	
C4	0.63772 (19)	0.1351 (2)	0.7594 (2)	0.0296 (5)	
H4	0.7048	0.0952	0.7697	0.036*	
C5	0.63592 (19)	0.2122 (2)	0.84538 (19)	0.0298 (5)	
H5	0.7018	0.2251	0.9145	0.036*	
C6	0.53846 (19)	0.2702 (2)	0.83053 (18)	0.0293 (5)	
H6	0.5376	0.3223	0.8897	0.035*	
C7	0.44182 (18)	0.2529 (2)	0.72969 (17)	0.0263 (5)	
H7	0.3752	0.2940	0.7195	0.032*	
C8	0.24840 (17)	0.2574 (2)	0.49774 (17)	0.0224 (4)	
H8	0.2316	0.2699	0.5604	0.027*	
C9	0.28388 (17)	0.4024 (2)	0.47324 (18)	0.0244 (5)	
H9A	0.2209	0.4694	0.4460	0.029*	
H9B	0.3436	0.4417	0.5442	0.029*	
C10	0.32375 (18)	0.3978 (2)	0.38745 (19)	0.0281 (5)	
H10A	0.3871	0.3317	0.4140	0.034*	
H10B	0.2642	0.3604	0.3155	0.034*	
C11	0.3578 (2)	0.5459 (3)	0.3688 (2)	0.0369 (6)	
H11A	0.2942	0.6104	0.3392	0.055*	
H11B	0.3850	0.5391	0.3151	0.055*	
H11C	0.4161	0.5836	0.4401	0.055*	
C12	0.10420 (19)	0.0616 (3)	0.4229 (2)	0.0315 (5)	

H12A	0.1437	0.0405	0.5042	0.038*
H12B	0.1125	-0.0211	0.3823	0.038*
C13	-0.01692 (19)	0.0917 (3)	0.3826 (2)	0.0337 (6)
H13A	-0.0618	0.0044	0.3503	0.040*
H13B	-0.0277	0.1265	0.4449	0.040*
C14	-0.04728 (19)	0.2071 (3)	0.29364 (19)	0.0325 (5)
H14A	-0.0592	0.1660	0.2219	0.039*
H14B	-0.1139	0.2602	0.2808	0.039*
C15	0.05371 (18)	0.3022 (3)	0.34626 (19)	0.0288 (5)
H15A	0.0580	0.3623	0.2889	0.035*
H15B	0.0529	0.3654	0.4040	0.035*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0438 (4)	0.0534 (4)	0.0259 (3)	-0.0135 (3)	0.0241 (3)	-0.0088 (3)
O1	0.0374 (9)	0.0259 (8)	0.0277 (8)	0.0010 (7)	0.0183 (7)	-0.0039 (7)
O2	0.0227 (12)	0.0512 (16)	0.0340 (13)	-0.0005 (10)	0.0094 (10)	0.0035 (10)
N1	0.0269 (10)	0.0266 (10)	0.0233 (9)	-0.0031 (7)	0.0163 (8)	-0.0009 (8)
C1	0.0317 (12)	0.0208 (11)	0.0246 (10)	-0.0019 (9)	0.0196 (10)	0.0020 (9)
C2	0.0295 (11)	0.0183 (10)	0.0243 (10)	-0.0013 (8)	0.0159 (9)	0.0031 (8)
C3	0.0327 (12)	0.0195 (10)	0.0311 (12)	-0.0011 (9)	0.0195 (10)	0.0009 (9)
C4	0.0289 (12)	0.0234 (11)	0.0385 (13)	0.0010 (9)	0.0180 (11)	0.0058 (10)
C5	0.0327 (12)	0.0237 (11)	0.0277 (12)	-0.0030 (9)	0.0105 (10)	0.0061 (9)
C6	0.0393 (13)	0.0251 (12)	0.0231 (11)	0.0004 (10)	0.0151 (10)	0.0023 (9)
C7	0.0315 (12)	0.0244 (11)	0.0253 (11)	0.0042 (9)	0.0157 (10)	0.0041 (9)
C8	0.0254 (11)	0.0251 (11)	0.0207 (10)	-0.0028 (9)	0.0142 (9)	-0.0033 (9)
C9	0.0237 (11)	0.0229 (11)	0.0261 (11)	0.0003 (8)	0.0118 (9)	-0.0017 (9)
C10	0.0293 (12)	0.0288 (12)	0.0289 (11)	-0.0049 (9)	0.0164 (10)	0.0007 (9)
C11	0.0341 (13)	0.0331 (13)	0.0457 (14)	-0.0013 (10)	0.0212 (12)	0.0098 (11)
C12	0.0370 (13)	0.0303 (12)	0.0314 (12)	-0.0092 (10)	0.0199 (11)	0.0001 (10)
C13	0.0350 (13)	0.0403 (14)	0.0329 (12)	-0.0127 (10)	0.0221 (11)	-0.0075 (11)
C14	0.0279 (12)	0.0433 (14)	0.0294 (12)	-0.0048 (10)	0.0162 (10)	-0.0049 (10)
C15	0.0266 (12)	0.0342 (12)	0.0279 (11)	0.0002 (9)	0.0151 (10)	0.0027 (10)

GEOMETRIC PARAMETERS ( $\text{\AA}$ ,  $^\circ$ )

O1—C1	1.219 (3)	C8—H8	1.0000
O2—H2A	0.84 (5)	C9—C10	1.526 (3)

O2—H2B	0.85 (5)	C9—H9A	0.9900
N1—C8	1.500 (3)	C9—H9B	0.9900
N1—C15	1.511 (3)	C10—C11	1.522 (3)
N1—C12	1.524 (3)	C10—H10A	0.9900
N1—H1	0.94 (3)	C10—H10B	0.9900
C1—C2	1.486 (3)	C11—H11A	0.9800
C1—C8	1.525 (3)	C11—H11B	0.9800
C2—C3	1.396 (3)	C11—H11C	0.9800
C2—C7	1.398 (3)	C12—C13	1.524 (3)
C3—C4	1.384 (3)	C12—H12A	0.9900
C3—H3	0.9500	C12—H12B	0.9900
C4—C5	1.391 (3)	C13—C14	1.522 (3)
C4—H4	0.9500	C13—H13A	0.9900
C5—C6	1.382 (3)	C13—H13B	0.9900
C5—H5	0.9500	C14—C15	1.515 (3)
C6—C7	1.388 (3)	C14—H14A	0.9900
C6—H6	0.9500	C14—H14B	0.9900
C7—H7	0.9500	C15—H15A	0.9900
C8—C9	1.533 (3)	C15—H15B	0.9900
H2A—O2—H2B	102 (4)	C8—C9—H9B	108.5
C8—N1—C15	113.49 (17)	H9A—C9—H9B	107.5
C8—N1—C12	113.76 (16)	C11—C10—C9	111.35 (19)
C15—N1—C12	106.48 (16)	C11—C10—H10A	109.4
C8—N1—H1	110.0 (15)	C9—C10—H10A	109.4
C15—N1—H1	105.8 (15)	C11—C10—H10B	109.4
C12—N1—H1	106.7 (15)	C9—C10—H10B	109.4
O1—C1—C2	122.23 (19)	H10A—C10—H10B	108.0
O1—C1—C8	119.93 (19)	C10—C11—H11A	109.5
C2—C1—C8	117.76 (17)	C10—C11—H11B	109.5
C3—C2—C7	119.7 (2)	H11A—C11—H11B	109.5
C3—C2—C1	118.05 (18)	C10—C11—H11C	109.5
C7—C2—C1	122.29 (19)	H11A—C11—H11C	109.5
C4—C3—C2	120.2 (2)	H11B—C11—H11C	109.5
C4—C3—H3	119.9	N1—C12—C13	105.34 (19)
C2—C3—H3	119.9	N1—C12—H12A	110.7
C3—C4—C5	119.9 (2)	C13—C12—H12A	110.7
C3—C4—H4	120.0	N1—C12—H12B	110.7
C5—C4—H4	120.0	C13—C12—H12B	110.7

C6—C5—C4	120.1 (2)	H12A—C12—H12B	108.8
C6—C5—H5	119.9	C14—C13—C12	104.20 (18)
C4—C5—H5	119.9	C14—C13—H13A	110.9
C5—C6—C7	120.5 (2)	C12—C13—H13A	110.9
C5—C6—H6	119.8	C14—C13—H13B	110.9
C7—C6—H6	119.8	C12—C13—H13B	110.9
C6—C7—C2	119.6 (2)	H13A—C13—H13B	108.9
C6—C7—H7	120.2	C15—C14—C13	101.74 (18)
C2—C7—H7	120.2	C15—C14—H14A	111.4
N1—C8—C1	108.67 (17)	C13—C14—H14A	111.4
N1—C8—C9	112.49 (17)	C15—C14—H14B	111.4
C1—C8—C9	109.46 (16)	C13—C14—H14B	111.4
N1—C8—H8	108.7	H14A—C14—H14B	109.3
C1—C8—H8	108.7	N1—C15—C14	104.08 (19)
C9—C8—H8	108.7	N1—C15—H15A	110.9
C10—C9—C8	114.93 (17)	C14—C15—H15A	110.9
C10—C9—H9A	108.5	N1—C15—H15B	110.9
C8—C9—H9A	108.5	C14—C15—H15B	110.9
C10—C9—H9B	108.5	H15A—C15—H15B	109.0
O1—C1—C2—C3	20.9 (3)	C12—N1—C8—C9	-174.02 (17)
C8—C1—C2—C3	-155.68 (18)	O1—C1—C8—N1	14.0 (3)
O1—C1—C2—C7	-158.8 (2)	C2—C1—C8—N1	-169.29 (16)
C8—C1—C2—C7	24.6 (3)	O1—C1—C8—C9	-109.2 (2)
C7—C2—C3—C4	0.3 (3)	C2—C1—C8—C9	67.5 (2)
C1—C2—C3—C4	-179.35 (19)	N1—C8—C9—C10	-65.5 (2)
C2—C3—C4—C5	0.0 (3)	C1—C8—C9—C10	55.4 (2)
C3—C4—C5—C6	0.0 (3)	C8—C9—C10—C11	-179.70 (19)
C4—C5—C6—C7	-0.4 (3)	C8—N1—C12—C13	126.51 (19)
C5—C6—C7—C2	0.8 (3)	C15—N1—C12—C13	0.7 (2)
C3—C2—C7—C6	-0.7 (3)	N1—C12—C13—C14	24.7 (2)
C1—C2—C7—C6	178.94 (19)	C12—C13—C14—C15	-40.5 (2)
C15—N1—C8—C1	-173.42 (16)	C8—N1—C15—C14	-151.95 (17)
C12—N1—C8—C1	64.6 (2)	C12—N1—C15—C14	-26.0 (2)
C15—N1—C8—C9	-52.1 (2)	C13—C14—C15—N1	40.9 (2)

APPENDIX 3 (G) – PENTYLONE HYDROCHLORIDE  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.97932 (3)	0.41147 (3)	0.25573 (3)	0.01695 (12)
O1	0.70258 (8)	0.21208 (8)	0.30983 (8)	0.0179 (2)
O2	0.24937 (8)	0.06549 (9)	0.54799 (9)	0.0215 (2)
O3	0.41749 (8)	0.09970 (8)	0.69851 (9)	0.0196 (2)
O4	0.07491 (8)	0.33169 (9)	0.66678 (9)	0.0206 (2)
H1	0.0592 (19)	0.3946 (9)	0.6947 (17)	0.048 (6)*
H2	0.0524 (17)	0.2780 (11)	0.7051 (15)	0.045 (6)*
N1	0.90706 (10)	0.26904 (10)	0.46549 (10)	0.0145 (2)
H3A	0.9034 (14)	0.3128 (11)	0.4039 (8)	0.021 (4)*
H4	0.9625 (15)	0.3059 (15)	0.5246 (16)	0.026 (4)*
C1	0.68631 (11)	0.21419 (11)	0.41253 (12)	0.0138 (3)
C2	0.56922 (11)	0.17657 (11)	0.44713 (12)	0.0147 (3)
C3	0.56047 (11)	0.16060 (11)	0.56753 (12)	0.0148 (3)
H3	0.6290	0.1741	0.6299	0.018*
C4	0.44821 (12)	0.12471 (11)	0.58976 (12)	0.0152 (3)
C5	0.34742 (11)	0.10440 (11)	0.49971 (13)	0.0169 (3)
C6	0.35329 (12)	0.11904 (12)	0.38181 (12)	0.0187 (3)
H6	0.2838	0.1049	0.3206	0.022*
C7	0.46692 (12)	0.15575 (11)	0.35698 (12)	0.0167 (3)
H7	0.4751	0.1669	0.2766	0.020*
C8	0.28556 (12)	0.08472 (13)	0.67410 (13)	0.0216 (3)
H8	0.2442	0.1552	0.6981	0.026*
H10	0.2617	0.0171	0.7187	0.026*
C9	0.78739 (11)	0.26329 (11)	0.50951 (11)	0.0138 (3)
H9A	0.7977	0.2104	0.5801	0.017*
C10	0.96050 (12)	0.15379 (11)	0.44170 (13)	0.0192 (3)
H11	0.9600	0.1019	0.5096	0.029*
H12	1.0459	0.1645	0.4296	0.029*
H13	0.9107	0.1192	0.3702	0.029*
C11	0.75109 (11)	0.38541 (11)	0.54686 (12)	0.0155 (3)
H14	0.6820	0.3773	0.5909	0.019*
H15	0.8224	0.4191	0.6021	0.019*

C12	0.71194 (13)	0.47076 (12)	0.44434 (12)	0.0210 (3)
H16	0.7786	0.4767	0.3970	0.025*
H17	0.6366	0.4411	0.3917	0.025*
C13	0.68578 (15)	0.59108 (13)	0.49057 (15)	0.0293 (4)
H18	0.6174	0.5858	0.5346	0.044*
H19	0.6631	0.6447	0.4235	0.044*
H20	0.7601	0.6201	0.5434	0.044*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.02390 (19)	0.0130 (2)	0.0155 (2)	-0.00227 (11)	0.00783 (13)	-0.00046 (10)
O1	0.0216 (5)	0.0187 (6)	0.0132 (6)	0.0008 (4)	0.0024 (4)	0.0002 (3)
O2	0.0150 (5)	0.0247 (6)	0.0249 (6)	-0.0019 (4)	0.0039 (4)	-0.0002 (4)
O3	0.0176 (5)	0.0241 (6)	0.0181 (6)	-0.0028 (4)	0.0061 (4)	-0.0019 (4)
O4	0.0213 (5)	0.0186 (6)	0.0216 (6)	-0.0016 (4)	0.0029 (4)	-0.0012 (4)
N1	0.0157 (5)	0.0141 (6)	0.0137 (6)	0.0007 (4)	0.0026 (4)	0.0008 (4)
C1	0.0182 (6)	0.0090 (7)	0.0137 (8)	0.0037 (5)	0.0014 (5)	0.0008 (5)
C2	0.0177 (6)	0.0091 (7)	0.0167 (8)	0.0022 (5)	0.0020 (5)	-0.0007 (5)
C3	0.0156 (6)	0.0123 (8)	0.0153 (7)	0.0009 (5)	0.0000 (5)	-0.0023 (5)
C4	0.0196 (6)	0.0108 (7)	0.0153 (7)	0.0029 (5)	0.0036 (5)	-0.0008 (5)
C5	0.0138 (6)	0.0112 (8)	0.0253 (8)	0.0021 (5)	0.0029 (5)	0.0001 (5)
C6	0.0170 (6)	0.0160 (8)	0.0204 (8)	0.0023 (5)	-0.0036 (5)	0.0004 (5)
C7	0.0209 (6)	0.0133 (8)	0.0147 (7)	0.0018 (5)	0.0001 (5)	0.0008 (5)
C8	0.0174 (7)	0.0234 (9)	0.0255 (9)	-0.0020 (5)	0.0079 (6)	-0.0028 (6)
C9	0.0142 (6)	0.0143	0.0133 (7)	-0.0001 (5)	0.0035 (5)	0.0007 (5)

	(7)				
C10 0.0207 (6)	0.0159 (8)	0.0218 (8)	0.0041 (5)	0.0060 (5)	0.0002 (5)
C11 0.0158 (6)	0.0158 (8)	0.0148 (7)	-0.0011 (5)	0.0026 (5)	-0.0026 (5)
C12 0.0275 (7)	0.0168 (8)	0.0187 (8)	0.0042 (5)	0.0044 (6)	0.0008 (5)
C13 0.0395 (9)	0.0181 (9)	0.0293 (10)	0.0086 (6)	0.0036 (7)	-0.0009 (6)

## GEOMETRIC PARAMETERS (Å, °)

O1—C1	1.2216 (16)	C6—C7	1.3947 (19)
O2—C5	1.3722 (16)	C6—H6	0.9500
O2—C8	1.4421 (18)	C7—H7	0.9500
O3—C4	1.3788 (17)	C8—H8	0.9900
O3—C8	1.4340 (16)	C8—H10	0.9900
O4—H1	0.8202 (10)	C9—C11	1.5381 (18)
O4—H2	0.8202 (10)	C9—H9A	1.0000
N1—C10	1.4914 (17)	C10—H11	0.9800
N1—C9	1.4930 (15)	C10—H12	0.9800
N1—H3A	0.8602 (10)	C10—H13	0.9800
N1—H4	0.925 (18)	C11—C12	1.5280 (18)
C1—C2	1.4776 (18)	C11—H14	0.9900
C1—C9	1.5256 (17)	C11—H15	0.9900
C2—C7	1.3988 (18)	C12—C13	1.524 (2)
C2—C3	1.4113 (19)	C12—H16	0.9900
C3—C4	1.3671 (18)	C12—H17	0.9900
C3—H3	0.9500	C13—H18	0.9800
C4—C5	1.3862 (18)	C13—H19	0.9800
C5—C6	1.373 (2)	C13—H20	0.9800
C5—O2—C8	105.17 (10)	O3—C8—H10	110.3
C4—O3—C8	104.79 (10)	O2—C8—H10	110.3
H1—O4—H2	110 (2)	H8—C8—H10	108.5
C10—N1—C9	115.01 (10)	N1—C9—C1	109.76 (10)
C10—N1—H3A	109.1 (11)	N1—C9—C11	110.05 (10)
C9—N1—H3A	113.0 (11)	C1—C9—C11	110.33 (10)
C10—N1—H4	108.1 (10)	N1—C9—H9A	108.9

C9—N1—H4	105.9 (10)	C1—C9—H9A	108.9
H3A—N1—H4	105.0 (15)	C11—C9—H9A	108.9
O1—C1—C2	122.75 (12)	N1—C10—H11	109.5
O1—C1—C9	119.47 (11)	N1—C10—H12	109.5
C2—C1—C9	117.70 (11)	H11—C10—H12	109.5
C7—C2—C3	120.57 (12)	N1—C10—H13	109.5
C7—C2—C1	118.17 (12)	H11—C10—H13	109.5
C3—C2—C1	121.26 (11)	H12—C10—H13	109.5
C4—C3—C2	116.55 (11)	C12—C11—C9	114.86 (11)
C4—C3—H3	121.7	C12—C11—H14	108.6
C2—C3—H3	121.7	C9—C11—H14	108.6
C3—C4—O3	127.57 (12)	C12—C11—H15	108.6
C3—C4—C5	122.39 (12)	C9—C11—H15	108.6
O3—C4—C5	110.00 (11)	H14—C11—H15	107.5
O2—C5—C6	128.17 (12)	C13—C12—C11	110.95 (12)
O2—C5—C4	109.46 (12)	C13—C12—H16	109.4
C6—C5—C4	122.33 (12)	C11—C12—H16	109.4
C5—C6—C7	116.29 (12)	C13—C12—H17	109.4
C5—C6—H6	121.9	C11—C12—H17	109.4
C7—C6—H6	121.9	H16—C12—H17	108.0
C6—C7—C2	121.87 (13)	C12—C13—H18	109.5
C6—C7—H7	119.1	C12—C13—H19	109.5
C2—C7—H7	119.1	H18—C13—H19	109.5
O3—C8—O2	107.19 (10)	C12—C13—H20	109.5
O3—C8—H8	110.3	H18—C13—H20	109.5
O2—C8—H8	110.3	H19—C13—H20	109.5

APPENDIX 3 (H) – DIBUTYLONE HYDROCHLORIDE 1.5 HYDRATE  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.57545 (12)	0.54884 (5)	0.42782 (3)	0.0265 (2)
Cl2	0.10485 (11)	0.41315 (5)	0.52923 (3)	0.02244 (19)
O1	0.5704 (3)	0.35450 (14)	0.33106 (8)	0.0237 (5)
O2	0.8272 (3)	0.01774 (16)	0.21170 (8)	0.0268 (6)
O3	0.7339 (3)	0.15882 (16)	0.18326 (8)	0.0292 (6)
O4	0.4191 (3)	0.65973 (14)	0.67708 (8)	0.0239 (5)
O5	0.1741 (3)	0.97088 (16)	0.81514 (8)	0.0283 (6)
O6	0.2571 (3)	0.82345 (15)	0.83552 (8)	0.0253 (5)
O7	0.4463 (3)	0.50905 (16)	0.57842 (9)	0.0272 (6)
H1A	0.369 (4)	0.478 (2)	0.5644 (12)	0.041*
H2A	0.531 (3)	0.514 (3)	0.5594 (10)	0.041*
O8	0.7626 (3)	0.55112 (18)	0.52718 (9)	0.0333 (6)
H3A	0.715 (5)	0.548 (3)	0.5007 (6)	0.050*
H4A	0.848 (4)	0.515 (2)	0.5279 (17)	0.050*
O9	0.1528 (4)	0.5640 (2)	0.44837 (11)	0.0487 (8)
H5A	0.125 (7)	0.528 (2)	0.4694 (11)	0.073*
H6A	0.261 (2)	0.554 (3)	0.4416 (18)	0.073*
N1	0.5882 (4)	0.33726 (17)	0.42679 (9)	0.0180 (5)
H1	0.590 (5)	0.3932 (7)	0.4176 (11)	0.022*
N2	0.4005 (4)	0.69552 (19)	0.58337 (10)	0.0263 (6)
H2	0.393 (6)	0.6395 (7)	0.5922 (12)	0.032*
C1	0.6508 (4)	0.2859 (2)	0.34428 (11)	0.0173 (7)
C2	0.7043 (4)	0.2120 (2)	0.31128 (11)	0.0172 (7)
C3	0.7653 (4)	0.1275 (2)	0.32774 (11)	0.0189 (7)
H3	0.7760	0.1177	0.3610	0.023*
C4	0.8112 (4)	0.0567 (2)	0.29639 (11)	0.0197 (7)
H4	0.8535	-0.0008	0.3075	0.024*
C5	0.7917 (4)	0.0749 (2)	0.24898 (11)	0.0201 (7)
C6	0.7341 (5)	0.1593 (2)	0.23221 (11)	0.0203 (7)
C7	0.6887 (5)	0.2290 (2)	0.26211 (11)	0.0200 (7)
H7	0.6484	0.2863	0.2503	0.024*
C8	0.7690 (6)	0.0660 (2)	0.16970 (12)	0.0328 (9)

H8A	0.8662	0.0636	0.1451	0.039*
H8B	0.6561	0.0379	0.1566	0.039*
C9	0.7088 (4)	0.2774 (2)	0.39660 (11)	0.0181 (7)
H9	0.6925	0.2126	0.4069	0.022*
C10	0.9147 (5)	0.3025 (2)	0.40021 (12)	0.0241 (7)
H10A	0.9519	0.3007	0.4341	0.029*
H10B	0.9875	0.2559	0.3830	0.029*
C11	0.9610 (5)	0.3962 (3)	0.38002 (15)	0.0344 (9)
H11A	0.9297	0.3978	0.3461	0.052*
H11B	1.0927	0.4080	0.3840	0.052*
H11C	0.8904	0.4429	0.3970	0.052*
C12	0.6490 (5)	0.3400 (2)	0.47752 (11)	0.0253 (8)
H12A	0.5571	0.3726	0.4966	0.038*
H12B	0.7673	0.3717	0.4797	0.038*
H12C	0.6623	0.2776	0.4895	0.038*
C13	0.3932 (5)	0.3064 (2)	0.42496 (11)	0.0231 (7)
H13A	0.3489	0.3091	0.3921	0.035*
H13B	0.3175	0.3462	0.4450	0.035*
H13C	0.3848	0.2435	0.4366	0.035*
C14	0.3403 (4)	0.7313 (2)	0.66790 (12)	0.0188 (7)
C15	0.2910 (4)	0.7987 (2)	0.70494 (11)	0.0184 (7)
C16	0.3049 (4)	0.7702 (2)	0.75322 (11)	0.0188 (7)
H16	0.3423	0.7102	0.7617	0.023*
C17	0.2613 (4)	0.8341 (2)	0.78661 (11)	0.0200 (7)
C18	0.2089 (4)	0.9220 (2)	0.77494 (11)	0.0204 (7)
C19	0.1934 (5)	0.9509 (2)	0.72882 (12)	0.0234 (7)
H19	0.1562	1.0113	0.7212	0.028*
C20	0.2351 (5)	0.8872 (2)	0.69362 (11)	0.0208 (7)
H20	0.2251	0.9044	0.6611	0.025*
C21	0.2216 (5)	0.9129 (2)	0.85459 (12)	0.0275 (8)
H21A	0.3322	0.9366	0.8710	0.033*
H21B	0.1192	0.9105	0.8777	0.033*
C22	0.2796 (5)	0.7496 (2)	0.61673 (11)	0.0197 (7)
H22	0.2925	0.8161	0.6096	0.024*
C23	0.0745 (5)	0.7216 (2)	0.61237 (12)	0.0285 (8)
H23A	0.0010	0.7601	0.6341	0.034*
H23B	0.0326	0.7344	0.5795	0.034*
C24	0.0360 (5)	0.6233 (2)	0.62346 (14)	0.0325 (9)

H24A	0.1067	0.5843	0.6018	0.049*
H24B	-0.0955	0.6111	0.6194	0.049*
H24C	0.0717	0.6103	0.6564	0.049*
C25	0.3333 (6)	0.6995 (3)	0.53287 (12)	0.0360 (9)
H25A	0.2133	0.6694	0.5306	0.054*
H25B	0.4213	0.6684	0.5121	0.054*
H25C	0.3213	0.7633	0.5230	0.054*
C26	0.5953 (5)	0.7312 (3)	0.58593 (13)	0.0315 (8)
H26A	0.6745	0.6945	0.5652	0.047*
H26B	0.6397	0.7272	0.6188	0.047*
H26C	0.5978	0.7949	0.5755	0.047*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0409 (5)	0.0173 (4)	0.0212 (4)	-0.0019 (3)	-0.0005 (4)	0.0034 (3)
Cl2	0.0260 (4)	0.0181 (4)	0.0232 (4)	-0.0007 (3)	-0.0006 (3)	0.0028 (3)
O1	0.0290 (14)	0.0205 (11)	0.0216 (11)	0.0053 (10)	0.0007 (10)	0.0012 (9)
O2	0.0332 (15)	0.0267 (13)	0.0205 (13)	0.0083 (10)	-0.0039 (10)	-0.0072 (10)
O3	0.0375 (16)	0.0314 (13)	0.0187 (12)	0.0116 (11)	-0.0041 (11)	-0.0040 (10)
O4	0.0311 (14)	0.0184 (11)	0.0222 (11)	0.0037 (10)	-0.0034 (10)	0.0009 (9)
O5	0.0381 (16)	0.0269 (14)	0.0200 (13)	0.0018 (10)	0.0029 (10)	-0.0054 (10)
O6	0.0306 (15)	0.0303 (13)	0.0151 (11)	0.0020 (10)	0.0002 (10)	-0.0013 (10)
O7	0.0303 (16)	0.0257 (13)	0.0256 (13)	0.0011 (11)	-0.0020 (10)	-0.0005 (11)
O8	0.0300 (15)	0.0401 (15)	0.0296 (14)	0.0075 (12)	-0.0036 (11)	-0.0103 (13)
O9	0.052 (2)	0.0481 (19)	0.0456 (18)	-0.0009 (15)	0.0007 (15)	0.0131 (15)
N1	0.0224 (15)	0.0171 (12)	0.0145 (13)	0.0002 (11)	-0.0019 (12)	0.0004 (11)
N2	0.0354 (18)	0.0217 (14)	0.0217 (15)	-0.0003 (13)	0.0000 (13)	0.0013 (12)
C1	0.0146 (17)	0.0166 (16)	0.0207 (17)	-0.0014 (12)	0.0026 (12)	0.0031 (13)
C2	0.0143 (17)	0.0186 (16)	0.0186 (16)	-0.0022 (12)	0.0002 (12)	0.0012 (13)
C3	0.0182 (18)	0.0192 (16)	0.0195 (16)	-0.0015 (13)	-0.0008 (13)	0.0021 (13)
C4	0.0199 (17)	0.0151 (16)	0.0240 (17)	-0.0005 (13)	-0.0021 (13)	0.0011 (13)
C5	0.0152 (17)	0.0212 (17)	0.0238 (17)	0.0019 (13)	-0.0013 (13)	-0.0055 (13)
C6	0.0197 (19)	0.0262 (17)	0.0151 (16)	0.0039 (13)	-0.0007 (13)	0.0005 (13)
C7	0.0183 (18)	0.0199 (17)	0.0219 (18)	0.0023 (13)	0.0002 (13)	0.0019 (14)
C8	0.045 (2)	0.033 (2)	0.0206 (18)	0.0128 (17)	-0.0092 (16)	-0.0072 (16)
C9	0.0189 (18)	0.0163 (16)	0.0190 (16)	0.0013 (13)	0.0012 (13)	0.0018 (13)
C10	0.0219 (19)	0.0255 (17)	0.0250 (17)	0.0019 (15)	-0.0016 (15)	0.0034 (14)

C11 0.020 (2) 0.031 (2) 0.051 (2) -0.0037 (15) -0.0002 (16) 0.0120 (18)  
 C12 0.037 (2) 0.0227 (18) 0.0164 (17) 0.0007 (14) -0.0055 (14) -0.0006 (14)  
 C13 0.0206 (19) 0.0248 (17) 0.0240 (17) 0.0006 (14) 0.0018 (14) -0.0049 (14)  
 C14 0.0157 (18) 0.0191 (17) 0.0216 (17) -0.0014 (12) -0.0008 (12) 0.0037 (14)  
 C15 0.0177 (18) 0.0209 (16) 0.0167 (16) 0.0004 (13) -0.0009 (13) -0.0003 (13)  
 C16 0.0158 (17) 0.0221 (17) 0.0184 (16) 0.0016 (13) -0.0010 (13) 0.0035 (13)  
 C17 0.0152 (18) 0.0299 (18) 0.0151 (16) -0.0029 (14) 0.0005 (12) 0.0025 (14)  
 C18 0.0197 (17) 0.0212 (16) 0.0202 (16) 0.0009 (13) 0.0031 (13) -0.0040 (14)  
 C19 0.0279 (19) 0.0188 (16) 0.0234 (17) 0.0021 (14) 0.0003 (14) 0.0012 (15)  
 C20 0.024 (2) 0.0209 (17) 0.0170 (16) -0.0022 (13) 0.0015 (13) 0.0036 (13)  
 C21 0.028 (2) 0.0339 (19) 0.0204 (17) -0.0002 (16) -0.0004 (14) -0.0041 (15)  
 C22 0.0254 (19) 0.0157 (16) 0.0180 (17) 0.0023 (13) 0.0033 (13) 0.0000 (13)  
 C23 0.031 (2) 0.0294 (19) 0.0253 (18) 0.0033 (16) -0.0012 (15) -0.0018 (15)  
 C24 0.027 (2) 0.0279 (19) 0.042 (2) 0.0000 (15) -0.0059 (16) 0.0030 (17)  
 C25 0.051 (3) 0.037 (2) 0.0203 (19) 0.0126 (17) -0.0025 (16) 0.0008 (17)  
 C26 0.024 (2) 0.039 (2) 0.032 (2) -0.0005 (17) 0.0081 (16) -0.0010 (16)

## GEOMETRIC PARAMETERS (Å, °)

O1—C1	1.221 (4)	C10—C11	1.524 (5)
O2—C5	1.367 (4)	C10—H10A	0.9900
O2—C8	1.440 (4)	C10—H10B	0.9900
O3—C6	1.377 (4)	C11—H11A	0.9800
O3—C8	1.436 (4)	C11—H11B	0.9800
O4—C14	1.223 (4)	C11—H11C	0.9800
O5—C18	1.362 (4)	C12—H12A	0.9800
O5—C21	1.440 (4)	C12—H12B	0.9800
O6—C17	1.384 (4)	C12—H12C	0.9800
O6—C21	1.440 (4)	C13—H13A	0.9800
O7—H1A	0.8201 (14)	C13—H13B	0.9800
O7—H2A	0.8200 (14)	C13—H13C	0.9800
O8—H3A	0.8202 (14)	C14—C15	1.480 (4)
O8—H4A	0.8200 (14)	C14—C22	1.529 (4)
O9—H5A	0.8204 (14)	C15—C20	1.396 (4)
O9—H6A	0.8203 (14)	C15—C16	1.424 (4)
N1—C13	1.490 (4)	C16—C17	1.364 (5)
N1—C12	1.494 (4)	C16—H16	0.9500
N1—C9	1.503 (4)	C17—C18	1.383 (5)

N1—H1	0.8600 (14)	C18—C19	1.369 (5)
N2—C25	1.503 (4)	C19—C20	1.395 (5)
N2—C22	1.511 (4)	C19—H19	0.9500
N2—C26	1.512 (5)	C20—H20	0.9500
N2—H2	0.8602 (14)	C21—H21A	0.9900
C1—C2	1.479 (4)	C21—H21B	0.9900
C1—C9	1.536 (4)	C22—C23	1.553 (5)
C2—C3	1.396 (4)	C22—H22	1.0000
C2—C7	1.409 (4)	C23—C24	1.500 (5)
C3—C4	1.402 (4)	C23—H23A	0.9900
C3—H3	0.9500	C23—H23B	0.9900
C4—C5	1.367 (4)	C24—H24A	0.9800
C4—H4	0.9500	C24—H24B	0.9800
C5—C6	1.389 (4)	C24—H24C	0.9800
C6—C7	1.363 (5)	C25—H25A	0.9800
C7—H7	0.9500	C25—H25B	0.9800
C8—H8A	0.9900	C25—H25C	0.9800
C8—H8B	0.9900	C26—H26A	0.9800
C9—C10	1.545 (5)	C26—H26B	0.9800
C9—H9	1.0000	C26—H26C	0.9800
C5—O2—C8	105.8 (2)	N1—C12—H12C	109.5
C6—O3—C8	105.7 (2)	H12A—C12—H12C	109.5
C18—O5—C21	106.5 (2)	H12B—C12—H12C	109.5
C17—O6—C21	105.7 (2)	N1—C13—H13A	109.5
H1A—O7—H2A	104 (4)	N1—C13—H13B	109.5
H3A—O8—H4A	108 (4)	H13A—C13—H13B	109.5
H5A—O9—H6A	107 (5)	N1—C13—H13C	109.5
C13—N1—C12	108.8 (3)	H13A—C13—H13C	109.5
C13—N1—C9	111.0 (2)	H13B—C13—H13C	109.5
C12—N1—C9	112.5 (2)	O4—C14—C15	122.5 (3)
C13—N1—H1	107 (2)	O4—C14—C22	119.0 (3)
C12—N1—H1	105 (2)	C15—C14—C22	118.4 (3)
C9—N1—H1	112 (2)	C20—C15—C16	120.7 (3)
C25—N2—C22	112.1 (3)	C20—C15—C14	122.0 (3)
C25—N2—C26	109.7 (3)	C16—C15—C14	117.2 (3)
C22—N2—C26	109.5 (3)	C17—C16—C15	116.0 (3)
C25—N2—H2	107 (2)	C17—C16—H16	122.0
C22—N2—H2	107 (3)	C15—C16—H16	122.0

C26—N2—H2	112 (3)	C16—C17—C18	122.7 (3)
O1—C1—C2	122.6 (3)	C16—C17—O6	127.7 (3)
O1—C1—C9	119.4 (3)	C18—C17—O6	109.5 (3)
C2—C1—C9	118.0 (3)	O5—C18—C19	127.4 (3)
C3—C2—C7	120.5 (3)	O5—C18—C17	110.2 (3)
C3—C2—C1	121.8 (3)	C19—C18—C17	122.4 (3)
C7—C2—C1	117.7 (3)	C18—C19—C20	116.5 (3)
C2—C3—C4	121.7 (3)	C18—C19—H19	121.7
C2—C3—H3	119.2	C20—C19—H19	121.7
C4—C3—H3	119.2	C15—C20—C19	121.6 (3)
C5—C4—C3	116.3 (3)	C15—C20—H20	119.2
C5—C4—H4	121.8	C19—C20—H20	119.2
C3—C4—H4	121.8	O6—C21—O5	107.1 (2)
O2—C5—C4	127.5 (3)	O6—C21—H21A	110.3
O2—C5—C6	110.1 (3)	O5—C21—H21A	110.3
C4—C5—C6	122.5 (3)	O6—C21—H21B	110.3
C7—C6—O3	128.4 (3)	O5—C21—H21B	110.3
C7—C6—C5	122.1 (3)	H21A—C21—H21B	108.6
O3—C6—C5	109.6 (3)	N2—C22—C14	108.9 (3)
C6—C7—C2	117.0 (3)	N2—C22—C23	111.8 (3)
C6—C7—H7	121.5	C14—C22—C23	107.8 (3)
C2—C7—H7	121.5	N2—C22—H22	109.4
O3—C8—O2	107.5 (3)	C14—C22—H22	109.4
O3—C8—H8A	110.2	C23—C22—H22	109.4
O2—C8—H8A	110.2	C24—C23—C22	114.7 (3)
O3—C8—H8B	110.2	C24—C23—H23A	108.6
O2—C8—H8B	110.2	C22—C23—H23A	108.6
H8A—C8—H8B	108.5	C24—C23—H23B	108.6
N1—C9—C1	109.5 (2)	C22—C23—H23B	108.6
N1—C9—C10	112.9 (3)	H23A—C23—H23B	107.6
C1—C9—C10	108.0 (3)	C23—C24—H24A	109.5
N1—C9—H9	108.8	C23—C24—H24B	109.5
C1—C9—H9	108.8	H24A—C24—H24B	109.5
C10—C9—H9	108.8	C23—C24—H24C	109.5
C11—C10—C9	113.8 (3)	H24A—C24—H24C	109.5
C11—C10—H10A	108.8	H24B—C24—H24C	109.5
C9—C10—H10A	108.8	N2—C25—H25A	109.5
C11—C10—H10B	108.8	N2—C25—H25B	109.5

C9—C10—H10B	108.8	H25A—C25—H25B	109.5
H10A—C10—H10B	107.7	N2—C25—H25C	109.5
C10—C11—H11A	109.5	H25A—C25—H25C	109.5
C10—C11—H11B	109.5	H25B—C25—H25C	109.5
H11A—C11—H11B	109.5	N2—C26—H26A	109.5
C10—C11—H11C	109.5	N2—C26—H26B	109.5
H11A—C11—H11C	109.5	H26A—C26—H26B	109.5
H11B—C11—H11C	109.5	N2—C26—H26C	109.5
N1—C12—H12A	109.5	H26A—C26—H26C	109.5
N1—C12—H12B	109.5	H26B—C26—H26C	109.5
H12A—C12—H12B	109.5		

APPENDIX 3 (I) – EPHYLONE HYDROCHLORIDE  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.21855 (2)	0.18398 (3)	0.84167 (2)	0.01565 (9)
O1	0.40031 (6)	0.06451 (11)	0.56932 (6)	0.02015 (19)
O2	0.72678 (7)	0.65538 (12)	0.60171 (7)	0.0246 (2)
O3	0.63480 (8)	0.76624 (13)	0.68643 (8)	0.0343 (3)
N1	0.29524 (7)	0.12238 (13)	0.67683 (7)	0.0136 (2)
H1A	0.2783 (9)	0.1248 (19)	0.7275 (6)	0.016*
H1B	0.3041 (10)	0.0068 (6)	0.6649 (9)	0.016*
C1	0.43165 (8)	0.19332 (15)	0.62509 (8)	0.0153 (2)
C2	0.51247 (8)	0.31446 (16)	0.62222 (8)	0.0154 (2)
C3	0.53048 (9)	0.49015 (16)	0.66596 (8)	0.0180 (2)
H3	0.4931	0.5361	0.7011	0.022*
C4	0.60494 (9)	0.59043 (16)	0.65487 (9)	0.0188 (2)
C5	0.65981 (8)	0.52498 (17)	0.60356 (8)	0.0173 (2)
C6	0.64338 (9)	0.35540 (17)	0.56004 (8)	0.0197 (3)
H6	0.6811	0.3118	0.5247	0.024*
C7	0.56819 (9)	0.25081 (17)	0.57068 (8)	0.0184 (3)
H7	0.5544	0.1323	0.5419	0.022*
C8	0.71827 (10)	0.80273 (18)	0.66192 (10)	0.0241 (3)
H8A	0.7794	0.8111	0.7217	0.029*
H8B	0.7090	0.9208	0.6266	0.029*
C9	0.38998 (8)	0.22728 (16)	0.70321 (8)	0.0144 (2)
H9	0.3759	0.3613	0.7052	0.017*
C10	0.46475 (9)	0.16687 (16)	0.80390 (8)	0.0164 (2)
H10A	0.5216	0.2531	0.8249	0.020*
H10B	0.4324	0.1762	0.8512	0.020*
C11	0.50413 (9)	-0.02802 (18)	0.80693 (9)	0.0237 (3)
H11A	0.4474	-0.1143	0.7829	0.028*
H11B	0.5401	-0.0361	0.7627	0.028*
C12	0.57334 (9)	-0.08600 (19)	0.90852 (9)	0.0255 (3)
H12A	0.6296	-0.0009	0.9328	0.038*
H12B	0.5978	-0.2106	0.9062	0.038*
H12C	0.5372	-0.0839	0.9520	0.038*

C13	0.21075 (8)	0.20317 (16)	0.59244 (8)	0.0176 (2)
H13A	0.2294	0.2115	0.5353	0.021*
H13B	0.1968	0.3289	0.6091	0.021*
C14	0.11867 (9)	0.08604 (17)	0.56733 (9)	0.0218 (3)
H14A	0.1322	-0.0377	0.5497	0.033*
H14B	0.0642	0.1410	0.5124	0.033*
H14C	0.0999	0.0789	0.6237	0.033*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.01918 (15)	0.01182 (15)	0.01821 (15)	0.00028 (9)	0.00969 (11)	0.00048 (9)
O1	0.0206 (4)	0.0202 (4)	0.0203 (4)	-0.0030 (3)	0.0086 (3)	-0.0067 (3)
O2	0.0269 (5)	0.0209 (5)	0.0344 (5)	-0.0053 (4)	0.0208 (4)	-0.0026 (4)
O3	0.0369 (6)	0.0206 (5)	0.0609 (7)	-0.0113 (4)	0.0361 (5)	-0.0153 (5)
N1	0.0140 (5)	0.0118 (5)	0.0151 (5)	-0.0003 (4)	0.0056 (4)	-0.0012 (4)
C1	0.0146 (5)	0.0150 (6)	0.0142 (5)	0.0029 (4)	0.0033 (4)	0.0008 (4)
C2	0.0147 (6)	0.0171 (6)	0.0128 (5)	0.0017 (4)	0.0036 (4)	0.0012 (4)
C3	0.0182 (6)	0.0182 (6)	0.0200 (6)	0.0013 (5)	0.0100 (5)	-0.0012 (5)
C4	0.0202 (6)	0.0150 (6)	0.0220 (6)	0.0005 (5)	0.0089 (5)	-0.0010 (5)
C5	0.0154 (5)	0.0205 (6)	0.0166 (6)	0.0001 (5)	0.0068 (5)	0.0039 (5)
C6	0.0192 (6)	0.0244 (6)	0.0179 (6)	0.0009 (5)	0.0100 (5)	-0.0018 (5)
C7	0.0189 (6)	0.0192 (6)	0.0160 (6)	0.0001 (5)	0.0057 (5)	-0.0031 (5)
C8	0.0250 (7)	0.0208 (6)	0.0305 (7)	-0.0057 (5)	0.0152 (6)	-0.0037 (5)
C9	0.0140 (5)	0.0127 (5)	0.0169 (6)	-0.0015 (4)	0.0063 (5)	-0.0020 (4)
C10	0.0147 (5)	0.0192 (6)	0.0149 (6)	-0.0019 (4)	0.0051 (5)	-0.0029 (4)
C11	0.0227 (6)	0.0218 (7)	0.0211 (6)	0.0040 (5)	0.0022 (5)	-0.0012 (5)

C12	0.0200 (6)	0.0276 (7)	0.0250 (6)	0.0005 (5)	0.0045 (5)	0.0057 (5)
C13	0.0152 (6)	0.0172 (6)	0.0176 (6)	0.0011 (4)	0.0032 (5)	0.0025 (5)
C14	0.0166 (6)	0.0201 (6)	0.0236 (6)	-0.0012 (5)	0.0022 (5)	0.0005 (5)

## GEOMETRIC PARAMETERS (Å, °)

O1—C1	1.2190 (14)	C8—H8A	0.9900
O2—C5	1.3702 (14)	C8—H8B	0.9900
O2—C8	1.4340 (15)	C9—C10	1.5403 (16)
O3—C4	1.3753 (15)	C9—H9	1.0000
O3—C8	1.4246 (15)	C10—C11	1.5249 (17)
N1—C9	1.4933 (14)	C10—H10A	0.9900
N1—C13	1.5007 (14)	C10—H10B	0.9900
N1—H1A	0.8801 (10)	C11—C12	1.5200 (17)
N1—H1B	0.8801 (10)	C11—H11A	0.9900
C1—C2	1.4862 (16)	C11—H11B	0.9900
C1—C9	1.5263 (15)	C12—H12A	0.9800
C2—C7	1.3949 (17)	C12—H12B	0.9800
C2—C3	1.4134 (16)	C12—H12C	0.9800
C3—C4	1.3706 (17)	C13—C14	1.5116 (16)
C3—H3	0.9500	C13—H13A	0.9900
C4—C5	1.3868 (17)	C13—H13B	0.9900
C5—C6	1.3720 (18)	C14—H14A	0.9800
C6—C7	1.3937 (17)	C14—H14B	0.9800
C6—H6	0.9500	C14—H14C	0.9800
C7—H7	0.9500		
C5—O2—C8	105.76 (9)	N1—C9—C10	110.30 (9)
C4—O3—C8	106.00 (9)	C1—C9—C10	110.81 (9)
C9—N1—C13	113.49 (9)	N1—C9—H9	109.1
C9—N1—H1A	107.5 (9)	C1—C9—H9	109.1
C13—N1—H1A	107.4 (9)	C10—C9—H9	109.1
C9—N1—H1B	110.4 (9)	C11—C10—C9	114.33 (10)
C13—N1—H1B	110.0 (9)	C11—C10—H10A	108.7
H1A—N1—H1B	107.7 (12)	C9—C10—H10A	108.7
O1—C1—C2	122.04 (10)	C11—C10—H10B	108.7
O1—C1—C9	119.28 (10)	C9—C10—H10B	108.7
C2—C1—C9	118.63 (10)	H10A—C10—H10B	107.6

C7—C2—C3	120.66 (11)	C12—C11—C10	112.71 (11)
C7—C2—C1	117.11 (10)	C12—C11—H11A	109.0
C3—C2—C1	122.18 (10)	C10—C11—H11A	109.0
C4—C3—C2	116.22 (11)	C12—C11—H11B	109.0
C4—C3—H3	121.9	C10—C11—H11B	109.0
C2—C3—H3	121.9	H11A—C11—H11B	107.8
C3—C4—O3	128.03 (11)	C11—C12—H12A	109.5
C3—C4—C5	122.40 (11)	C11—C12—H12B	109.5
O3—C4—C5	109.51 (10)	H12A—C12—H12B	109.5
O2—C5—C6	127.60 (11)	C11—C12—H12C	109.5
O2—C5—C4	109.91 (10)	H12A—C12—H12C	109.5
C6—C5—C4	122.46 (11)	H12B—C12—H12C	109.5
C5—C6—C7	116.10 (11)	N1—C13—C14	110.56 (9)
C5—C6—H6	122.0	N1—C13—H13A	109.5
C7—C6—H6	122.0	C14—C13—H13A	109.5
C6—C7—C2	122.16 (11)	N1—C13—H13B	109.5
C6—C7—H7	118.9	C14—C13—H13B	109.5
C2—C7—H7	118.9	H13A—C13—H13B	108.1
O3—C8—O2	108.01 (10)	C13—C14—H14A	109.5
O3—C8—H8A	110.1	C13—C14—H14B	109.5
O2—C8—H8A	110.1	H14A—C14—H14B	109.5
O3—C8—H8B	110.1	C13—C14—H14C	109.5
O2—C8—H8B	110.1	H14A—C14—H14C	109.5
H8A—C8—H8B	108.4	H14B—C14—H14C	109.5
N1—C9—C1	108.46 (9)		

APPENDIX 4 (A) – THE ERDMANN'S SALT OF COCAINE  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.95697 (10)	0.32274 (7)	0.13992 (4)	0.0117 (2)
Co2	0.92055 (10)	0.58272 (7)	0.90371 (4)	0.0121 (2)
C10	0.2653 (9)	0.1094 (6)	0.5165 (3)	0.0156 (13)
C14	0.4426 (10)	0.2764 (6)	0.6152 (4)	0.0254 (15)
H14	0.5693	0.3277	0.6376	0.030*
C11	0.0748 (10)	0.1240 (6)	0.5527 (3)	0.0202 (14)
H11	-0.0508	0.0710	0.5310	0.024*
C12	0.0694 (10)	0.2154 (6)	0.6196 (3)	0.0223 (15)
H12	-0.0592	0.2259	0.6442	0.027*
C15	0.4464 (10)	0.1870 (6)	0.5477 (3)	0.0242 (15)
H15	0.5742	0.1790	0.5226	0.029*
C13	0.2542 (10)	0.2914 (6)	0.6504 (4)	0.0263 (16)
H13	0.2516	0.3548	0.6962	0.032*
C9	0.2591 (8)	0.0066 (5)	0.4452 (3)	0.0136 (12)
O1	0.1289 (6)	-0.0805 (4)	0.4233 (2)	0.0192 (10)
O2	0.4324 (6)	0.0237 (4)	0.4077 (2)	0.0162 (9)
C5	0.3325 (9)	-0.1288 (6)	0.2012 (3)	0.0183 (14)
H5	0.2102	-0.1290	0.1643	0.022*
C3	0.4549 (9)	-0.0691 (6)	0.3379 (3)	0.0152 (13)
H3	0.4544	-0.1552	0.3455	0.018*
C2	0.6794 (8)	-0.0340 (5)	0.3173 (3)	0.0124 (12)
H2	0.7908	-0.0647	0.3473	0.015*
C6	0.4122 (9)	-0.2624 (5)	0.1891 (3)	0.0207 (13)
H6A	0.3858	-0.3126	0.1366	0.025*
H6B	0.3390	-0.3078	0.2199	0.025*
C1	0.7044 (9)	-0.0959 (5)	0.2351 (3)	0.0149 (13)
H1	0.8500	-0.0731	0.2216	0.018*
C8	0.5708 (9)	-0.0745 (6)	0.1114 (3)	0.0185 (13)
H8A	0.5842	-0.1650	0.0885	0.028*
H8B	0.7053	-0.0269	0.1089	0.028*
H8C	0.4522	-0.0455	0.0851	0.028*
C7	0.6569 (9)	-0.2396 (5)	0.2127 (3)	0.0210 (14)

H7A	0.6939	-0.2735	0.2547	0.025*
H7B	0.7410	-0.2814	0.1711	0.025*
C4	0.2727 (8)	-0.0683 (5)	0.2800 (3)	0.0148 (12)
H4A	0.2373	0.0202	0.2853	0.018*
H4B	0.1429	-0.1151	0.2890	0.018*
N1	0.5263 (7)	-0.0532 (4)	0.1899 (2)	0.0138 (11)
H1A	0.5098	0.0325	0.2111	0.017*
C16	0.7133 (8)	0.1106 (5)	0.3356 (3)	0.0157 (11)
O3	0.6053 (6)	0.1745 (3)	0.30722 (19)	0.0177 (8)
O4	0.8794 (6)	0.1553 (3)	0.3857 (2)	0.0274 (9)
N2	1.1939 (7)	0.3267 (5)	0.0792 (3)	0.0156 (11)
H2A	1.1411	0.3234	0.0327	0.023*
H2B	1.2735	0.2590	0.0775	0.023*
H2C	1.2784	0.3996	0.0990	0.023*
N3	0.7124 (8)	0.3205 (5)	0.1974 (3)	0.0178 (12)
H3A	0.7077	0.3976	0.2311	0.027*
H3B	0.7255	0.2600	0.2213	0.027*
H3C	0.5890	0.3028	0.1669	0.027*
N4	0.8029 (7)	0.1937 (5)	0.0558 (3)	0.0148 (11)
N5	1.1110 (8)	0.4477 (5)	0.2241 (3)	0.0192 (12)
N6	1.0838 (8)	0.1855 (5)	0.1739 (3)	0.0150 (11)
N7	0.8402 (7)	0.4608 (4)	0.1094 (2)	0.0113 (11)
O5	0.6063 (7)	0.1855 (4)	0.0487 (2)	0.0268 (11)
O6	0.9064 (7)	0.1216 (4)	0.0116 (3)	0.0309 (12)
O12	0.9666 (6)	0.5434 (4)	0.0986 (2)	0.0174 (9)
O8	1.0084 (7)	0.5190 (5)	0.2712 (2)	0.0350 (13)
O10	0.9798 (7)	0.1314 (4)	0.2105 (3)	0.0292 (11)
O7	1.3076 (6)	0.4584 (4)	0.2299 (2)	0.0241 (10)
O11	0.6453 (6)	0.4705 (4)	0.1027 (2)	0.0196 (9)
O9	1.2671 (6)	0.1539 (4)	0.1605 (2)	0.0248 (11)
N9	0.6828 (7)	0.5745 (5)	0.9633 (3)	0.0157 (11)
H9A	0.6054	0.4989	0.9444	0.024*
H9B	0.5966	0.6387	0.9630	0.024*
H9C	0.7349	0.5822	1.0105	0.024*
N8	1.1632 (7)	0.5864 (5)	0.8448 (3)	0.0175 (12)
H8D	1.2756	0.6348	0.8739	0.026*
H8E	1.1245	0.6200	0.8075	0.026*
H8F	1.2030	0.5062	0.8255	0.026*

N11	0.7993 (8)	0.7217 (5)	0.8721 (3)	0.0170 (11)
N10	1.0399 (8)	0.4448 (5)	0.9340 (3)	0.0153 (11)
N13	1.0732 (8)	0.7112 (5)	0.9878 (3)	0.0166 (12)
N12	0.7663 (8)	0.4566 (5)	0.8180 (3)	0.0172 (12)
O13	0.6934 (6)	0.9785 (4)	0.6106 (2)	0.0215 (10)
O14	0.3695 (6)	0.8902 (4)	0.6223 (2)	0.0169 (9)
C19	0.3771 (9)	0.9747 (6)	0.6969 (3)	0.0138 (12)
H19	0.4203	1.0630	0.6967	0.017*
C26	0.5511 (10)	0.7929 (6)	0.5167 (3)	0.0175 (14)
C25	0.5486 (9)	0.8974 (6)	0.5864 (3)	0.0147 (13)
C23	0.2732 (10)	1.1656 (6)	0.8308 (4)	0.0280 (15)
H23A	0.2172	1.2182	0.8764	0.034*
H23B	0.2561	1.2092	0.7919	0.034*
C27	0.7395 (10)	0.7814 (6)	0.4812 (3)	0.0225 (15)
H27	0.8606	0.8395	0.5007	0.027*
C20	0.5436 (8)	0.9307 (5)	0.7471 (3)	0.0143 (12)
H20	0.6912	0.9553	0.7361	0.017*
C31	0.3752 (10)	0.7098 (6)	0.4881 (4)	0.0245 (15)
H31	0.2474	0.7182	0.5132	0.029*
C29	0.5747 (11)	0.6003 (7)	0.3873 (4)	0.0347 (18)
H29	0.5839	0.5339	0.3432	0.042*
C18	0.1511 (9)	0.9699 (6)	0.7218 (3)	0.0209 (14)
H18A	0.0939	0.8806	0.7104	0.025*
H18B	0.0550	1.0139	0.6949	0.025*
C28	0.7487 (11)	0.6837 (7)	0.4166 (4)	0.0299 (17)
H28	0.8781	0.6746	0.3924	0.036*
C21	0.5162 (8)	0.9968 (5)	0.8281 (3)	0.0156 (13)
H21	0.6275	0.9728	0.8612	0.019*
C24	0.2629 (9)	0.9858 (6)	0.9246 (3)	0.0224 (15)
H24A	0.3086	1.0746	0.9500	0.034*
H24B	0.3506	0.9306	0.9452	0.034*
H24C	0.1110	0.9697	0.9315	0.034*
C30	0.3828 (10)	0.6130 (7)	0.4224 (4)	0.0314 (17)
H30	0.2600	0.5568	0.4018	0.038*
C17	0.1563 (9)	1.0343 (6)	0.8057 (3)	0.0208 (14)
H17	0.0074	1.0373	0.8223	0.025*
C22	0.5138 (9)	1.1409 (5)	0.8454 (3)	0.0219 (14)
H22A	0.6051	1.1728	0.8128	0.026*

H22B	0.5666	1.1830	0.8974	0.026*
N14	0.2911 (7)	0.9592 (5)	0.8435 (3)	0.0157 (11)
H14A	0.2596	0.8733	0.8203	0.019*
C32	0.5165 (8)	0.7871 (5)	0.7268 (3)	0.0179 (12)
O16	0.6691 (6)	0.7354 (3)	0.6832 (2)	0.0285 (10)
O15	0.3735 (7)	0.7278 (4)	0.7442 (2)	0.0286 (10)
O17	0.9177 (6)	0.3589 (4)	0.9415 (2)	0.0181 (9)
O20	0.8995 (6)	0.7777 (4)	0.8338 (2)	0.0210 (10)
O22	0.8718 (7)	0.3882 (5)	0.7714 (2)	0.0349 (13)
O24	1.2696 (6)	0.7272 (4)	0.9918 (2)	0.0260 (11)
O23	0.9685 (7)	0.7792 (4)	1.0354 (2)	0.0243 (11)
O21	0.5709 (7)	0.4463 (4)	0.8127 (2)	0.0283 (11)
O18	1.2381 (6)	0.4442 (4)	0.9464 (2)	0.0179 (9)
O19	0.6208 (7)	0.7581 (4)	0.8912 (3)	0.0314 (12)
C33	0.9296 (11)	0.2905 (6)	0.4044 (4)	0.0474 (18)
H33A	0.9801	0.3122	0.3613	0.071*
H33B	1.0424	0.3159	0.4453	0.071*
H33C	0.8002	0.3350	0.4192	0.071*
C34	0.6492 (12)	0.5973 (5)	0.6565 (3)	0.0443 (19)
H34A	0.6577	0.5623	0.6987	0.066*
H34B	0.7661	0.5674	0.6253	0.066*
H34C	0.5104	0.5693	0.6277	0.066*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.0112 (5)	0.0121 (5)	0.0130 (5)	0.0024 (4)	0.0041 (4)	0.0044 (4)
Co2	0.0107 (5)	0.0125 (5)	0.0135 (5)	0.0010 (4)	0.0024 (4)	0.0039 (4)
C10	0.023 (3)	0.014 (3)	0.011 (3)	-0.001 (3)	-0.001 (2)	0.006 (3)
C14	0.023 (4)	0.016 (3)	0.036 (4)	-0.003 (3)	-0.002 (3)	0.007 (3)
C11	0.021 (3)	0.025 (4)	0.017 (3)	-0.001 (3)	0.004 (2)	0.009 (3)
C12	0.022 (3)	0.025 (4)	0.022 (3)	0.003 (3)	0.011 (3)	0.008 (3)
C15	0.026 (4)	0.026 (4)	0.020 (3)	0.007 (3)	0.007 (3)	0.004 (3)
C13	0.039 (4)	0.019 (4)	0.020 (4)	0.009 (3)	0.008 (3)	0.003 (3)
C9	0.011 (3)	0.016 (3)	0.016 (3)	0.003 (2)	-0.001 (2)	0.010 (3)
O1	0.019 (2)	0.021 (2)	0.018 (2)	-0.0040 (19)	0.0064 (17)	0.0047 (19)
O2	0.017 (2)	0.020 (2)	0.012 (2)	0.0007 (16)	0.0051 (15)	0.0031 (17)
C5	0.017 (3)	0.022 (3)	0.016 (3)	-0.003 (3)	0.004 (2)	0.007 (3)

C3	0.015 (3)	0.020 (3)	0.009 (3)	0.000 (3)	0.001 (2)	0.001 (3)
C2	0.011 (3)	0.014 (3)	0.011 (3)	-0.002 (2)	-0.003 (2)	0.002 (2)
C6	0.024 (3)	0.012 (3)	0.023 (3)	-0.006 (3)	0.001 (2)	0.002 (2)
C1	0.009 (3)	0.018 (3)	0.017 (3)	0.004 (2)	-0.001 (2)	0.004 (2)
C8	0.026 (3)	0.016 (3)	0.014 (3)	-0.001 (3)	0.003 (2)	0.004 (3)
C7	0.028 (3)	0.014 (3)	0.020 (3)	0.009 (3)	0.003 (3)	0.003 (3)
C4	0.011 (3)	0.016 (3)	0.018 (3)	0.001 (2)	0.001 (2)	0.005 (2)
N1	0.017 (3)	0.012 (3)	0.009 (2)	0.004 (2)	-0.0009 (18)	-0.002 (2)
C16	0.018 (3)	0.014 (3)	0.012 (3)	-0.003 (2)	0.007 (2)	-0.001 (2)
O3	0.024 (2)	0.0128 (19)	0.017 (2)	0.0020 (17)	0.0039 (17)	0.0045 (16)
O4	0.039 (2)	0.018 (2)	0.023 (2)	-0.0079 (18)	-0.0128 (17)	0.0069 (18)
N2	0.012 (3)	0.019 (3)	0.017 (3)	0.004 (2)	0.005 (2)	0.007 (2)
N3	0.022 (3)	0.018 (3)	0.015 (3)	0.007 (2)	0.003 (2)	0.007 (2)
N4	0.012 (3)	0.014 (3)	0.024 (3)	0.002 (2)	0.005 (2)	0.012 (2)
N5	0.022 (3)	0.017 (3)	0.022 (3)	0.005 (2)	0.005 (2)	0.009 (2)
N6	0.015 (3)	0.013 (3)	0.015 (3)	0.000 (2)	0.000 (2)	0.002 (2)
N7	0.014 (3)	0.011 (3)	0.008 (2)	0.003 (2)	0.0037 (19)	0.001 (2)
O5	0.015 (2)	0.034 (3)	0.027 (3)	0.000 (2)	-0.0007 (19)	0.002 (2)
O6	0.022 (3)	0.032 (3)	0.030 (3)	0.007 (2)	0.004 (2)	-0.006 (2)
O12	0.015 (2)	0.014 (2)	0.023 (2)	-0.0040 (17)	0.0058 (16)	0.0059 (18)
O8	0.027 (3)	0.040 (3)	0.025 (3)	0.007 (2)	0.004 (2)	-0.013 (2)
O10	0.020 (2)	0.032 (3)	0.048 (3)	0.004 (2)	0.015 (2)	0.029 (2)
O7	0.015 (2)	0.030 (3)	0.024 (2)	-0.002 (2)	-0.0038 (18)	0.003 (2)
O11	0.015 (2)	0.017 (2)	0.026 (2)	0.0034 (17)	0.0015 (17)	0.0060 (19)
O9	0.016 (2)	0.030 (3)	0.036 (3)	0.012 (2)	0.0100 (19)	0.017 (2)
N9	0.020 (3)	0.015 (3)	0.011 (3)	0.006 (2)	-0.001 (2)	0.002 (2)
N8	0.010 (3)	0.023 (3)	0.024 (3)	0.004 (2)	0.010 (2)	0.011 (2)
N11	0.014 (3)	0.017 (3)	0.018 (3)	-0.002 (2)	-0.001 (2)	0.003 (2)
N10	0.019 (3)	0.016 (3)	0.011 (3)	0.001 (2)	0.005 (2)	0.005 (2)
N13	0.021 (3)	0.013 (3)	0.018 (3)	0.006 (2)	0.006 (2)	0.006 (2)
N12	0.015 (3)	0.023 (3)	0.016 (3)	0.003 (2)	0.008 (2)	0.008 (2)
O13	0.025 (2)	0.017 (2)	0.022 (2)	-0.0018 (19)	0.0061 (17)	0.0039 (19)
O14	0.016 (2)	0.021 (2)	0.013 (2)	0.0009 (17)	0.0047 (16)	0.0033 (17)
C19	0.013 (3)	0.012 (3)	0.017 (3)	0.000 (2)	0.001 (2)	0.006 (3)
C26	0.024 (3)	0.017 (3)	0.016 (3)	0.008 (3)	0.008 (3)	0.010 (3)
C25	0.014 (3)	0.019 (3)	0.015 (3)	0.005 (3)	-0.001 (2)	0.011 (3)
C23	0.039 (4)	0.017 (3)	0.027 (4)	0.009 (3)	0.006 (3)	0.004 (3)
C27	0.024 (3)	0.023 (4)	0.022 (3)	0.004 (3)	0.003 (3)	0.009 (3)

C20	0.010 (3)	0.016 (3)	0.015 (3)	-0.003 (2)	0.003 (2)	0.001 (2)
C31	0.016 (3)	0.032 (4)	0.023 (4)	0.001 (3)	-0.003 (2)	0.005 (3)
C29	0.037 (4)	0.041 (5)	0.016 (4)	0.008 (4)	-0.004 (3)	-0.007 (3)
C18	0.016 (3)	0.026 (3)	0.022 (3)	0.002 (3)	0.004 (2)	0.006 (3)
C28	0.035 (4)	0.034 (4)	0.019 (4)	0.006 (3)	0.011 (3)	0.002 (3)
C21	0.010 (3)	0.018 (3)	0.016 (3)	-0.001 (2)	-0.003 (2)	0.001 (2)
C24	0.022 (3)	0.028 (4)	0.016 (3)	0.005 (3)	0.006 (3)	0.003 (3)
C30	0.026 (4)	0.035 (4)	0.018 (4)	-0.008 (3)	-0.011 (3)	-0.013 (3)
C17	0.012 (3)	0.032 (4)	0.018 (3)	0.010 (3)	0.007 (2)	0.004 (3)
C22	0.021 (3)	0.020 (3)	0.021 (3)	-0.004 (3)	0.003 (2)	0.001 (3)
N14	0.016 (3)	0.015 (3)	0.016 (3)	0.000 (2)	0.007 (2)	0.004 (2)
C32	0.026 (3)	0.018 (3)	0.009 (3)	0.008 (2)	-0.001 (2)	0.002 (2)
O16	0.038 (3)	0.027 (2)	0.020 (2)	0.0176 (19)	0.0078 (17)	0.0016 (18)
O15	0.048 (3)	0.019 (2)	0.020 (2)	-0.001 (2)	0.014 (2)	0.0062 (18)
O17	0.020 (2)	0.016 (2)	0.019 (2)	-0.0007 (18)	0.0017 (17)	0.0072 (19)
O20	0.022 (2)	0.023 (2)	0.023 (2)	0.0019 (19)	0.0054 (18)	0.013 (2)
O22	0.025 (3)	0.043 (3)	0.022 (3)	0.001 (2)	0.004 (2)	-0.016 (2)
O24	0.013 (2)	0.026 (3)	0.032 (3)	-0.005 (2)	-0.0037 (19)	-0.001 (2)
O23	0.023 (2)	0.018 (2)	0.025 (3)	0.001 (2)	0.0029 (19)	-0.004 (2)
O21	0.021 (3)	0.034 (3)	0.023 (3)	0.004 (2)	-0.0042 (19)	-0.002 (2)
O18	0.009 (2)	0.021 (2)	0.027 (2)	0.0020 (18)	0.0025 (17)	0.0118 (19)
O19	0.021 (2)	0.037 (3)	0.050 (3)	0.016 (2)	0.015 (2)	0.029 (2)
C33	0.072 (5)	0.023 (4)	0.036 (4)	-0.023 (3)	-0.027 (3)	0.002 (3)
C34	0.076 (5)	0.027 (4)	0.032 (4)	0.026 (4)	0.014 (3)	0.006 (3)

GEOMETRIC PARAMETERS ( $\text{\AA}$ ,  $^\circ$ )

Co1—N7	1.931 (5)	N5—O7	1.222 (6)
Co1—N3	1.937 (5)	N5—O8	1.245 (6)
Co1—N2	1.939 (4)	N6—O9	1.233 (6)
Co1—N5	1.948 (6)	N6—O10	1.231 (6)
Co1—N4	1.968 (5)	N7—O11	1.227 (6)
Co1—N6	1.982 (5)	N7—O12	1.247 (6)
Co2—N10	1.934 (5)	N11—O19	1.243 (6)
Co2—N9	1.937 (5)	N11—O20	1.256 (6)
Co2—N8	1.945 (4)	N10—O17	1.235 (6)
Co2—N13	1.962 (5)	N10—O18	1.244 (6)
Co2—N11	1.962 (5)	N13—O24	1.224 (6)

Co2—N12	1.971 (5)	N13—O23	1.243 (6)
C10—C15	1.376 (9)	N12—O21	1.214 (6)
C10—C11	1.405 (8)	N12—O22	1.236 (6)
C10—C9	1.495 (8)	O13—C25	1.210 (7)
C14—C13	1.383 (8)	O14—C25	1.358 (6)
C14—C15	1.379 (9)	O14—C19	1.452 (7)
C11—C12	1.383 (9)	C19—C18	1.520 (7)
C12—C13	1.384 (9)	C19—C20	1.548 (8)
C9—O1	1.189 (7)	C26—C31	1.373 (9)
C9—O2	1.366 (6)	C26—C27	1.387 (8)
O2—C3	1.446 (6)	C26—C25	1.488 (8)
C5—N1	1.499 (7)	C23—C17	1.525 (8)
C5—C4	1.532 (7)	C23—C22	1.558 (8)
C5—C6	1.539 (7)	C27—C28	1.389 (9)
C3—C4	1.527 (7)	C20—C21	1.524 (7)
C3—C2	1.540 (7)	C20—C32	1.519 (7)
C2—C16	1.534 (7)	C31—C30	1.397 (9)
C2—C1	1.534 (7)	C29—C28	1.368 (10)
C6—C7	1.550 (8)	C29—C30	1.401 (9)
C1—C7	1.530 (7)	C18—C17	1.543 (8)
C1—N1	1.530 (7)	C21—N14	1.517 (7)
C8—N1	1.485 (7)	C21—C22	1.531 (7)
C16—O3	1.204 (6)	C24—N14	1.504 (7)
C16—O4	1.333 (6)	C17—N14	1.493 (7)
O4—C33	1.446 (6)	C32—O15	1.201 (6)
N4—O5	1.222 (6)	C32—O16	1.342 (5)
N4—O6	1.222 (6)	O16—C34	1.460 (6)
N7—Co1—N3	88.90 (19)	O3—C16—C2	124.1 (5)
N7—Co1—N2	89.16 (19)	O4—C16—C2	111.2 (4)
N3—Co1—N2	177.6 (2)	C16—O4—C33	115.3 (4)
N7—Co1—N5	88.4 (2)	O5—N4—O6	120.8 (5)
N3—Co1—N5	89.8 (2)	O5—N4—Co1	120.1 (4)
N2—Co1—N5	91.6 (2)	O6—N4—Co1	119.1 (4)
N7—Co1—N4	92.8 (2)	O7—N5—O8	119.9 (6)
N3—Co1—N4	90.0 (2)	O7—N5—Co1	120.3 (4)
N2—Co1—N4	88.7 (2)	O8—N5—Co1	119.8 (4)
N5—Co1—N4	178.8 (2)	O9—N6—O10	118.7 (5)
N7—Co1—N6	178.0 (2)	O9—N6—Co1	121.6 (4)

N3—Co1—N6	91.4 (2)	O10—N6—Co1	119.7 (4)
N2—Co1—N6	90.57 (19)	O11—N7—O12	119.8 (5)
N5—Co1—N6	89.6 (2)	O11—N7—Co1	121.3 (4)
N4—Co1—N6	89.2 (2)	O12—N7—Co1	118.9 (4)
N10—Co2—N9	88.76 (19)	O19—N11—O20	118.3 (5)
N10—Co2—N8	89.37 (19)	O19—N11—Co2	120.0 (4)
N9—Co2—N8	178.1 (2)	O20—N11—Co2	121.7 (4)
N10—Co2—N13	92.6 (2)	O17—N10—O18	120.8 (5)
N9—Co2—N13	89.5 (2)	O17—N10—Co2	119.4 (4)
N8—Co2—N13	90.6 (2)	O18—N10—Co2	119.8 (4)
N10—Co2—N11	179.5 (2)	O24—N13—O23	120.4 (5)
N9—Co2—N11	91.5 (2)	O24—N13—Co2	120.1 (4)
N8—Co2—N11	90.4 (2)	O23—N13—Co2	119.5 (4)
N13—Co2—N11	87.8 (2)	O21—N12—O22	121.5 (6)
N10—Co2—N12	88.6 (2)	O21—N12—Co2	119.6 (4)
N9—Co2—N12	91.0 (2)	O22—N12—Co2	118.9 (4)
N8—Co2—N12	89.0 (2)	C25—O14—C19	115.2 (4)
N13—Co2—N12	178.7 (2)	O14—C19—C18	106.8 (5)
N11—Co2—N12	91.0 (2)	O14—C19—C20	109.2 (4)
C15—C10—C11	119.8 (6)	C18—C19—C20	112.1 (5)
C15—C10—C9	123.3 (5)	C31—C26—C27	120.5 (6)
C11—C10—C9	116.9 (5)	C31—C26—C25	122.0 (5)
C13—C14—C15	119.9 (6)	C27—C26—C25	117.5 (6)
C12—C11—C10	120.2 (6)	O13—C25—O14	122.7 (5)
C13—C12—C11	119.0 (6)	O13—C25—C26	124.2 (5)
C10—C15—C14	120.1 (6)	O14—C25—C26	113.0 (5)
C12—C13—C14	120.9 (6)	C17—C23—C22	104.7 (5)
O1—C9—O2	123.3 (5)	C26—C27—C28	119.1 (6)
O1—C9—C10	126.6 (5)	C21—C20—C32	114.0 (4)
O2—C9—C10	110.1 (5)	C21—C20—C19	110.0 (4)
C9—O2—C3	117.6 (4)	C32—C20—C19	107.6 (5)
N1—C5—C4	107.1 (5)	C26—C31—C30	120.5 (6)
N1—C5—C6	103.1 (4)	C28—C29—C30	120.0 (6)
C4—C5—C6	113.5 (5)	C19—C18—C17	109.7 (5)
O2—C3—C4	111.8 (4)	C29—C28—C27	121.1 (6)
O2—C3—C2	104.0 (5)	N14—C21—C20	107.6 (4)
C4—C3—C2	113.7 (5)	N14—C21—C22	102.5 (4)
C16—C2—C3	109.4 (4)	C20—C21—C22	113.3 (5)

C16—C2—C1	110.2 (4)	C31—C30—C29	118.8 (6)
C3—C2—C1	111.0 (5)	N14—C17—C23	103.2 (5)
C5—C6—C7	104.5 (5)	N14—C17—C18	107.4 (4)
C7—C1—N1	102.4 (5)	C23—C17—C18	114.0 (5)
C7—C1—C2	112.4 (5)	C21—C22—C23	104.8 (5)
N1—C1—C2	108.3 (4)	C17—N14—C24	114.0 (4)
C1—C7—C6	105.7 (4)	C17—N14—C21	101.8 (4)
C3—C4—C5	112.1 (4)	C24—N14—C21	113.1 (5)
C8—N1—C5	114.5 (5)	O15—C32—O16	124.6 (5)
C8—N1—C1	112.9 (4)	O15—C32—C20	125.0 (4)
C5—N1—C1	101.8 (4)	O16—C32—C20	110.3 (4)
O3—C16—O4	124.7 (5)	C32—O16—C34	114.7 (4)

APPENDIX 4 (B) – THE ERDMANN'S SALT OF METHAMPHETAMINE  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.88121 (19)	0.00010 (8)	0.81717 (5)	0.0174 (3)
Co2	0.60979 (18)	0.38722 (8)	0.67542 (5)	0.0166 (3)
O1	0.8813 (8)	0.0563 (4)	0.6925 (2)	0.0230 (14)
O2	1.1921 (8)	0.0327 (5)	0.7363 (2)	0.0360 (17)
O3	0.8184 (8)	-0.1742 (4)	0.7465 (2)	0.0321 (15)
O4	0.5436 (9)	-0.1260 (5)	0.7897 (2)	0.0313 (15)
O5	0.8378 (8)	-0.1028 (5)	0.9270 (2)	0.0358 (15)
O6	0.6365 (9)	0.0266 (5)	0.9154 (2)	0.0470 (19)
O7	0.9571 (9)	0.2024 (5)	0.8583 (3)	0.0458 (18)
O8	1.2195 (9)	0.1062 (4)	0.8786 (3)	0.0476 (18)
O9	0.6267 (8)	0.4790 (5)	0.5599 (2)	0.0387 (17)
O10	0.9093 (8)	0.3992 (4)	0.5891 (2)	0.0294 (14)
O11	0.3367 (8)	0.2782 (4)	0.5900 (2)	0.0313 (14)
O12	0.5147 (8)	0.1801 (5)	0.6527 (2)	0.0301 (15)
O13	0.6162 (8)	0.3412 (4)	0.8001 (2)	0.0252 (14)
O14	0.3066 (9)	0.3368 (5)	0.7556 (2)	0.0348 (16)
O15	0.6421 (9)	0.5672 (5)	0.7411 (2)	0.0338 (16)
O16	0.9424 (8)	0.5105 (5)	0.7177 (2)	0.0320 (15)
N1	0.6413 (9)	0.0879 (5)	0.7938 (2)	0.0196 (16)
H1A	0.6343	0.1000	0.7524	0.029*
H1B	0.6561	0.1486	0.8146	0.029*
H1C	0.5214	0.0562	0.8036	0.029*
N2	1.1164 (9)	-0.0923 (5)	0.8389 (2)	0.0209 (16)
H2A	1.0848	-0.1337	0.8707	0.031*
H2B	1.2331	-0.0548	0.8506	0.031*
H2C	1.1409	-0.1315	0.8055	0.031*
N3	0.9986 (11)	0.0330 (5)	0.7395 (3)	0.0231 (17)
N4	0.7286 (10)	-0.1139 (6)	0.7796 (3)	0.0232 (16)
N5	0.7697 (10)	-0.0295 (6)	0.8961 (3)	0.0218 (17)
N6	1.0353 (11)	0.1169 (5)	0.8557 (3)	0.0216 (17)
N7	0.3631 (9)	0.4704 (5)	0.6529 (2)	0.0194 (15)
H7A	0.2760	0.4688	0.6841	0.029*

H7B	0.2946	0.4452	0.6177	0.029*
H7C	0.4030	0.5364	0.6464	0.029*
N8	0.8563 (9)	0.3027 (5)	0.6994 (3)	0.0202 (17)
H8A	0.9590	0.3163	0.6738	0.030*
H8B	0.8206	0.2351	0.6964	0.030*
H8C	0.9041	0.3175	0.7391	0.030*
N9	0.7260 (10)	0.4260 (5)	0.5986 (3)	0.0199 (16)
N10	0.4693 (10)	0.2689 (5)	0.6344 (3)	0.0182 (16)
N11	0.4959 (10)	0.3506 (5)	0.7529 (3)	0.0184 (16)
N12	0.7464 (10)	0.5031 (5)	0.7157 (3)	0.0204 (16)
N13	1.1381 (10)	0.0635 (5)	0.5890 (3)	0.0205 (16)
H13A	1.2191	0.1209	0.5883	0.025*
H13B	1.0623	0.0678	0.6227	0.025*
N14	0.3855 (10)	0.3116 (5)	-0.0943 (3)	0.0215 (16)
H14A	0.4409	0.3290	-0.1303	0.026*
H14B	0.3148	0.2515	-0.1013	0.026*
C1	0.9881 (11)	0.0623 (5)	0.5317 (3)	0.0206 (18)
H1	1.0717	0.0511	0.4952	0.025*
C2	0.8815 (10)	0.1671 (5)	0.5242 (3)	0.0223 (17)
H2D	0.7654	0.1705	0.5518	0.027*
H2E	0.9843	0.2213	0.5374	0.027*
C4	0.9282 (12)	0.1879 (6)	0.4109 (3)	0.0214 (19)
H4D	1.0726	0.1720	0.4198	0.026*
C3	0.7955 (12)	0.1880 (6)	0.4590 (3)	0.0176 (18)
C5	0.8550 (12)	0.2104 (5)	0.3508 (3)	0.0236 (19)
H5D	0.9487	0.2087	0.3190	0.028*
C6	0.6459 (12)	0.2352 (6)	0.3365 (3)	0.028 (2)
H6D	0.5951	0.2509	0.2952	0.034*
C7	0.5110 (12)	0.2368 (6)	0.3841 (3)	0.025 (2)
H7D	0.3669	0.2536	0.3754	0.030*
C8	0.5883 (12)	0.2138 (6)	0.4442 (3)	0.0214 (19)
H8D	0.4952	0.2159	0.4762	0.026*
C9	0.8361 (11)	-0.0267 (6)	0.5349 (3)	0.025 (2)
H9A	0.9136	-0.0917	0.5346	0.038*
H9B	0.7322	-0.0243	0.4991	0.038*
H9C	0.7643	-0.0218	0.5730	0.038*
C10	1.2790 (11)	-0.0280 (6)	0.5964 (3)	0.019
H10A	1.1970	-0.0881	0.6073	0.028*

H10B	1.3901	-0.0149	0.6294	0.028*
H10C	1.3422	-0.0412	0.5575	0.028*
C11	0.5651 (12)	0.2917 (6)	-0.0463 (3)	0.0236 (19)
H11	0.6727	0.2510	-0.0668	0.028*
C12	0.4905 (11)	0.2262 (5)	0.0054 (3)	0.0244 (18)
H12A	0.4211	0.1642	-0.0131	0.029*
H12B	0.3836	0.2653	0.0262	0.029*
C13	0.6613 (12)	0.1923 (6)	0.0539 (3)	0.0211 (19)
C14	0.8623 (12)	0.1657 (6)	0.0384 (3)	0.026 (2)
H14C	0.8947	0.1687	-0.0036	0.031*
C15	1.0130 (12)	0.1354 (6)	0.0833 (3)	0.031 (2)
H15A	1.1493	0.1182	0.0720	0.037*
C16	0.9703 (13)	0.1293 (6)	0.1443 (4)	0.033 (2)
H16A	1.0765	0.1089	0.1750	0.039*
C17	0.7702 (13)	0.1534 (6)	0.1605 (3)	0.029 (2)
H17A	0.7371	0.1480	0.2023	0.035*
C18	0.6191 (12)	0.1855 (6)	0.1149 (3)	0.025 (2)
H18A	0.4831	0.2033	0.1261	0.030*
C19	0.6675 (11)	0.3933 (6)	-0.0254 (3)	0.0248 (19)
H19A	0.5698	0.4329	-0.0022	0.037*
H19B	0.7023	0.4327	-0.0617	0.037*
H19C	0.7960	0.3795	0.0011	0.037*
C20	0.2290 (11)	0.3924 (6)	-0.0808 (3)	0.0295 (19)
H20A	0.1768	0.3790	-0.0403	0.044*
H20B	0.1114	0.3909	-0.1128	0.044*
H20C	0.2964	0.4600	-0.0804	0.044*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.0130 (8)	0.0212 (8)	0.0180 (6)	0.0003 (6)	0.0009 (6)	0.0009 (6)
Co2	0.0121 (7)	0.0195 (8)	0.0179 (6)	0.0004 (6)	-0.0002 (6)	0.0001 (6)
O1	0.023 (3)	0.035 (4)	0.010 (2)	0.008 (3)	-0.001 (2)	0.008 (2)
O2	0.009 (3)	0.069 (5)	0.031 (3)	-0.006 (3)	0.006 (3)	0.010 (3)
O3	0.024 (3)	0.032 (4)	0.041 (3)	-0.003 (3)	0.007 (3)	-0.015 (3)
O4	0.017 (3)	0.038 (4)	0.039 (3)	-0.010 (3)	0.006 (3)	-0.010 (3)
O5	0.040 (4)	0.037 (4)	0.033 (3)	0.014 (3)	0.014 (3)	0.018 (3)
O6	0.041 (4)	0.068 (5)	0.036 (3)	0.030 (3)	0.021 (3)	0.015 (3)

O7	0.026 (4)	0.027 (4)	0.083 (5)	0.005 (3)	-0.004 (3)	-0.024 (4)
O8	0.028 (4)	0.035 (4)	0.074 (4)	-0.003 (3)	-0.032 (4)	-0.003 (3)
O9	0.020 (3)	0.073 (5)	0.022 (3)	0.010 (3)	-0.001 (3)	0.022 (3)
O10	0.023 (3)	0.038 (4)	0.029 (3)	0.005 (3)	0.011 (3)	0.002 (3)
O11	0.027 (3)	0.029 (3)	0.035 (3)	0.001 (3)	-0.016 (3)	-0.002 (3)
O12	0.021 (3)	0.023 (4)	0.043 (3)	-0.005 (3)	-0.014 (3)	0.002 (3)
O13	0.019 (3)	0.036 (4)	0.020 (3)	0.000 (3)	-0.005 (3)	0.005 (2)
O14	0.015 (3)	0.057 (5)	0.031 (3)	-0.001 (3)	-0.001 (3)	0.007 (3)
O15	0.032 (4)	0.029 (4)	0.039 (3)	0.014 (3)	-0.007 (3)	-0.015 (3)
O16	0.018 (4)	0.043 (4)	0.035 (3)	-0.009 (3)	0.002 (3)	-0.011 (3)
N1	0.019 (4)	0.020 (4)	0.020 (3)	-0.001 (3)	0.000 (3)	0.004 (3)
N2	0.009 (4)	0.027 (4)	0.026 (3)	0.002 (3)	-0.002 (3)	0.005 (3)
N3	0.023 (5)	0.023 (5)	0.023 (4)	-0.002 (3)	0.001 (3)	0.001 (3)
N4	0.021 (4)	0.024 (4)	0.023 (3)	-0.001 (4)	-0.004 (3)	-0.003 (3)
N5	0.014 (4)	0.032 (5)	0.018 (3)	-0.001 (3)	-0.004 (3)	0.001 (3)
N6	0.021 (5)	0.029 (5)	0.015 (3)	-0.008 (3)	-0.001 (3)	-0.002 (3)
N7	0.018 (4)	0.021 (4)	0.019 (3)	0.000 (3)	-0.001 (3)	0.002 (3)
N8	0.005 (4)	0.027 (4)	0.028 (4)	0.002 (3)	-0.006 (3)	0.003 (3)
N9	0.018 (4)	0.020 (4)	0.021 (3)	-0.001 (3)	0.001 (3)	-0.005 (3)
N10	0.012 (4)	0.022 (4)	0.020 (3)	-0.002 (3)	0.000 (3)	-0.002 (3)
N11	0.015 (4)	0.025 (4)	0.014 (3)	0.002 (3)	-0.005 (3)	0.001 (3)
N12	0.023 (4)	0.019 (4)	0.017 (3)	-0.007 (3)	-0.007 (3)	0.002 (3)
N13	0.019 (4)	0.023 (4)	0.019 (3)	-0.002 (3)	0.000 (3)	-0.002 (3)
N14	0.023 (4)	0.019 (4)	0.023 (3)	-0.002 (3)	-0.001 (3)	0.001 (3)
C1	0.023 (5)	0.024 (5)	0.014 (4)	-0.004 (4)	-0.002 (3)	0.004 (3)
C2	0.015 (4)	0.026 (5)	0.025 (4)	0.005 (3)	-0.001 (4)	-0.004 (3)
C4	0.018 (5)	0.020 (4)	0.026 (4)	-0.002 (4)	-0.003 (4)	0.001 (4)
C3	0.017 (5)	0.015 (4)	0.019 (4)	-0.003 (3)	-0.007 (4)	0.003 (3)
C5	0.033 (5)	0.021 (5)	0.018 (4)	-0.004 (4)	0.005 (4)	-0.001 (4)
C6	0.035 (6)	0.025 (5)	0.023 (4)	0.002 (4)	-0.005 (4)	0.003 (4)
C7	0.014 (5)	0.022 (5)	0.038 (5)	-0.003 (4)	-0.006 (4)	0.000 (4)
C8	0.015 (5)	0.026 (5)	0.023 (4)	-0.004 (4)	0.000 (4)	0.000 (4)
C9	0.014 (5)	0.035 (5)	0.025 (4)	-0.007 (4)	-0.006 (4)	0.000 (4)
C10	0.015	0.020	0.021	0.003	-0.004	-0.003
C11	0.024 (5)	0.027 (5)	0.018 (4)	-0.002 (4)	-0.007 (4)	-0.003 (3)
C12	0.024 (5)	0.028 (5)	0.021 (4)	0.001 (4)	0.003 (4)	-0.006 (4)
C13	0.024 (5)	0.020 (5)	0.018 (4)	-0.003 (4)	-0.004 (4)	0.005 (4)
C14	0.027 (5)	0.030 (5)	0.021 (4)	-0.003 (4)	-0.003 (4)	0.002 (4)

C15	0.018 (5)	0.030 (5)	0.045 (5)	-0.007 (4)	-0.002 (4)	0.006 (4)
C16	0.032 (6)	0.030 (6)	0.034 (5)	-0.005 (4)	-0.013 (5)	0.008 (4)
C17	0.047 (6)	0.022 (5)	0.017 (4)	-0.008 (4)	-0.004 (4)	0.001 (4)
C18	0.016 (5)	0.028 (5)	0.032 (5)	0.000 (4)	0.003 (4)	-0.002 (4)
C19	0.022 (5)	0.024 (5)	0.028 (4)	0.005 (4)	-0.002 (4)	0.000 (4)
C20	0.031 (5)	0.032 (5)	0.025 (4)	0.007 (4)	-0.002 (4)	0.000 (4)

## GEOMETRIC PARAMETERS (Å, °)

Co1—N4	1.920 (7)	O14—N11	1.229 (7)
Co1—N5	1.945 (6)	O15—N12	1.226 (8)
Co1—N3	1.946 (6)	O16—N12	1.253 (7)
Co1—N1	1.945 (6)	N13—C10	1.494 (8)
Co1—N2	1.952 (6)	N13—C1	1.507 (8)
Co1—N6	1.961 (7)	N14—C20	1.496 (8)
Co2—N12	1.917 (6)	N14—C11	1.507 (8)
Co2—N7	1.941 (6)	C1—C9	1.518 (10)
Co2—N11	1.942 (6)	C1—C2	1.527 (9)
Co2—N9	1.943 (6)	C2—C3	1.499 (8)
Co2—N8	1.956 (6)	C4—C5	1.378 (8)
Co2—N10	1.960 (6)	C4—C3	1.397 (9)
O1—N3	1.252 (7)	C3—C8	1.378 (9)
O2—N3	1.244 (7)	C5—C6	1.385 (9)
O3—N4	1.235 (8)	C6—C7	1.397 (9)
O4—N4	1.230 (7)	C7—C8	1.387 (9)
O5—N5	1.225 (8)	C11—C12	1.516 (9)
O6—N5	1.219 (8)	C11—C19	1.528 (10)
O7—N6	1.223 (8)	C12—C13	1.518 (9)
O8—N6	1.247 (7)	C13—C18	1.372 (9)
O9—N9	1.222 (7)	C13—C14	1.397 (10)
O10—N9	1.255 (7)	C14—C15	1.370 (9)
O11—N10	1.234 (7)	C15—C16	1.373 (9)
O12—N10	1.249 (8)	C16—C17	1.389 (11)
O13—N11	1.235 (7)	C17—C18	1.389 (9)
N4—Co1—N5	90.6 (3)	O7—N6—Co1	122.2 (5)
N4—Co1—N3	91.2 (3)	O8—N6—Co1	120.5 (6)
N5—Co1—N3	178.2 (3)	O9—N9—O10	118.9 (7)
N4—Co1—N1	89.0 (3)	O9—N9—Co2	121.4 (5)

N5—Co1—N1	90.5 (3)	O10—N9—Co2	119.7 (5)
N3—Co1—N1	89.8 (3)	O11—N10—O12	117.7 (6)
N4—Co1—N2	88.9 (3)	O11—N10—Co2	122.4 (5)
N5—Co1—N2	89.8 (3)	O12—N10—Co2	119.8 (5)
N3—Co1—N2	90.1 (3)	O14—N11—O13	119.6 (6)
N1—Co1—N2	177.8 (3)	O14—N11—Co2	121.1 (5)
N4—Co1—N6	179.6 (3)	O13—N11—Co2	119.3 (5)
N5—Co1—N6	89.2 (3)	O15—N12—O16	120.7 (7)
N3—Co1—N6	89.0 (3)	O15—N12—Co2	119.8 (5)
N1—Co1—N6	90.7 (3)	O16—N12—Co2	119.5 (6)
N2—Co1—N6	91.5 (3)	C10—N13—C1	114.7 (5)
N12—Co2—N7	90.3 (3)	C20—N14—C11	117.9 (6)
N12—Co2—N11	89.3 (3)	N13—C1—C9	109.6 (6)
N7—Co2—N11	90.0 (3)	N13—C1—C2	109.0 (6)
N12—Co2—N9	89.7 (3)	C9—C1—C2	113.9 (6)
N7—Co2—N9	89.9 (3)	C3—C2—C1	112.8 (6)
N11—Co2—N9	179.0 (3)	C5—C4—C3	121.7 (7)
N12—Co2—N8	89.7 (3)	C8—C3—C4	117.1 (6)
N7—Co2—N8	179.0 (2)	C8—C3—C2	122.4 (7)
N11—Co2—N8	89.0 (3)	C4—C3—C2	120.4 (6)
N9—Co2—N8	91.1 (3)	C4—C5—C6	120.5 (7)
N12—Co2—N10	179.8 (3)	C5—C6—C7	118.7 (7)
N7—Co2—N10	89.6 (3)	C8—C7—C6	119.7 (7)
N11—Co2—N10	90.6 (3)	C3—C8—C7	122.3 (7)
N9—Co2—N10	90.5 (3)	N14—C11—C12	109.9 (6)
N8—Co2—N10	90.4 (3)	N14—C11—C19	109.9 (6)
O2—N3—O1	119.1 (6)	C12—C11—C19	114.8 (6)
O2—N3—Co1	120.2 (5)	C11—C12—C13	115.2 (6)
O1—N3—Co1	120.7 (5)	C18—C13—C14	118.2 (7)
O4—N4—O3	121.4 (7)	C18—C13—C12	120.0 (7)
O4—N4—Co1	119.0 (6)	C14—C13—C12	121.8 (6)
O3—N4—Co1	119.6 (5)	C15—C14—C13	120.4 (7)
O6—N5—O5	120.4 (7)	C14—C15—C16	121.1 (8)
O6—N5—Co1	119.9 (5)	C15—C16—C17	119.3 (8)
O5—N5—Co1	119.7 (5)	C18—C17—C16	119.2 (8)
O7—N6—O8	117.3 (7)	C13—C18—C17	121.7 (7)

APPENDIX 4 (C) – THE ERDMANN'S SALT OF METHYLONE  
 FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC OR EQUIVALENT  
 ISOTROPIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.0000	0.5000	0.5000	0.0684 (9)
O1	0.4189 (16)	0.3121 (9)	0.0161 (11)	0.162 (5)
O2	0.5149 (9)	-0.1466 (6)	0.3727 (6)	0.0629 (17)
O3	0.7084 (11)	-0.0510 (8)	0.2382 (11)	0.137 (4)
O4	0.2916 (12)	0.3873 (9)	0.4639 (11)	0.155 (4)
O5	-0.0014 (14)	0.2441 (12)	0.4154 (9)	0.110 (3)
O6	-0.0126 (10)	0.3314 (9)	0.6978 (6)	0.093 (3)
O7	0.1746 (13)	0.5407 (10)	0.7681 (8)	0.100 (3)
N1	0.1803 (12)	0.4543 (9)	0.0495 (7)	0.077 (2)
H1A	0.0615	0.4775	0.0271	0.092*
H1B	0.2286	0.4581	-0.0208	0.092*
N2	0.2766 (10)	0.6366 (8)	0.5434 (7)	0.072 (3)
H2A	0.3724	0.5948	0.5416	0.109*
H2B	0.3092	0.6798	0.6245	0.109*
H2C	0.2777	0.6991	0.4845	0.109*
N3	0.1059 (17)	0.3601 (12)	0.4485 (10)	0.085 (3)
N4	0.0605 (14)	0.4520 (13)	0.6761 (9)	0.079 (3)
C1	0.3520 (14)	0.1522 (9)	0.1653 (10)	0.064 (3)
C2	0.5190 (18)	0.1082 (12)	0.1580 (15)	0.129 (6)
H2	0.6000	0.1459	0.1021	0.155*
C3	0.5604 (15)	0.0106 (10)	0.2331 (12)	0.084 (3)
C4	0.4423 (14)	-0.0471 (9)	0.3109 (9)	0.052 (2)
C5	0.2813 (13)	-0.0065 (9)	0.3207 (8)	0.053 (2)
H5	0.2019	-0.0463	0.3769	0.064*
C6	0.2358 (12)	0.0947 (9)	0.2463 (8)	0.046 (2)
H6	0.1233	0.1248	0.2513	0.055*
C7	0.3105 (18)	0.2622 (11)	0.0859 (12)	0.092 (4)
C8	0.1354 (13)	0.3162 (9)	0.0886 (9)	0.056 (2)
H8	0.1192	0.3166	0.1779	0.067*
C9	-0.0667 (15)	0.2231 (9)	-0.0096 (9)	0.083 (3)
H9A	-0.1840	0.2534	-0.0058	0.125*
H9B	-0.0928	0.1283	0.0118	0.125*

H9C	-0.0523	0.2281	-0.0975	0.125*
C10	0.3443 (15)	0.5536 (11)	0.1625 (11)	0.100 (4)
H10A	0.2870	0.5546	0.2354	0.150*
H10B	0.3833	0.6459	0.1350	0.150*
H10C	0.4683	0.5244	0.1899	0.150*
C11	0.7032 (14)	-0.1360 (11)	0.3389 (10)	0.077 (3)
H11A	0.8280	-0.0959	0.4152	0.093*
H11B	0.7014	-0.2278	0.3095	0.093*

ATOMIC DISPLACEMENT PARAMETERS ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.0497 (14)	0.137 (2)	0.0621 (14)	0.0663 (14)	0.0423 (11)	0.0704 (14)
O1	0.212 (10)	0.163 (8)	0.266 (12)	0.158 (8)	0.198 (10)	0.134 (8)
O2	0.050 (4)	0.063 (4)	0.077 (4)	0.034 (3)	0.005 (3)	0.004 (3)
O3	0.084 (5)	0.085 (6)	0.307 (12)	0.070 (5)	0.111 (7)	0.095 (7)
O4	0.059 (5)	0.147 (8)	0.311 (14)	0.065 (5)	0.102 (7)	0.061 (8)
O5	0.088 (7)	0.168 (9)	0.124 (7)	0.079 (7)	0.066 (6)	0.047 (7)
O6	0.072 (5)	0.161 (7)	0.084 (5)	0.067 (5)	0.048 (4)	0.093 (5)
O7	0.087 (6)	0.168 (9)	0.071 (5)	0.061 (6)	0.038 (5)	0.072 (6)
N1	0.084 (6)	0.100 (7)	0.088 (6)	0.073 (5)	0.043 (5)	0.033 (5)
N2	0.050 (5)	0.134 (7)	0.074 (5)	0.065 (5)	0.041 (4)	0.070 (5)
N3	0.075 (8)	0.145 (10)	0.103 (8)	0.085 (7)	0.070 (6)	0.100 (8)
N4	0.054 (6)	0.156 (10)	0.078 (7)	0.071 (6)	0.053 (5)	0.085 (7)
C1	0.059 (6)	0.051 (6)	0.107 (8)	0.037 (5)	0.040 (6)	0.024 (6)
C2	0.109 (10)	0.091 (9)	0.277 (17)	0.079 (8)	0.139 (11)	0.102 (11)
C3	0.054 (7)	0.052 (7)	0.174 (11)	0.040 (6)	0.053 (8)	0.039 (7)
C4	0.041 (6)	0.049 (6)	0.065 (6)	0.024 (5)	0.003 (5)	0.004 (5)
C5	0.046 (6)	0.065 (6)	0.060 (6)	0.031 (5)	0.018 (5)	0.008 (5)
C6	0.039 (5)	0.056 (6)	0.047 (5)	0.028 (5)	0.005 (4)	0.000 (5)
C7	0.105 (9)	0.096 (8)	0.143 (10)	0.075 (8)	0.092 (8)	0.049 (8)
C8	0.068 (6)	0.051 (6)	0.072 (6)	0.038 (5)	0.036 (5)	0.015 (5)
C9	0.098 (8)	0.060 (6)	0.081 (7)	0.027 (6)	0.008 (6)	-0.004 (6)
C10	0.060 (7)	0.087 (8)	0.122 (10)	0.011 (6)	-0.006 (7)	-0.007 (7)
C11	0.048 (7)	0.075 (8)	0.107 (8)	0.042 (6)	-0.003 (6)	0.001 (7)

## GEOMETRIC PARAMETERS (Å, °)

Co1—N4 <sup>i</sup>	1.929 (8)	C1—C6	1.378 (11)
Co1—N4	1.929 (8)	C1—C2	1.405 (12)
Co1—N2 <sup>i</sup>	1.943 (7)	C1—C7	1.481 (13)
Co1—N2	1.943 (7)	C2—C3	1.349 (14)
Co1—N3	1.956 (10)	C2—H2	0.9500
Co1—N3 <sup>i</sup>	1.956 (10)	C3—C4	1.359 (12)
O1—C7	1.226 (11)	C4—C5	1.353 (11)
O2—C4	1.381 (9)	C5—C6	1.385 (11)
O2—C11	1.445 (10)	C5—H5	0.9500
O3—C3	1.368 (11)	C6—H6	0.9500
O3—C11	1.404 (12)	C7—C8	1.509 (12)
O4—N3	1.212 (10)	C8—C9	1.533 (12)
O5—N3	1.188 (11)	C8—H8	1.0000
O6—N4	1.244 (11)	C9—H9A	0.9800
O7—N4	1.242 (11)	C9—H9B	0.9800
N1—C8	1.455 (10)	C9—H9C	0.9800
N1—C10	1.521 (11)	C10—H10A	0.9800
N1—H1A	0.9100	C10—H10B	0.9800
N1—H1B	0.9100	C10—H10C	0.9800
N2—H2A	0.9100	C11—H11A	0.9900
N2—H2B	0.9100	C11—H11B	0.9900
N2—H2C	0.9100		
N4 <sup>i</sup> —Co1—N4	180.0	C1—C2—H2	121.1
N4 <sup>i</sup> —Co1—N2 <sup>i</sup>	89.9 (4)	C2—C3—C4	121.8 (9)
N4—Co1—N2 <sup>i</sup>	90.1 (4)	C2—C3—O3	128.0 (11)
N4 <sup>i</sup> —Co1—N2	90.1 (4)	C4—C3—O3	110.1 (9)
N4—Co1—N2	89.9 (4)	C5—C4—C3	121.8 (9)
N2 <sup>i</sup> —Co1—N2	180.0 (6)	C5—C4—O2	128.7 (10)
N4 <sup>i</sup> —Co1—N3	89.7 (4)	C3—C4—O2	109.5 (8)
N4—Co1—N3	90.3 (4)	C4—C5—C6	118.0 (8)
N2 <sup>i</sup> —Co1—N3	88.9 (4)	C4—C5—H5	121.0
N2—Co1—N3	91.1 (4)	C6—C5—H5	121.0
N4 <sup>i</sup> —Co1—N3 <sup>i</sup>	90.3 (4)	C1—C6—C5	120.7 (7)
N4—Co1—N3 <sup>i</sup>	89.7 (4)	C1—C6—H6	119.7
N2 <sup>i</sup> —Co1—N3 <sup>i</sup>	91.1 (4)	C5—C6—H6	119.7

N2—Co1—N3 <sup>i</sup>	88.9 (4)	O1—C7—C1	120.5 (8)
N3—Co1—N3 <sup>i</sup>	180.0	O1—C7—C8	118.2 (9)
C4—O2—C11	105.3 (7)	C1—C7—C8	121.3 (9)
C3—O3—C11	106.5 (8)	N1—C8—C7	109.5 (7)
C8—N1—C10	108.9 (7)	N1—C8—C9	108.7 (7)
C8—N1—H1A	109.9	C7—C8—C9	108.2 (8)
C10—N1—H1A	109.9	N1—C8—H8	110.2
C8—N1—H1B	109.9	C7—C8—H8	110.2
C10—N1—H1B	109.9	C9—C8—H8	110.2
H1A—N1—H1B	108.3	C8—C9—H9A	109.5
Co1—N2—H2A	109.5	C8—C9—H9B	109.5
Co1—N2—H2B	109.5	H9A—C9—H9B	109.5
H2A—N2—H2B	109.5	C8—C9—H9C	109.5
Co1—N2—H2C	109.5	H9A—C9—H9C	109.5
H2A—N2—H2C	109.5	H9B—C9—H9C	109.5
H2B—N2—H2C	109.5	N1—C10—H10A	109.5
O5—N3—O4	117.5 (11)	N1—C10—H10B	109.5
O5—N3—Co1	122.3 (8)	H10A—C10—H10B	109.5
O4—N3—Co1	119.7 (10)	N1—C10—H10C	109.5
O7—N4—O6	119.6 (9)	H10A—C10—H10C	109.5
O7—N4—Co1	120.3 (9)	H10B—C10—H10C	109.5
O6—N4—Co1	120.1 (9)	O3—C11—O2	107.0 (7)
C6—C1—C2	119.8 (9)	O3—C11—H11A	110.3
C6—C1—C7	122.3 (8)	O2—C11—H11A	110.3
C2—C1—C7	117.9 (9)	O3—C11—H11B	110.3
C3—C2—C1	117.9 (10)	O2—C11—H11B	110.3
C3—C2—H2	121.1	H11A—C11—H11B	108.6