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Tetrachloroplatinate(II) and Hexachloroplatinate(IV) Salts of N,N,N′,N′-Tetramethylethylenediammonium: Significant Differences in the Conformation of the Cation, as Shown by Infrared and X-Ray Diffraction Data

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The structures of $(H_2tmen)[PtCl_4]$, *(1),* $(H_2tmen$ = *N,N,N′,N′-tetramethylethylenediammonium),* [*triclinic,* $P\bar{1}$; $a = 7.344(3)$, $b = 8.345(3)$, $c = 6.216(2)$ Å, $\alpha = 84.53(3)$, $\beta = 109.22(3)$, $\gamma = 69.43(3)^\circ$, $Z = 1$] *and* $(H_2tmen)[PtCl_6]$, *(2),* [*monoclinic,* $P2_1/a$; $a = 14.409(4)$, $b = 12.736(7)$, $c = 8.601(3)$ Å, $\beta = 99.58(3)^\circ$, $Z = 4$] *were determined from diffractometric data by Patterson and Fourier methods and refined by full-matrix least-squares to* $R = 0.027$ *and 0.039 for (1) and (2) respectively. In both cases the anions and cations are joined in polymeric chains through hydrogen bonds involving the protonated nitrogens and the co-ordinated chlorine atoms. The square-planar* $[PtCl_4]^{2-}$ *and octahedral* $[PtCl_6]^{2-}$ *anions are centrosymmetric; the* H_2tmen^{2+} *cations are centrosymmetric in (1) with a N–C–C–N dihedral angle of exactly 180°, while in (2) the dihedral angle is 166°. The different symmetry of the organic moieties [*C_i *and* C_1 *in (1) and (2) respectively] results in a different i.r. spectrum which is more complex the lower the symmetry; moreover the spectrum of a KBr pellet of (2) changes with time, finally resembling that of (1) and of the* $(H_2tmen)Cl_2$ *salt.*

Introduction

In a recent study on the reactivity of the cationic complex containing ethylene, $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$ [1], (tmen = N,N,N′,N′-tetramethylethylenediamine) in concentrated hydrochloric acid, two coordination compounds containing the tmen ligand either mono-coordinated to platinum with the free end protonated, $[PtCl_3(Htmen)]$, or *cis* chelated to the metal, $[PtCl_2(tmen)]$, were found [2]. The different configuration of the diamine in the two complexes was reflected by the i.r. spectrum which was much more complex in the former than in the latter.

In the same reaction two side products were also formed, namely $(H_2tmen)[PtCl_4]$, (1), and $(H_2tmen)[PtCl_6]$, (2); both could be obtained in crystalline form and their yields could be increased by prolonging the reaction time. Apart from the platinum–chlorine stretchings, i.r. spectra were very different although both species contained the same cation; moreover the spectrum of a KBr pellet of (2) changed with time, finally resembling that of (1) and of $(H_2tmen)Cl_2$ in the region below 1200 cm^{-1}. We took this unique opportunity to investigate, by a X-ray diffraction study, how the i.r. spectra could reflect a different conformation of the organic moieties which would be predicted to be *trans* in both cases.

Results and Discussion

The structure of (1) consists of tetramethylethylenediammonium cations (H_2tmen^{2+}) and square-planar tetrachloroplatinate(II) anions; that of (2) of H_2tmen^{2+} cations and octahedral hexachloroplatinate(IV) anions. In both structures cations and anions are joined in chains by hydrogen bonds (Figs. 1 and 2); relevant bond distances

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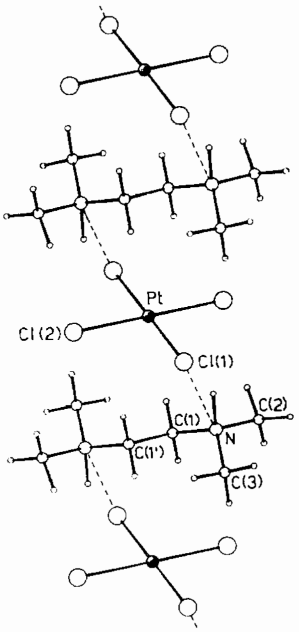

Fig. 1. Chain of $[PtCl_4]^{2-}$ anions and H_2tmen^{2+} cations in compound (1).

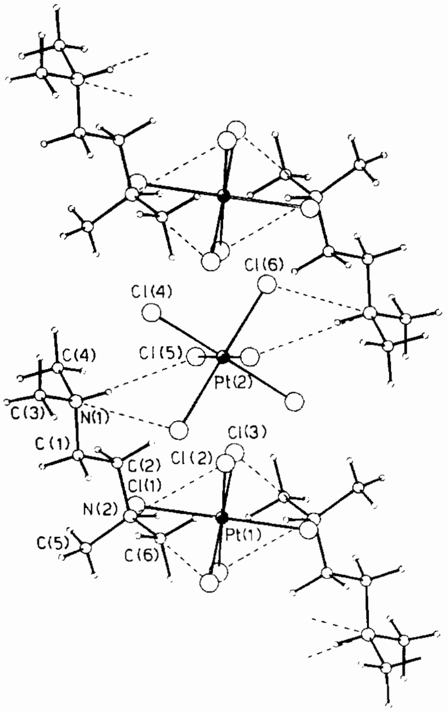

Fig. 2. Chain of $[PtCl_6]^{2-}$ anions and H_2tmen^{2+} cations in compound (2).

TABLE I. Bond Distances and Angles of $(H_2tmen)[PtCl_4]$, (1).

a) in the anion			
Pt–Cl(1)	2.304(2) Å	Cl(1)–Pt–Cl(2)	91.0(1)°
Pt–Cl(2)	2.303(2)		
b) In the cation			
N(1)–C(1)	1.506(8)	C(1)–N(1)–C(3)	113.2(5)
N(1)–C(2)	1.493(8)	C(1)–N(1)–C(2)	109.2(5)
N(1)–C(3)	1.512(9)	C(2)–N(1)–C(3)	110.7(5)
C(1)–C(1^i)	1.509(7)	N(1)–C(1)–C(1^i)	110.9(5)
c) Hydrogen Bonds			
N(1)···Cl(1)	3.190(7) Å	N(1)–H(1)–Cl(1)	142°
H(1)···Cl(1)	2.18		

and angles with hydrogen bonds are given in Tables I and II.

While in (1) the cation and the anion are both centrosymmetric, in (2) only the platinum atom lies on a centre of symmetry. The Pt–Cl bond lengths range from 2.303 to 2.304 Å in (1) and from 2.304 to 2.316 Å in (2) and are comparable to those found in other tetrachloroplatinate(II) [3, 4] and hexachloroplatinate(IV) structures [5, 6].

The C–N bonds in the two halves of N–C–C–N system of H_2tmen^{2+} are equal either in (1) [exactly 1.506(8) Å for imposed symmetry restrictions] or in (2) [1.49(2) Å]. These distances are comparable to those found for the protonated end of diamine in $[PtCl_5(Hen)] \cdot H_2O$ and $[PtCl_3(Hen)]$ (Hen = monoprotonated ethylenediamine) [1.489(15) and 1.501(7) Å respectively] [7, 8]; in the latter compounds the C–N distances involving the coordinated nitrogens were significantly shorter [1.465(12) and 1.420(8) Å respectively].

The conformation of the N–C–C–N system in the H_2tmen^{2+} cations is *trans* in both compounds; while in (1) the dihedral angle is exactly 180° for symmetry restrictions, in (2) the angle is 166°.

The alternating $[PtCl_4]^{2-}$ and H_2tmen^{2+} ions in compound (1) are linked by hydrogen bonds involving the protonated nitrogens of the cations and *trans* halogens of the anions; in compound (2) the linkage of the $[PtCl_6]^{2-}$ with the H_2tmen^{2+} ions is realized through bifurcated hydrogen bonds that each protonated nitrogen of the cation forms with two chlorine atoms of an adjacent anion.

The packing of the chains is determined, in compound (1), by normal van der Waals contacts. In (2), beyond van der Waals contacts, a significant role is also played by C–H···Cl interactions involving a carbon atom of the ethylene moiety of the cation and a chlorine atom of a $[PtCl_6]^{2-}$ anion from a different chain [C(1)···Cl(2) = 3.494(19), H(12)···Cl(2) = 2.51 Å, C(1)–H(12)–Cl(2) = 161°].

As a result of the structural investigation it appears that the different symmetry of the cation in the two compounds results in significant differences in the i.r. spectra. Compound (1) has a centrosymmetric H_2tmen^{2+} moiety (symmetry group C_i) and a more simple spectrum (Fig. 3c); compound (2)

TABLE II. Bond Distances and Angles of (H_2tmen)[$PtCl_6$], (2).

a) In the two independent anions			
Pt(1)–Cl(1)	2.312(4) Å	Cl(1)–Pt(1)–Cl(2)	88.2(2)°
Pt(1)–Cl(2)	2.315(6)	Cl(1)–Pt(1)–Cl(3)	91.3(2)
Pt(1)–Cl(3)	2.309(5)	Cl(2)–Pt(1)–Cl(3)	90.6(2)
Pt(2)–Cl(4)	2.304(5)	Cl(4)–Pt(2)–Cl(5)	89.0(2)
Pt(2)–Cl(5)	2.316(5)	Cl(4)–Pt(2)–Cl(6)	91.5(2)
Pt(2)–Cl(6)	2.311(6)	Cl(5)–Pt(2)–Cl(6)	88.9(2)
b) In the cation			
N(1)–C(1)	1.49(2)	C(1)–N(1)–C(3)	108.8(14)
N(1)–C(3)	1.52(3)	C(1)–N(1)–C(4)	113.3(15)
N(1)–C(4)	1.51(3)	C(3)–N(1)–C(4)	108.7(15)
C(1)–C(2)	1.53(3)	N(1)–C(1)–C(2)	109.8(15)
C(2)–N(2)	1.49(2)	C(1)–C(2)–N(2)	112.1(15)
N(2)–C(5)	1.49(3)	C(2)–N(2)–C(5)	113.5(15)
N(2)–C(6)	1.53(3)	C(2)–N(2)–C(6)	113.6(15)
		C(5)–N(2)–C(6)	111.1(15)
c) Hydrogen bonds			
N(1)···Cl(5^{i})	3.484(17) Å	N(1)–H(1)–Cl(5^{i})	135°
H(1)···Cl(5^{i})	2.74		
N(1)···Cl(6^{ii})	3.368(16)	N(1)–H(1)–Cl(6^{ii})	138
H(1)···Cl(6^{ii})	2.60		
N(2)···Cl(2^{i})	3.264(18)	N(2)–H(2)–Cl(2^{i})	137
H(2)···Cl(2^{i})	2.39		
N(2)···Cl(3^{iii})	3.300(16)	N(2)–H(2)–Cl(3^{iii})	132
H(2)···Cl(3^{iii})	2.48		

Asymmetric units:

i $-\frac{1}{2}+x, \frac{1}{2}-y, z$
ii $-\frac{1}{2}-x, -\frac{1}{2}+y, 1-z$
iii $-\frac{1}{2}-x, \frac{1}{2}+y, -z$

has the H_2tmen^{2+} cation without symmetry elements (group C_1) and a more complex spectrum (Fig. 3a).

It was interesting to note that the i.r. spectrum of a KBr pellet of (2) changed with time (Fig. 3b), finally resembling that of (1) in the region below 1200 cm^{-1}. Big changes also occurred in the region above 2000 cm^{-1}, indicative of extensive rearrangements in hydrogen bonding, and in the Pt–Cl stretching region where a sharp band appeared at a different wavenumber. These modifications are in agreement with a relaxation of the crystal lattice and consequent rearrangement of the cations towards a centrosymmetric conformation and of the anions towards the situation of the other hexachloroplatinate(IV) salts [9].

It is also worth noting that, especially in the region below 1200 cm^{-1}, the final spectrum of (2) and that of (1) resemble that of (H_2tmen)Cl_2 (spectra **b**, **c**, and **d** of Fig. 3 respectively), pointing to a similar conformation of the cation in the three cases.

A detailed analysis of the i.r. spectra is beyond the scope of this work, but we emphasize the fact that an overall minor change in the conformation of a molecule (such as a 14° variation in the N–C–C–N dihedral angle in the diammonium cation) can cause relevant symmetry changes and big differences in the corresponding spectra. This must be kept in mind whenever the conformation of a molecule is deduced on the basis of spectroscopic data.

Experimental

Starting Materials

All chemicals were reagent-grade products and were used without further purification. [Pt(η^2-C_2H_4)Cl(tmen)](ClO_4) (tmen = N,N,N′,N′-tetramethylethylenediamine) was prepared from Zeise's salt and diamine according to the method of ref. 1.

Preparation of Compounds

Crystals of (H_2tmen)[$PtCl_4$], (1), and (H_2tmen)-[$PtCl_6$], (2), were obtained in the decomposition

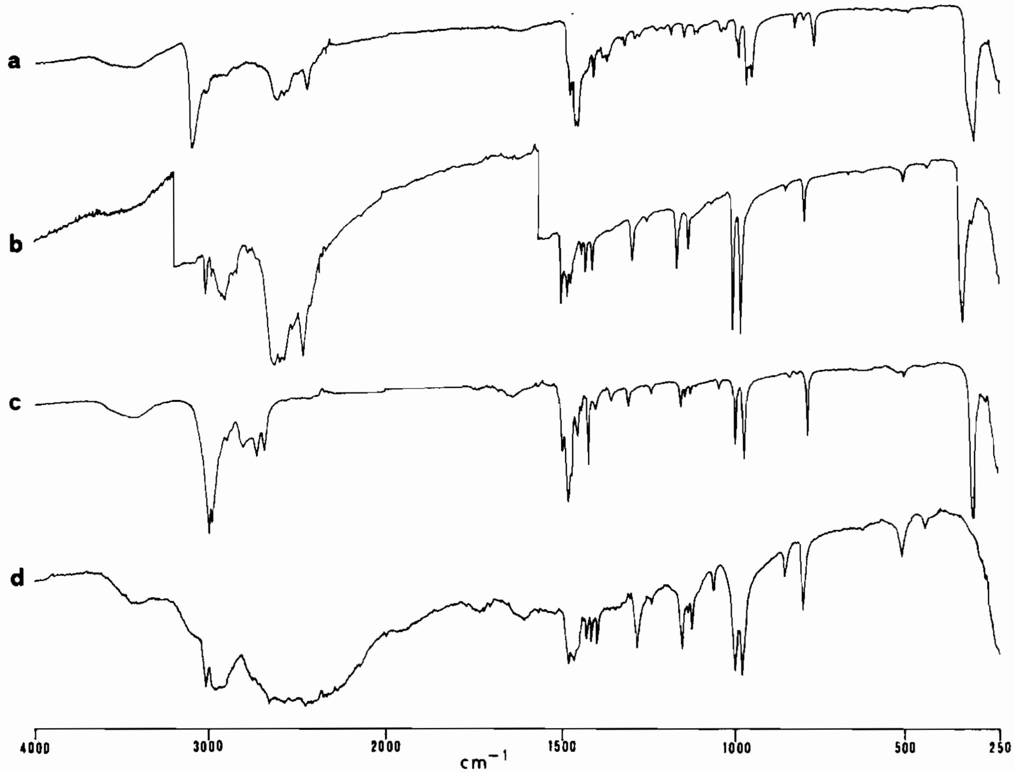

Fig. 3. Infrared spectra of $(H_2tmen)[PtCl_6]$, (2), right after the preparation of the KBr pellet, a, and two weeks later, b; $(H_2tmen)[PtCl_4]$, (1), c; and $(H_2tmen)Cl_2$, d.

of $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)](ClO_4)$ in concentrated hydrochloric acid. In a typical experiment 200 mg of $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)](ClO_4)$ were dissolved in 5 cm^3 of concentrated HCl (37% in water), and placed in a desiccator containing a beaker of concentrated sulphuric acid (96% in water) and KOH in pellets. Under vacuum the evaporation of the solvent took place in 3–4 d and $[PtCl_3(Htmen)]$ was the major product [10]; at atmospheric pressure however the evaporation was much slower (2–3 weeks) and crystals of H_2tmen^{2+} cations and $[PtCl_4]^{2-}$ or $[PtCl_6]^{2-}$ anions were formed [compounds (**1**) and (**2**) respectively]. The relative yield of the two salts was different from case to case; the reason of this is not clear and was not investigated. *Anal.*: Calcd. for $(C_6H_{18}N_2)[PtCl_4]$: C, 15.8; H, 4.0; Cl, 31.2; N, 6.2. Found: C, 15.5; H, 4.1; Cl, 31.0; N, 6.1. Calcd. for $(C_6H_{18}N_2)[PtCl_6]$: C, 13.7; H, 3.4; Cl, 40.4; N, 5.3. Found: C, 13.8; H, 3.4; Cl, 40.2; N, 5.3%.

Crystal Data

Compound (**1**): $(C_6H_{18}N_2)[PtCl_4]$, M = 455.12. Triclinic, a = 7.344(3), b =8.345(3), c = 6.216(2) Å, α = 84.53(3), β = 109.22(3), γ = 69.43(3)°, V = 327.0(2) Å^3 (by least-squares refinement from the θ values of 28 reflections accurately measured, λ = 0.71069 Å), space group $P\bar{1}$, Z = 1, D_x = 2.311 g cm^{-3}. A flattened yellow crystal, of approximate dimensions 0.09 × 0.27 × 0.28 mm, was used for the X-ray analysis, μ(Mo-Kα) = 116.29 cm^{-1} (max. and min. transmission factor values: 1.4678 and 0.7892) [11].

Compound (**2**), $(C_6H_{18}N_2)[PtCl_6]$, M = 526.03. Monoclinic, a = 14.409(4), b = 12.736(7), c = 8.601(3) Å, β = 99.58(3)°, V = 1556(1) Å^3 (by least-squares refinement from the θ values of 26 reflections accurately measured, λ = 0.71069 Å), space group $P2_1/a$, Z = 4, D_x = 2.245 g cm^{-3}. A yelllow-orange prismatic crystal, of approximate dimensions 0.34 × 0.44 × 0.64 mm, was used for the X-ray analysis, μ(Mo-Kα) = 101.27 cm^{-1} (max. and min. transmission factor values: 1.4364 and 0.7656) [11].

Data Collection and Processing

Siemens AED diffractometer, $\theta/2\theta$ mode, niobium-filtered Mo-Kα radiation for both compounds; all the reflections in the range of $3 < \theta < 27°$ for (**1**) and (**2**) were measured. Of 1302 and 3630 independent reflections 1302 and 1559, having $I > 2\sigma(I)$, were considered observed and used in the analyses for (**1**) and (**2**) respectively.

Structure Analyses and Refinements

Patterson and Fourier methods, full-matrix least-squares refinement with all non-hydrogen atoms

TABLE III. Fractional Atomic Coordinates ($\times 10^4$) with E.s.d.'s in Parentheses for the Non-hydrogen Atoms of (H_2tmen)[$PtCl_4$], (1).

Atom	*x/a*	*y/b*	*z/c*
Pt	0	0	0
Cl(1)	1250(3)	1276(2)	2959(3)
Cl(2)	1945(3)	−2765(2)	2488(3)
N(1)	3479(8)	2422(6)	−155(10)
C(1)	4390(9)	811(7)	−1002(10)
C(2)	2320(13)	3997(8)	−2179(14)
C(3)	5119(13)	2708(8)	1808(14)

TABLE IV. Fractional Atomic Coordinates ($\times 10^4$) with E.s.d.'s in Parentheses for the Non-hydrogen Atoms of (H_2tmen)[$PtCl_6$], (2).

Atom	*x/a*	*y/b*	*z/c*
Pt(1)	0	0	0
Pt(2)	0	5000	5000
Cl(1)	1612(3)	−43(5)	815(5)
Cl(2)	−59(4)	1408(4)	1684(7)
Cl(3)	−230(4)	−1156(4)	1969(6)
Cl(4)	1335(4)	5451(5)	6739(7)
Cl(5)	504(4)	3271(4)	5139(7)
Cl(6)	−814(4)	4667(5)	7047(6)
N(1)	−2265(11)	1101(13)	4360(17)
N(2)	−3290(11)	2411(13)	504(18)
C(1)	−2315(12)	1394(16)	2673(21)
C(2)	−3040(14)	2264(16)	2242(21)
C(3)	−1600(15)	178(17)	4725(27)
C(4)	−1929(17)	1987(19)	5488(28)
C(5)	−2467(17)	2684(18)	−269(25)
C(6)	−3849(16)	1493(19)	−342(27)

anisotropic in the last cycles, hydrogen clearly localized in the ΔF map, but not refined, were used for both compounds. The weighting scheme used in the last cycles was $w = 1/[\sigma^2(F_o) + 0.005F_o]$ for (1) while unit weights were used for (2). Final R and R' values were 0.027 and 0.035 for (1) and 0.039 and 0.047 for (2). Programs and computers used and sources of scattering factors are given in ref. 12. Final atomic coordinates for non-hydrogen atoms of (1) and (2) are given in Tables III and IV respectively.

Apparatus

The i.r. spectra were recorded as KBr pellets on a Perkin-Elmer 683 spectrophotometer.

Acknowledgements

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References

1 L. Maresca, G. Natile and G. Rizzardi, *Inorg. Chim. Acta, 38,* 53 (1980).

2 L. Maresca, G. Natile and G. Rizzardi, *Inorg. Chim. Acta, 38,* 137 (1980).

3 R. G. Purnell and D. J. Hodgson, *J. Am. Chem. Soc., 98,* 4759 (1979).

4 J. Britten and C. J. L. Lock, *Acta Cryst., B35,* 3065 (1979).

5 P. L'Haridon, J. Lang, J. Pastuszak and J. Dobrowolski, *Acta Cryst., B34,* 2436 (1978).

6 M. Biagini-Cingi, A. M. Manotti-Lanfredi, A. Tiripicchio, C. G. van Kralingen and J. Reedijk, *Inorg. Chim. Acta, 39,* 265 (1980).

7 F. P. Fanizzi, G. Natile, L. Maresca, A. M. Manotti-Lanfredi and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.,* (1984) in press.

8 L. Maresca, G. Natile, F. P. Fanizzi, A. M. Manotti-Lanfredi and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.,* submitted for publication.

9 D. M. Adams, 'Metal–Ligand and Related Vibrations', Edward Arnold, London, 1967.

10 G. Annibale, L. Maresca, L. Cattalini and G. Natile, *J. Chem. Soc., Dalton Trans.,* 1 (1982).

11 Absorption corrections following E. Walker and D. Stuard, *Acta Cryst., A39,* 158 (1983) and using the program ASSORB (written by F. Ugozzoli, University of Parma).

12 SHELX, System of Computing Programs (G. M. Sheldrick, University of Cambridge, 1976); atomic scattering factors, corrected for anomalous dispersion of Pt and Cl, from 'International Tables for X-Ray Crystallography', Vol. IV, Kynoch Press, Birmingham, 1974.