

Platinum(II) Complexes containing a Cationic Amine Ligand: Crystal Structure of [(2-Aminoethyl)ammonium]trichloroplatinum(II)†

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The complex [PtCl(dms)(en)]Cl (dms = dimethyl sulphide and en = 1,2-diaminoethane) reacts with concentrated hydrochloric acid displacing one end of en and substituting dms by Cl⁻, to form [PtCl₃(Hen)] (Hen = monoprotonated en). The structure of this compound has been solved by Patterson and Fourier methods and refined by full-matrix least squares to *R* = 0.030 for 1 326 observed reflections. The structure consists of zwitterionic molecules in which the co-ordination around the metal is square planar with three chlorine and one nitrogen atom from the monoprotonated en ligand. The conformation of the organic ligand is *gauche* with a hydrogen bond between the ammonium group and a *cis* chlorine atom; the same ligand in [PtCl₅(Hen)] had a perfectly *trans* conformation.

Complexes in which a polyfunctional ligand is only partially co-ordinated to a metal have attracted the attention of several investigators.¹⁻¹²

Powerful chelators such as 1,2-diaminoethane (en) usually fail to give complexes of this type except in some special cases, such as [PtCl₄(dms)(Hen)]Cl⁶ (dms = dimethyl sulphide, Hen = monoprotonated en), [PtCl₅(Hen)]⁶ and *cis*-[PtCl₂(L)(Hen)]⁺ [L = C₂H₄ or dimethyl sulphoxide (dms)],^{4,13} in which the metal centre is either six- or four-co-ordinate but having a strong *trans*-labilizing ligand.

We have now succeeded in preparing the complex [PtCl₃(Hen)] which has also been characterized by a single-crystal X-ray analysis.

Results and Discussion

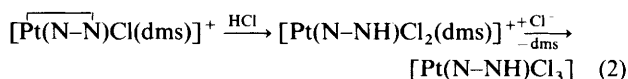
A general procedure for the preparation of metal complexes with partially co-ordinated polyamine ligands consists of the partial displacement of the polydentate ligand, fully co-ordinated to the metal, under the action of concentrated acid [equation (1)]. This route is particularly suitable for com-



plexes in which one end of the polydentate ligand is loosely bound to the metal because of the presence of a strong *trans*-labilizing ligand (L). Hence the complexes *cis*-[Pt(η²-C₂H₄)-Cl₂(Htmen)]^{+,4}, *cis*-[Pt(η²-C₂H₄)Cl₂(Htmpn)]^{+,4} and *cis*-[PtCl₂(dms)(Hen)]^{+,13} (tmen = *N,N,N',N'*-tetramethyl-1,2-diaminoethane and tmpn = *N,N,N',N'*-tetramethyl-1,3-diaminopropane) could be obtained from the corresponding *cis*-chelate species under the action of hydrochloric acid. In the first two cases the olefin could, in turn, be displaced by Cl⁻ giving rise to the formation of [PtCl₃(Htmen)] and [PtCl₃(Htmpn)]; in the third case an internal redox process led to the formation of

[PtCl₄(dms)(Hen)]⁺ which afterwards underwent dms displacement by Cl⁻ to give [PtCl₅(Hen)]⁶.

In order to avoid the redox process caused by dms and prepare [PtCl₃(Hen)] we performed an analogous reaction starting with [PtCl(dms)(en)]Cl. Dimethyl sulphide has a *trans*-labilizing power which is comparable to that of dms and could, in principle, be displaced by excess chloride. As expected the reaction [equation (2); N-N = en, N-NH = Hen] led to the



formation of [PtCl₃(Hen)] in *ca.* 30% yield. The major by-product was the neutral bis-sulphide complex [PtCl₂(dms)₂] formed by reaction of free dms [equation (2)] with an intermediate species [PtCl₂(dms)(Hen)]⁺, to give Hen⁺ displacement. This side reaction was less important in the case of six-co-ordinate [PtCl₄(dms)(Hen)]^{+,6} since ligand substitution in six-co-ordinate Pt^{IV} species is less sensitive to the entering-group effect.

The isolation of [PtCl₃(Hen)] in crystalline form allowed us to determine its molecular structure and compare it with that of [PtCl₅(Hen)], already reported.⁶ This gave the rather unique opportunity to see how the different oxidation state and co-ordination geometry of the metal could influence the conformation of the ligand and the bond distances within the complex. In fact it was surprising to see, in the i.r. spectra of [PtCl₃(Hen)] and [PtCl₅(Hen)], significant differences in the region of NH₂ and CH₂ rocking and skeletal stretching and bending which pointed to an overall different configuration of the organic moiety in the two complexes.¹⁴

X-Ray Structure of [PtCl₃(Hen)].—The crystal structure consists of zwitterionic [(2-aminoethyl)ammonium]trichloroplatinum(II) molecules in which the co-ordination of the metal is square planar with three chlorine atoms and a nitrogen atom, N(1), from the monoprotonated Hen ligand; deviations of Pt, Cl(1), Cl(2), Cl(3), and N(1) from the mean plane passing through them are 0.019(1), 0.012(2), -0.061(3), -0.047(3), and 0.152(8) Å respectively. A view of the complex with the atomic

† Supplementary data available (No. SUP 56148, 3 pp.): H-atom coordinates, anisotropic thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii-xix. Structure factors are available from the editorial office.

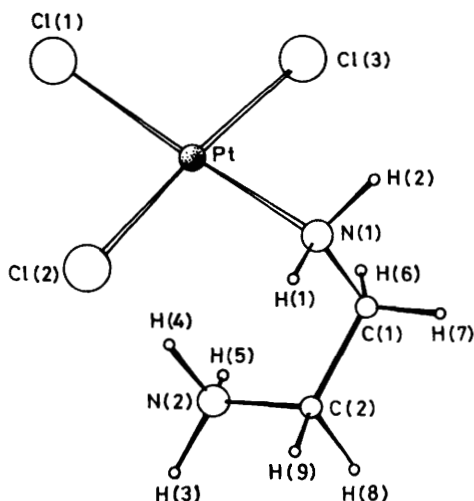


Figure. View of the complex $[\text{PtCl}_3(\text{Hen})]$ with the atomic numbering scheme

numbering scheme is given in the Figure, bond distances and angles are given in Table 1. The three Pt–Cl bonds are equal, ranging from 2.287 to 2.305 Å, and are almost identical to those of the six-co-ordinate Pt^{IV} complex $[\text{PtCl}_3(\text{Hen})]$ which fall in the range 2.297–2.302 Å.⁶ In addition the Pt–N(1) bonds are identical in the Pt^{II} [2.041(8) Å] and in the Pt^{IV} [2.050(4) Å] species. Therefore it appears that the combined effects of oxidation state and co-ordination number give the same results in terms of bond lengths in the two complexes. The C–N bonds in the Hen^+ ligand are slightly different [$\text{C}(1)\text{--N}(1) = 1.465(12)$, $\text{C}(2)\text{--N}(2) = 1.489(15)$ Å], the longer involving the protonated nitrogen; this trend resembles that observed in the Pt^{IV} complex.

The two complexes differ significantly in the conformation of the Hen^+ ligand, which is *gauche* in the four-co-ordinate Pt^{II} complex [dihedral angle $\text{N}(1)\text{--C}(1)\text{--C}(2)\text{--N}(2)$ of $73(1)^\circ$] and *trans* in the six-co-ordinate Pt^{IV} species (dihedral angle of exactly 180° for imposed symmetry restrictions). The *gauche* conformation appears to be determined by an intramolecular hydrogen bond involving the ammonium group and a chlorine atom in the *cis* position [$\text{N}(2)\cdots\text{Cl}(2) = 3.315(9)$, $\text{H}(4)\cdots\text{Cl}(2) = 2.27$ Å; $\text{N}(2)\text{--H}(4)\text{--Cl}(2) = 157^\circ$]. Although one obvious explanation for the different conformation of the ligand in the two complexes is that it arises from crystal packing, it is relevant, nevertheless, that such an interaction between a 'hanging' ammonium ion and a *cis* chlorine, which has been invoked in some occasions to explain the bigger substitutional lability of the *cis* ligands, can take place.¹⁵

The packing of the molecules in the crystal lattice appears to be determined by some $\text{N}\cdots\text{Cl}$ intermolecular hydrogen bonds [$\text{N}(1)\cdots\text{Cl}(1^{\text{I}}) = 3.476(8)$ Å, $\text{N}(1)\text{--H}(1)\text{--Cl}(1^{\text{I}}) = 150^\circ$; $\text{N}(2)\cdots\text{Cl}(1^{\text{II}}) = 3.362(9)$ Å, $\text{N}(2)\text{--H}(5)\text{--Cl}(1^{\text{II}}) = 156^\circ$; $\text{N}(1)\cdots\text{Cl}(1^{\text{III}}) = 3.443(9)$ Å, $\text{N}(1)\text{--H}(2)\text{--Cl}(1^{\text{III}}) = 146^\circ$].*

Complexes of this type could find useful application as anticancer agents. It is generally agreed that cytostatic activity results from substitution reactions involving displacement of anionic ligands from a metal complex.¹⁶ In *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$ the Cl^- leaving groups are *trans* to ammonia and therefore rather inert since ammonia is at the lower end of the *trans*-effect series. In $[\text{PtCl}_3(\text{Hen})]$ the reactivity of one Cl^- should be enhanced since it is *trans* to a chlorine atom which lies above NH_3 in the *trans*-effect series. Moreover in this complex the

Table 1. Bond distances (Å) and angles ($^\circ$)

Pt–Cl(1)	2.305(3)	Cl(1)–Pt–Cl(2)	91.6(1)
Pt–Cl(2)	2.305(3)	Cl(1)–Pt–Cl(3)	91.9(1)
Pt–Cl(3)	2.287(3)	Cl(2)–Pt–N(1)	89.7(2)
Pt–N(1)	2.041(8)	Cl(3)–Pt–N(1)	87.0(2)
C(1)–N(1)	1.465(12)	Pt–N(1)–C(1)	118.1(6)
C(1)–C(2)	1.498(14)	N(1)–C(1)–C(2)	114.0(8)
C(2)–N(2)	1.489(15)	C(1)–C(2)–N(2)	113.3(8)

Table 2. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses for the non-hydrogen atoms

Atom	X/a	Y/b	Z/c
Pt	2 831(1)	2 662(1)	2 161(1)
Cl(1)	2 321(3)	4 756(2)	2 951(2)
Cl(2)	5 037(3)	2 207(3)	4 136(3)
Cl(3)	548(3)	2 927(2)	215(2)
N(1)	3 348(9)	871(7)	1 372(8)
N(2)	2 011(11)	–195(9)	3 745(9)
C(1)	2 189(12)	–281(9)	1 378(10)
C(2)	2 577(14)	–982(10)	2 719(9)

neutrality, and hence the ability to cross the cell membrane, should be preserved and, at any stage, by a ring closing process the adduct formed with biological substrates would become similar to that given by $[\text{PtCl}_2(\text{en})]$.

Experimental

Commercial reagent-grade chemicals were used without further purification. *trans*- $[\text{PtCl}_2(\text{dms})_2]$ was prepared from K_2PtCl_4 and dms by the method of Kauffman and Cowan.¹⁷ $[\text{PtCl}(\text{dms})(\text{en})]\text{Cl}$ was prepared by reaction of the former complex with en.¹⁸ I.r. spectra were recorded for KBr pellets on a Perkin-Elmer 683 spectrophotometer.

[(2-Aminoethyl)ammonium]trichloroplatinum(II).— $[\text{PtCl}(\text{dms})(\text{en})]\text{Cl}$ (0.2 g) was dissolved in concentrated HCl (37%, 5 cm^3) and the resulting yellow solution filtered and placed in a desiccator containing concentrated sulphuric acid and pellets of potassium hydroxide. At atmospheric pressure the solution concentrated slowly and afforded yellow crystals of the desired product in ca. 30% yield. These were collected, washed with ethanol, and air dried (Found: C, 6.50; H, 2.60; Cl, 29.0, N, 7.60. Calc. for $\text{C}_2\text{H}_9\text{Cl}_3\text{N}_2\text{Pt}$: C, 6.60; H, 2.50; Cl, 29.3; N, 7.70%).

Crystal Data.— $\text{C}_2\text{H}_9\text{Cl}_3\text{N}_2\text{Pt}$, $M = 362.55$, monoclinic, $a = 7.934(6)$, $b = 9.884(8)$, $c = 10.345(8)$ Å, $\beta = 107.31(4)^\circ$, $U = 775(1)$ Å³ (by least-squares refinement from the θ values of 23 reflections accurately measured, $\lambda = 0.71069$ Å), space group $P2_1/c$, $Z = 4$, $D_c = 3.109$ g cm^{-3} , $F(000) = 656$. A yellow irregularly shaped crystal of approximate dimensions $0.19 \times 0.36 \times 0.48$ mm was used for the X-ray analysis, $\mu(\text{Mo-K}\alpha) = 192.64$ cm^{-1} .

Data Collection and Processing.—Siemens AED diffractometer, $\theta/2\theta$ mode, niobium-filtered $\text{Mo-K}\alpha$ radiation; 1 862 reflections measured ($3 \leq \theta \leq 27^\circ$, $+h, k, l$), 1 677 unique [merging $R = 0.018$ after absorption correction (transmission factors = max. 1.2252, min. 0.8067)], $\dagger 1\ 326$ with $I \geq 2\sigma(I)$.

* The roman numeral superscripts refer to the following transformations: I $I - x, y - \frac{1}{2}, \frac{1}{2} - z$; II $-x, y - \frac{1}{2}, \frac{1}{2} - z$; III $x, \frac{1}{2} - y, z - \frac{1}{2}$.

\dagger Absorption correction following E. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158 and using the program ASSORB, written by F. Ugozzoli, University of Parma.

Structure Analysis and Refinement.—Patterson and Fourier methods, full-matrix least-squares refinement with all non-hydrogen atoms anisotropic in the last cycles, hydrogens clearly localized in the ΔF map, but not refined. Weighting scheme used in the last cycles: $w = 0.4145/[\sigma^2(F_o) + 0.005F_o]$, with $\sigma(F_o)$ from counting statistics. Final R and R' values are 0.030 and 0.043 respectively. Calculations were performed on the CYBER 76 computer (Centro di Calcolo Elettronico dell'Italia Nord-Orientale, Bologna) using SHELX.¹⁹ Atomic scattering factors, corrected for anomalous dispersion of Pt and Cl, were from ref. 20. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 2.

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References

- 1 D. Berglund and D. W. Meek, *Inorg. Chem.*, 1969, **8**, 2602; *J. Am. Chem. Soc.*, 1968, **90**, 518.
- 2 L. M. Vallarino, J. V. Quagliano, and V. L. Goedken, *Inorg. Chem.*, 1973, **12**, 102 and refs. therein.
- 3 K. P. Beaumont and C. A. McAuliffe, *Inorg. Chim. Acta*, 1975, **14**, L9 and refs. therein.
- 4 L. Maresca, G. Natile, and G. Rizzardi, *Inorg. Chim. Acta*, 1980, **38**, 137.
- 5 F. Galsbøl and B. S. Rasmussen, *Acta Chem. Scand., Ser. A*, 1982, **36**, 439; Proceedings of the 20th International Conference on Coordination Chemistry, Budapest, 1982, p. 666.
- 6 F. P. Fanizzi, G. Natile, L. Maresca, A. M. Manotti-Lanfredi, and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1984, 1467.
- 7 M. G. Carter and J. K. Beattie, *Inorg. Chem.*, 1970, **9**, 1233.
- 8 G. Natile, G. Albertin, E. Bordignon, and A. A. Orio, *J. Chem. Soc., Dalton Trans.*, 1976, 626.
- 9 R. Romeo, S. Lanza, D. Minniti, and M. L. Tobe, *Inorg. Chem.*, 1978, **9**, 2436 and refs. therein.
- 10 G. Albertin, E. Bordignon, A. A. Orio, B. Pavoni, and H. B. Gray, *Inorg. Chem.*, 1979, **18**, 1451.
- 11 G. Annibale, L. Maresca, L. Cattalini, and G. Natile, *J. Chem. Soc., Dalton Trans.*, 1982, 1.
- 12 D. B. Brown, A. R. Khokhar, M. P. Hacker, L. Lokys, J. H. Burchenal, R. A. Newman, J. J. McCormack, and D. Frost, *J. Med. Chem.*, 1982, **25**, 952.
- 13 R. Romeo, S. Lanza, and M. L. Tobe, *Inorg. Chem.*, 1977, **16**, 785.
- 14 D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 1959, 791, 3089.
- 15 F. Basolo and G. Pearson, 'Mechanism of Inorganic Reactions,' 2nd edn., John Wiley, New York, 1967.
- 16 B. Rosenberg, *Cancer Treat. Rep.*, 1979, **63**, 1433.
- 17 J. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, 1960, **6**, 211.
- 18 M. Bonivento, L. Canovese, L. Cattalini, G. Marangoni, G. Michelon, and M. L. Tobe, *Inorg. Chem.*, 1981, **20**, 1493.
- 19 G. M. Sheldrick, SHELX, System of Computing Programs, University of Cambridge, 1976.
- 20 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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