Inorganica Chimica Acta, 66 (1982) 79–84

Preparation, Characterisation and Crystal Structure of Dichloro Tetrakis-(1-methylimidazoline-2(3H)-thione) Platinum(II) Dihyderate

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Received October 15, 1981

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*The preparation of a complex of methylimidazoline-2(3H)-thione (*MImt*) with platinum chloride is described. The stoichiometry, Pt(*MImt*)$_4$Cl$_2$·2H$_2$O, has been established by chemical, crystallographic and thermogravimetric analysis. The compound has been characterised by means of infrared spectroscopy, electronic spectroscopy and ^{13}C-NMR spectroscopy. The single-crystal X-ray study has confirmed the presence of uncoordinated H_2O molecules, ionic chloride ions and square-planar PtS_4^{2+} entities linked by H-bonds.*

Introduction

The coordination chemistry of heterocyclic molecules containing the thioamide (–NH–C(S)–NH–) group with platinum and palladium salts has been widely investigated [1–11], a major stimulus for this research being the discovery of anti-tumour activity among the Pt(II) and Pd(IV) complexes of 6-mercaptopurine [1, 2]. In view of the established anti-tumour activity among *cis*-dichloro bis-ammine Pt(II) complexes [12] interest has centred on the identification of the donor atom(s) among the potentially ambidentate S,N-containing heterocyclic molecules studied. In this respect infrared spectroscopy, though most frequently used is not regarded as diagnostically definitive [11], and consequently, ^{13}C NMR spectroscopy as well as crystal structure analysis are currently regarded as the more reliable means of identifying the donor atom(s) in these important complexes [11, 13].

Of particular relevance, in view of our sustained interest in the complexes of 1-methylimidazoline-2(3H)-thione (*MImt*), is the investigation into the carcinostatic activity of Pt(*MImt*)$_2$Cl$_2$ and the assertion that the complex is N-bonded [9, 10].

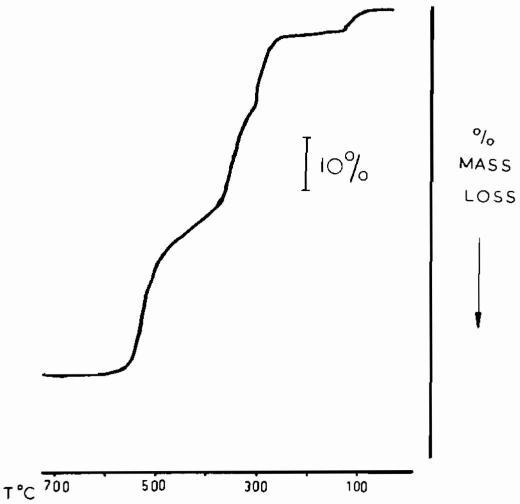

Fig. 1. TG curve in air.

Although the ligand is potentially ambidentate previous work has shown it to be S-donating rather than N-donating with M(II) ions (M(II) = Co, Ni, Zn and Cd) [14–18].

Consequently we have prepared, characterised and performed the crystal structure analysis of Pt(*MImt*)$_4$Cl$_2$·2H$_2$O as a further contribution to this series of complexes.

Results

Preparation, analysis and characterisation

Platinum chloride (1 mmol) and *MImt* (4.0 mmol) were refluxed in ethanol (25 ml) for four hours. Yellow–orange crystals formed upon overnight refrigeration; these were removed, washed with a little cold ethanol and vacuum dried at room

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temperature. Chemical analysis gave: C, 25.6; H, 3.77, N, 14.6. Pt(*MImt*)$_4$Cl$_2$·2H$_2$O requires: C, 25.3; H, 3.64, N, 14.8%.

Thermogravimetric analysis (Fig. 1) gave an initial weight loss of 4.8% in the temperature range 50–120 °C which is consistent with the presence of two water molecules in the complex. A total weight loss of 74.0% is consistent with overall reduction to the metal.

$$\mathrm{Pt}(MImt)_4\cdot\mathrm{Cl_2\,2H_2O(s)} = \mathrm{Pt(s)} + 4MImt\mathrm{(g)} + \\ + \mathrm{Cl_2(g)} + \mathrm{2H_2O(g)}$$

and confirms the stoichiometry of the complex.

The infrared spectrum has bands attributable to the water molecules at 3490, 3420 cm^{-1} (ν_3, ν_1); 1610 cm^{-1} (ν_2) and also a lattice mode, ρ_w, at 550 cm^{-1} [19].

The effect of coordination upon the 'thioamide' bands [20, 21] is largely restricted to the thioamide IV band. In the free ligand this is a composite band consisting of a peak at 740 cm^{-1} and a broad, less intense component 770 cm^{-1}. In the complex these bands are replaced by two sharply defined bands at 730 and 770 cm^{-1}. In previous instances of coordination by *MImt* this band was frequently reduced to a single absorption in the region of 730 cm^{-1} [14, 21]. In the low-frequency region a ν(Pt–S) absorption occurs at 340 cm^{-1}. These observations suggest the ligand is S-donating in this complex. The absence of ν(Pt–Cl) absorption suggests ionic, rather than coordinated, chloride in the complex.

Several bands were observed in the solid state diffuse reflectance electronic spectrum of the complex. An intense charge-transfer band was centred at 25,000 cm^{-1}. The first major d–d band, at 12,500 cm^{-1} is assigned to the $^1B_{1g} \leftarrow {}^1A_{1g}$ transition; the second band at 8696 cm^{-1} is assigned to the $^1A_{2g} \leftarrow {}^1A_{1g}$ transition The remaining absorption, at 6750 cm^{-1}, is weaker than the others and is assigned to a spin-forbidden triplet ← singlet absorption whose intensity has been increased due to spin-orbit coupling [22]. The value of Δ_1, calculated by standard methods [23, 24], is 14,600 cm^{-1} and is lower than those reported for other PtS$_4$ systems which are for S,S-chelated ligands [24]. The complex is diamagnetic at room temperature.

The ^{13}C NMR spectrum of the free ligand consists of a methyl-C signal at 33.6 ppm, two vinyl-C signals at 119.3 and 113.9 ppm and a thioketonic-C signal at 160.8 ppm [25, 26]. The effect of S-coordination of this spectrum usually causes a high-field shift of the thioketonic signal of the order of 2.0 ppm [26]. In the ^{13}C-NMR spectrum of Pt(*MImt*)$_4$Cl$_2$·2H$_2$O the signals due to the methyl and vinyl-C atoms were not shifted; the signal due to the thioketonic C-atom was indistinct due to its relatively low intensity and the poor solubility of the complex in DMSO-d$_6$, but the expected shift was indicated.

The electrolytic conductivity of a 10^{-3} *M* solution of the complex in nitromethane produced Λ_m = 35 ohm^{-1} cm^2 mol^{-1}.

Crystal and Molecular Structure of Pt(MImt)$_4$Cl$_2$·2H$_2$O

Crystal Data

Amber, plate-like, crystals of the complex were obtained by recrystallisation from anhydrous ethanol. Cell constants were obtained from Weissenberg and precession photographs. Subsequent analysis identified the space group as $P\bar{1}$. PtC$_{16}$H$_{24}$N$_8$S$_4^{2+}$ - 2Cl$^-$2H$_2$O; *Mr* 714.27; a = 8.817(4); b = 9.897(5), c = 8.752(5) Å; α = 92.49(10)°; β = 106.28(12)°; γ = 66.00(10)°; U = 673.20 Å; D_m = 3.54 g·cm^{-3}; D_c = 3.50; Z = 1 *F(000)* = 362, μ(MoKα) = 5.50 mm^{-1}; Triclinic.

Data collection and reduction

A crystal of dimensions 0.76 × 0.48 × 0.16 mm was mounted with the *a*-axis coincident with the rotation (w) axis of a Stoe Stadi-2 two-circle diffractometer. Monochromated Mo-K$_\alpha$ (λ = 0.7107 Å) radiation and the background-*w*scan-background technique were used to collect 3728 unique reflections of which 2913 had $I > 2.5\ \sigma(I)$ and were considered observed. Data were corrected for Lorentz and polarisation but not for absorption effects.

Structure determination and refinement

The Pt(II) ions occupy centres of symmetry in the unit cell and have their coordinates constrained. The coordinates of the Cl$^-$ ion and the S-atoms were located by Patterson methods. The remaining atoms were obtained by difference-Fourier methods and their coordinates were refined by full-matrix least-squares calculations with anisotropic temperature factors for the non-H atoms. The O-atom of the unique water molecule was well defined and was anisotropically refined but the associated H-atoms could not be satisfactorily located. Methyl H-atoms were refined as rigid groups (C–H = 1.08 Å) with one overall isotropic temperature factor (final U = 0.200(118) Å^2). Positional parameters for the H-atoms attached to the ligands were included in the calculations and common isotropic temperature factors were applied (final U = 0.0727(4) Å^2). Scattering factors for all atoms were calculated using an analytical approximation (International Tables for X-ray crystallography, 1974) [27].

The function minimised was $\Sigma w(\Delta F)^2$ with w = 0.7758/[σ^2](F) + 0.023108(F)^2]. Final R = 0.0958 and R_w = 0.0891.

All calculations were performed on the NUMAC IBM 370/165 computer at the SERC computing centre,

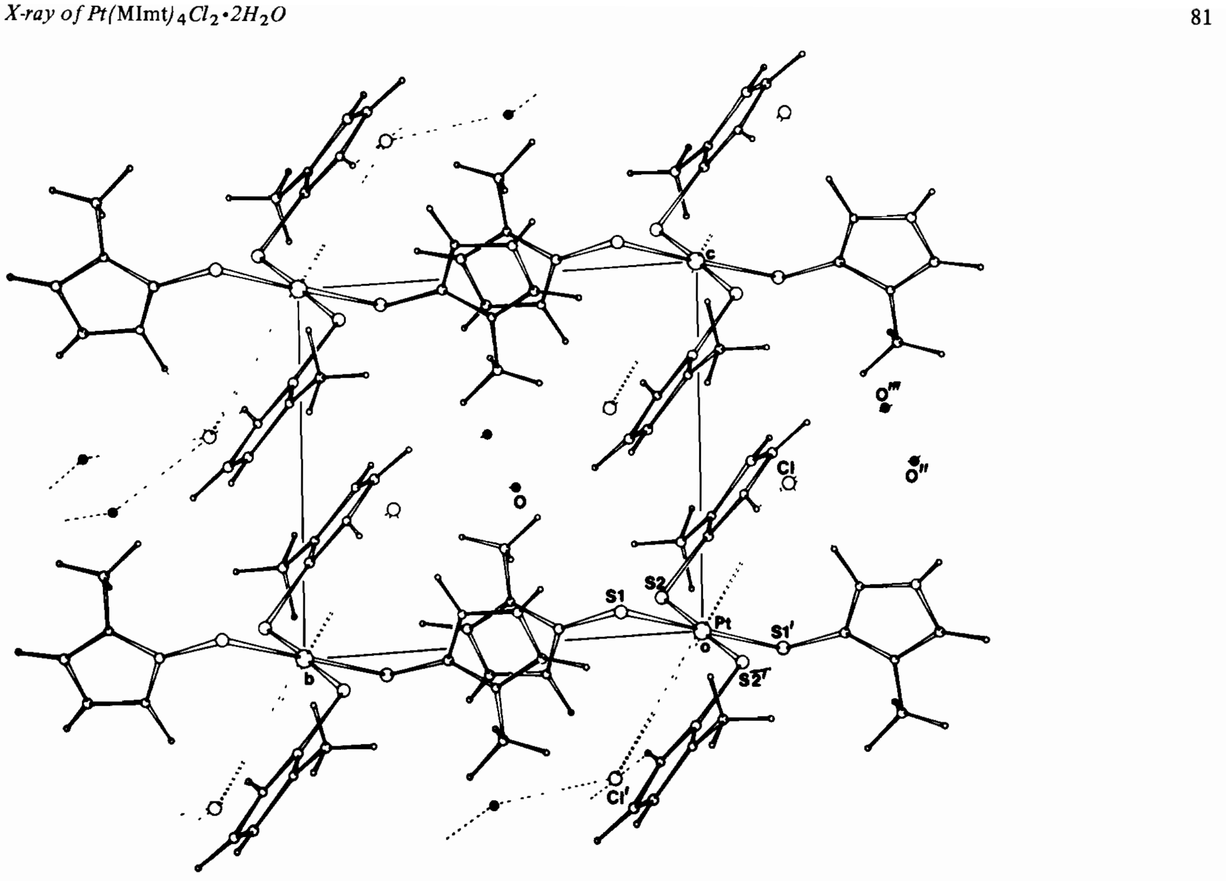

Fig. 2. Unit cell contents viewed down a^*.

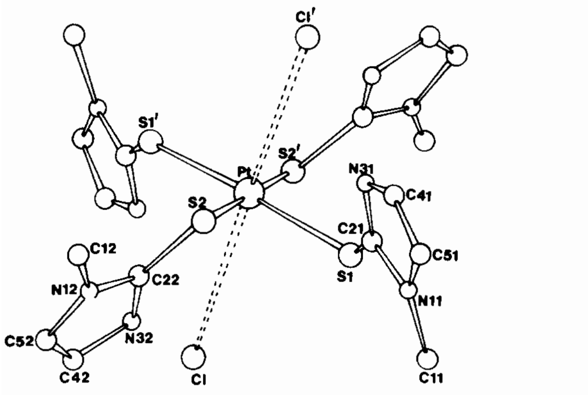

Fig. 3. Perspective diagram of the complex with atomic labelling.

Daresbury, SHELX [35] and related programs were used in the analysis. [Anisotropic temperature factors, observed and calculated structure factors have been deposited with the Editor].

Description of the Structure

The crystal structure of Pt(*MImt*)$_4$Cl$_2$·2H$_2$O consists of square-planar complexed cations, ionic chlorides and water molecules which are held together by an extensive network of H-bonds. Final atomic parameters are in Table I, bond lengths and angles are in Table II, equations of mean planes are in Table III.

The PtS$_4^{2+}$ entity is essentially square planar with the S(1)–Pt–S(2) and S(1)–Pt–S(2') angles close to 90° at 92.7(2)° and 87.3(2)° respectively. The methyl groups of the ligand have an '*anti*' arrangement with respect to the PtS$_4$ plane.

The two unique Pt–S distances (Pt–S(1), 2.339(4) Å; Pt–S(2), 2.307(4) Å) are significantly different from one another, both of these distances are significantly shorter than the sum of the covalent radii (2.36 ± 0.01 Å [28]). The bond length variations are accompanied by differences in the corresponding Pt–S(1)–C(2A) angles of 108.8(6)° and 104.1(5)° respectively.

The geometry of the two unique ligands is essentially the same. No significant differences are observed between the thioamide C–N and the ethylenic C–N distances; the C–S distances correspond to about 40% SCF π-bond order [29].

The ligand molecule 'twists' around the Pt–S(1)–C(2A) bond. The resulting dihedral angles (35.2 and 22.4°) are significantly different from one another

TABLE I. Final Fractional Coordinates ($\times 10^4$) (e.s.d.s are in parentheses).

	x	y	z
Pt	0	0	0
S1	0701(6)	2040(3)	0638(5)
S2	–2396(5)	0978(3)	0921(4)
N11	–1374(21)	4820(11)	1129(16)
N31	–2660(20)	3972(12)	–0905(16)
N12	–3034(18)	–0309(11)	3156(13)
N32	–0313(14)	–1065(11)	3515(13)
C11	–0028(30)	4937(17)	2556(21)
C21	–1175(22)	3607(11)	0292(16)
C41	–3753(19)	5378(14)	–0813(20)
C51	–3016(25)	5925(13)	0440(22)
C12	–4920(26)	0506(18)	2514(23)
C22	–1888(17)	–0182(10)	2553(13)
C42	–0475(19)	–1755(14)	4728(18)
C52	–2182(20)	–1273(16)	4519(21)
Cl	3696(7)	–2252(4)	3875(6)
O	–6993(27)	4696(23)	4317(30)
H111	–0505	6021	2986
H112	1134	4753	2240
H113	0253	4111	3476
H121	–5554	0183	3231
H122	–5341	0251	1301
H123	–5246	1679	2548
H31	–2731	3315	–1843
H41	–4888	5936	–1768
H51	–3220	6869	1010
H32	0780	–0982	3404
H42	0498	–2754	5306
H52	–2993	–1419	5050

TABLE II. Bond Distances (Å) and Angles (°) (with e.s.d.s in parentheses).

Symmetry code, superscript, none x, y, z; (′) = $-x, -y, -z$; (″) $-x, -1+y, z$, (‴) $1.0-x, -y, 1.0-z$.

(a) The coordination sphere

Bond	A	Angle	(°)
Pt–S1	2.339(4)	S1–Pt–S2	92.7(2)
Pt–S2	2.307(4)	S1–Pt–S2′	87.3(2)
S1···S2	3.362(7)	Pt–S1–C21	108 8(6)
S1···S2′	3 205(5)	Pt–S2–C22	104 1(5)
Pt···Cl	3.981(4)	Cl–Pt–S(1)	92.5(6)
		Cl–Pt–S(2)	85.4(5)

(b) Geometry of the ligand molecules

A	ligand 1	ligand 2
C2(A)–N3(A)	1.355(20)	1.360(14) (Å)
N3(A)–C4(A)	1.356(16)	1.359(22)
C4(A)–C5(A)	1.324(23)	1.345(24)
C5(A)–N1(A)	1.403(19)	1.390(19)
N1(A)–C2(A)	1.356(17)	1.313(23)
N1(A)–C1(A)	1 502(25)	1.478(23)
S(A)–C2(A)	1 720(13)	1.717(12)
C4(A)–H4(A)	1.07	1.05
C5(A)–H5(A)	1.02	1.01
N3(A)–H1(A)	1.03	1.03
C2A–N3A–C4A	109.9(12)	110.8(13) (°)
N3A–C4A–C5A	108.9(12)	105.5(12)
C4A–C5A–N1A	106.4(11)	108.1(17)
C5A–N1A–C2A	109.0(13)	109.1(13)
N1A–C2A–N3A	105.7(11)	106.5(11)
SA–C2A–N3A	129.4(10)	129.4(13)
C5A–N1A–C1A	126.3(12)	126.2(17)
ClA–N1A–SA	124.6(12)	124.1(9)
C2A–N3A–H3A	120.3 1	119.9
H3A–N3A–C4A	128.3	128.0
N3A–C4A–H4A	121.0	123.2
H4A–C4A–C5A	129.1	127.8
C4A–C5A–H5A	141.3	138.6
H5A–C5A–N1A	112.1	113.2

(c) Hydrogen bonded contacts

Bond	Å	Angle	(°)
Cl–O″	3.027	O″–Cl–O‴	92.1
Cl–O‴	3 084	O″–Cl–N31′	103 8
Cl–N31′	3 169	N32–Cl–N31′	92.9
Cl–H31′	2.171	N32–Cl–O‴	125.4
Cl–N32	3.176		
Cl–H32	2.291		

TABLE III. Equations of the Mean Planes Referred to Orthogonal Axes with Distance (Å) of Relevant Atoms from the Planes in Square Brackets

Plane A

Pt, S1, C21
$-3.0277X - 1.6826Y + 8\ 7098Z = 0\ 0$

Plane B

Pt, S2, C22
$4.6654X + 7.7603Y + 3\ 9250Z = 0.0$

Plane C

Ligand 1
$6.5519X + 5\ 8435Y - 6.5524Z - 1\ 1959 = 0.0$
[S1, 0.037, C21, –0 046, N11, –0.003, C51, 0 014, C41, 0.026; N31, –0.022; C11, –0.006]

(continued on facing page)

TABLE III. *(continued)*

Plane D

Ligand 2
$1.5937X + 7.9253Y + 4.9346Z - 0.8410 = 0.0$
[S2, 0.006, C22, −0.018; N12, −0.014; C52, −0.014, C42, 0.020; N32, 0.004; C12, 0.017]

Plane E

Pt, S1, S2, S1, S2
$1.5627X - 2.7140Y + 6.9664Z = 0.0$

Dihedral Angles

Planes	Angles (°)
A/C	35.15
B/D	22.35
C/E	58.27
D/E	75.27
C/D	87.69

(e.s.d.s are in the range 1.0–2.0°)

and much smaller than the corresponding angles in tetrahedral Co(II) and Zn(II) complexes [15, 16, 18]. The dihedral angles resulting from the 'tilt' of the ligands about the PtS$_4$ plane are 58.3° and 75.3° (Table III).

The chloride ion occupies an approximately axial position, relative to the PtS$_4$ plane, (Cl–Pt–S(1), S(2) = 92.5, 83.4°), and shows a long metal–halogen distance, 3.981 Å. Each chloride ion is involved in four H-bonds to two water H-atoms and to two ligand imido H-atoms, thus the water molecules effectively bridge the chloride ions by means of H-bonds; angles around the chloride ion range from 92.1–125.4°.

Discussion

MImt forms two complexes with Pt(II). Pt(*MImt*)$_2$Cl$_2$ [9, 10] and Pt(*MImt*)$_4$Cl$_2$·2H$_2$O. The reported existence of Pt–N contacts in the former is somewhat surprising in view of the *soft* character of Pt(II) and the established S-donor behaviour of the ligand [14–18].

The spectroscopic and magnetic properties of Pt(*MImt*)$_4$Cl$_2$·2H$_2$O are consistent with a square-planar PtS$_4$ entity and uncoordinated chloride ions. The non-electrolytic behaviour of the complex in nitromethane is unexpected and suggests that an equilibrium of the type:

$$PtL_4Cl_2 \rightleftarrows PtL_2Cl_2 + 2L$$

exists in this solvent. Such equilibria have been previously reported for Co(II) complexes of *MImt* [18]. In addition, this equilibrium rationalizes the existence of the two Pt(II) complexes.

The Pt–S distances in the Pt(*MImt*)$_4^{2+}$ ion occur in the range of previously reported values for monodentate S-donors [30–33]. Similar differences between Pt–S distances, in the same complex, have also been reported for thiourea [32] and ethylenethiourea [30] Pt(II) complexes. Such variations have been variously attributed to the (a) differences in the character of the Pt–S bonds (b) H-bonding and (c) crystal packing effects.

The variation in the Pt–S distances, as well as the 'twisting' and 'tilting' of the ligands, in this structure, are probably a consequence of inter-related effects which seek to maximise the π-character of the Pt–S bonds and optimise the orientation of the ligands relative to the water molecules and the chloride ions for effective H-bonding.

The major factors contributing to these effects are the *trans*-influencing character of the S-donor atoms [34], the competition for the d-orbitals of sulphur between the Pt(II) species and the C2A ligand atoms and also the steric repulsion arising from the relatively short S·····S contacts within the PtS$_4^{2+}$ entities.

Experimental

Starting Materials

The ligand was used as supplied by the Aldrich Chemical Company Limited, PtCl$_2$ was supplied by ICI Limited.

Physical Methods

Chemical analysis for C, H, N was performed at the ICI Corporate Laboratory, Runcorn, Cheshire. The remaining physical techniques have all been described elsewhere [14, 18].

Acknowledgement

We are grateful to ICI Limited for the provision of PtCl$_2$, the chemical analysis and the ^{13}C NMR data, and to SERC for an equipment grant as well as computing facilities to I.W.N.

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