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

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The preparation of a complex of 1-methylimidazoline-2(3H)-thione (MImt) with palladium dichloride in acid solution is described. The stoichiometry, $Pd(MImt)_4Cl_2 \cdot 2H_2O$ has been established by chemical and thermal analysis. The compound has been characterised by means of infrared spectroscopy and a single crystal X-ray study. The latter has confirmed the presence of uncoordinated water molecules, ionic chloride ions and square-planar $[PdS_4]^{2+}$ units bridged by H-bonds.

Introduction

Interactions between palladium(II) and 1-methylimidazoline-2(3H)thione (MImt) have been previously reported [1, 2]. The complexes have the formula $Pd(MImt)_2Cl_2$ and possess nitrogen donating MImt molecules [1, 2]; in one instance both *cis* and *trans* isomers are described [2]. The influence of pH on the coordinating behaviour of MImt has also been described [2]. The molecule is reputedly nitrogen donating between pH 3.5–6.0 and both sulphur and nitrogen donating between pH 6–10 [2].

We believe the reactivity of MImt to be more varied than this. Although the molecule will be completely protonated in highly acid media (pH 0–3) (Fig. 1(a)) it is also potentially ambidentate. Coordination may occur through either sulphur or nitrogen together with the simultaneous ejection of a proton from the imidazolium-thione cation. In alkaline media, (pH 7<), the thiolate anion (Fig. 1(d)) may use either or both sulphur and nitrogen as well as a choice of bridging, chelating or monodentate coordination. At intermediate pH levels either the thiol (Fig. 1(b)) or thione (Fig. 1(c)) form is possible and the molecule will be monodentate and either nitrogen or sulphur donating.

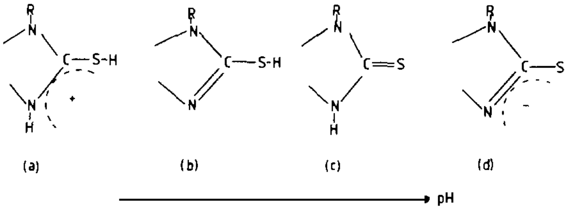

Fig. 1. Molecular forms of the ligand in solution as a function of pH.

An X-ray study has shown that the thione form is the dominant tautomer in the solid [3]. Proton magnetic resonance has demonstrated that the thione form is also retained in solution [3]. Another study has demonstrated that both thiol and thione forms are present in solution however [2]. Structural studies with a variety of metals have also demonstrated that the monodentate sulphur donating thione form is retained in complexes obtained from neutral media [4–9]. The thiolate anion has been shown to be bridging in a polynuclear complex which contains both +1 and +2 copper [10] and has also been complexed with platinum(II) and palladium(II) [2].

As a further contribution to this versatile system we now report the behaviour of MImt with palladium dichloride in acid media.

Experimental

Starting Materials

The ligand was used as supplied by the Aldrich Chemical Company Limited, $PdCl_2$ was supplied by ICI.

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0020-1693/83/$3.00

TABLE I. Crystallographic Data.

Compound	$PdC_{16}H_{24}N_8S_4Cl_2 \cdot 2H_2O$
M_r	669.5
a, Å	8.795(1)
b, Å	8.866(2)
c, Å	9.826(1)
α, deg	66.75(2)
β, deg	93.00(2)
γ, deg	108.02(2)
U, Å^3	667.3
Z	1
D_c g cm^{-3}	1.67
Space group	$P\bar{1}$
Radiation Å	MoKα, 0.71073
F(000)	340
μ, cm^{-1}	11.30
Diffractometer	CAD-4
2θ range, deg	5 to 52.0
Total data	3876
$F_o > 3\sigma(F_o)$	3576
R	0.069
R_w	0.083
w	$1.0000[(\sigma^2)F_o + 0.009853\ F_o^2]^{-1}$

TABLE II. Final Fractional Coordinates ($\times 10^4$) with E.s.d. s in Parentheses for Non-H Atoms and B Equivalent Values [20].

	x	y	z	B_{eq}(Å^2)
(a) *Non-H atoms*				
Pd	0	0	0	1.5(1)
Cl	6131(3)	−3669(2)	2229(2)	3.3(1)
O	4329(12)	−3048(11)	4653(9)	5.3(1)
S21	960(2)	−2363(2)	1023(1)	2.4(1)
C21	2559(6)	−1902(6)	−144(5)	1.9(2)
N11	3141(5)	−3053(5)	−281(4)	2.1(2)
C11	2460(7)	−4927(7)	521(7)	2.7(2)
N31	3541(6)	−325(5)	−1047(5)	2.2(2)
C41	4723(7)	−544(9)	−1756(7)	2.7(2)
C51	4481(7)	−2241(8)	−1277(7)	2.7(2)
S22	511(2)	690(2)	2066(1)	2.5(1)
C22	233(6)	−1158(6)	3622(5)	9.1(2)
N12	1151(6)	−1330(6)	4805(5)	2.5(2)
C12	2582(7)	−33(9)	4885(8)	3.4(2)
N32	−953(6)	−2688(6)	4022(5)	2.3(2)
C42	−771(8)	−3784(7)	5397(6)	3.1(2)
C52	575(9)	−2995(9)	5899(6)	3.3(2)
(b) *H-atoms*				
H1	4257	−3871	5637	
H2	4797	−3329	4093	
H31	3411	608	−1197	
H32	−1729	−2917	3497	

Chemical Analysis

C, H and N analyses were performed by Elemental Micro-Analysis Limited, Beaworthy, Devon.

Preparation

$PdCl_2$ (1 mmol) was dissolved in hot distilled water (10 cm^3) and acidified with concentrated hydrochloric acid to about 1 *M* (H$^+$) concentration. MImt (4 mmol) was dissolved in 1 *M* hydrochloric acid (10 cm^3). The two solutions were mixed and refluxed for two hours. The deep-red reaction mixture was cooled in an ice-bath from which orange-red crystals were obtained. These were washed with cold ethanol (5 cm^3) then dried in a moisture oven (70 °C), Yield 70%. Chemical analysis, (%), calculated (expt), gave C, 28.70 (29.0); H, 4.19 (4.5); N, 16.74 (16.2).

Single crystals suitable for X-ray analysis were grown at the interface of an acidified aqueous solution of the complex and chloroform.

Physical Methods

Infrared spectra of MImt and the complex were run as CsI discs in the range 4000–200 cm^{-1} from a Perkin-Elmer 577 grating spectrophotometer. Thermal analysis measurements were made with a Stanton-Redcroft TG 750 thermal analyser using column dried (molecular sieve, 13X) flowing air, platinum crucibles and sample masses in the range 2–5 mg. X-ray powder photographs of the end-products from the TG curves in air were taken with a Guinier X-ray camera using Cu(Kα) radiation (λ = 1.5405 Å) and Kodirex single-coated X-ray film.

Crystal Structure

Relevant crystal data are listed in Table 1; the intensity data were corrected for Lorentz, polarisation and absorption effects. With one formula unit in the cell the Pd(II) atoms are required to occupy inversion centres. A Fourier synthesis with the Pd(II) atom at the origin generated the sulphur and chlorine atomic coordinates; successive difference Fourier syntheses generated the remaining non-H atoms. The coordinates of these atoms were refined by full-matrix, least squares methods with anisotropic temperature factors. Positional parameters for the H-atoms were included in the calculations but they were not refined. Hydrogen atoms involved in H-bonding were located by difference Fourier methods the remainder were fixed by the program (C–H = 1.08 Å). Common isotropic temperature factors were also applied and refined, to water, imido, olefinic

TABLE III. Bond Distances (Å) and Angles (°) (with E.s.d.s. in parentheses). Symmetry code, superscript: none x, y, z; (i) = 1 − x, −1 −y, 1 − z; (ii) = 1 − x, −y, −z; (iii) = −1 + x, +y, +z.

(a) *The coordination sphere*

Bond	(Å)	Angle	(°)
Pd–S21	2.336(2)	S21–Pd–S22	92.9(1)
Pd–S22	2.327(1)	Pd–S21–C21	105.6(2)
Pd····Cl	3.907(2)	Pd–S22–C22	109.3(2)
S21····S22	3.380(2)	Cl···Pd···S21	78.8(2)
		Cl···Pd···S22	88.4(2)

(b) *Geometry of the ligand molecules*

(A = 1 or 2)	Ligand 1	Ligand 2
C2(A)–S2(A)	1.704(6)	1.701(4)
C2(A)–N1(A)	1.327(8)	1.366(7)
N1(A)–C1(A)	1.463(6)	1.441(8)
C2(A)–N3(A)	1.357(5)	1.353(6)
N3(A)–C4(A)	1.382(10)	1.354(7)
C4(A)–C5(A)	1.336(10)	1.318(10)
C5(A)–N1(A)	1.381(7)	1.395(7)
N3(A)–H3(A)	0.824	0.856
S2(A)–C2(A)–N1(A)	125.6(3)	125.0(4)
S2(A)–C2(A)–N3(A)	128.1(5)	129.5(4)
N1(A)–C2(A)–N3(A)	106.2(5)	105.3(4)
C2(A)–N1(A)–C1(A)	124.6(4)	125.6(4)
C1(A)–N1(A)–C5(A)	124.6(6)	125.6(5)
C2(A)–N1(A)–C5(A)	110.8(4)	108.7(5)
C2(A)–N3(A)–H3(A)	125.4(6)	124.9(4)
H3(A)–N3(A)–C4(A)	125.5(5)	124.8(5)
C2(A)–N3(A)–C4(A)	109.0(5)	110.2(5)
N3(A)–C4(A)–C5(A)	107.6(5)	108.7(4)
C4(A)–C5(A)–N1(A)	106.5(7)	107.0(5)

(c) *Hydrogen bonded contacts*

Bond	Lengths			Angle
A···H–D	A····D	A···H	H–D	A···H–D
$Cl^{(i)}$–H(1)–O	3.224	2.296	0.944	167.3
Cl–H(2)–O	3.234	2.388	0.854	170.8
$Cl^{(ii)}$–H31–N31	3.182	2.398	0.824	159.3
$Cl^{(iii)}$–H32–N31	3.129	2.274	0.856	176.5

and methyl hydrogen atoms. Final U-values ($Å^2$) are 0.067(1), 0.037(14), 0.057(21) and 0.061(4) respectively. Scattering factors for all atoms were calculated from an analytical approximation [11]. Final atomic parameters are in Table II.

All calculations were performed on the NUMAC, IBM 370/168 computer at the University of Newcastle upon Tyne. SHELX [12] and related programs were used in the solution. Anisotropic temperature factors, observed and calculated structure factors and structurally insignificant H-atom coordinates have been deposited with the Editor.

Results and Discussion

Thermogravimetric analysis of the compound in air gave an initial mass loss of 5.0% in the region of 100 °C. A total mass loss of 84.2% occurred at 550 °C with an end product of PdS which was identified by X-ray powder diffraction. The initial mass

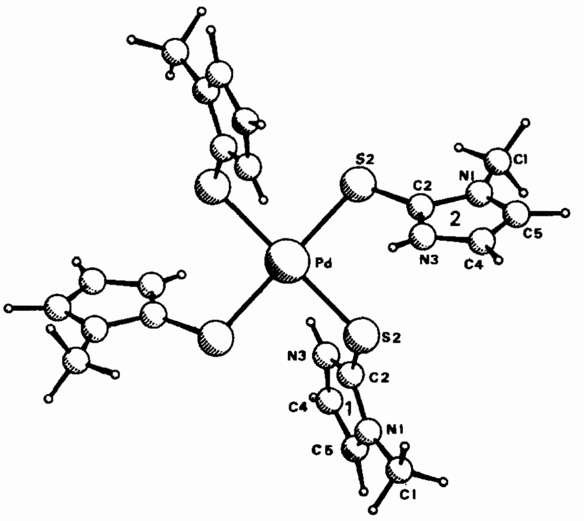

Fig. 2. Perspective diagram of the complex cation with atomic labelling.

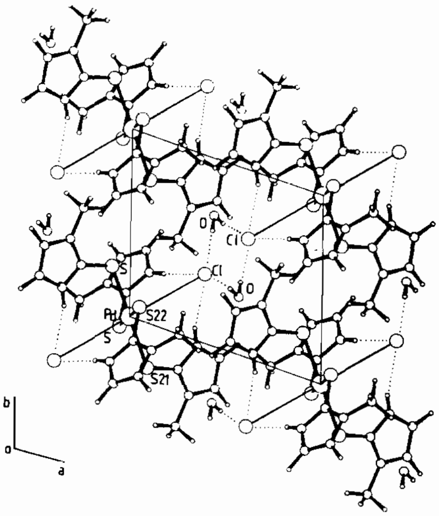

Fig. 3. Unit cell contents viewed down c^*.

loss is indicative of two water molecules in the compound (theoretical mass 5.37%) and the theoretical overall mass loss to PdS of 84.0% is in excellent agreement with the experimental value and confirms the stoichiometry of the compound.

The infrared spectrum of the compound has bands attributable to the water molecules at 3500 cm^{-1} (ν_3) and 1620 cm^{-1} (ν_2) [13]. The presence of a broad and intense absorption in the range 3600–3200 cm^{-1} indicates H-bonding in the solid and contains, in addition to ν(OH), both ν(NH) and ν(CH). The 'thioamide' bands (I, II, III and IV) occur at 1460, 1275, 1090 and 770, 740 cm^{-1} respectively, in the free MImt molecule [14]. In this complex, thioamide I is split into two components, thioamide II and III show slight (10 cm^{-1}) positive shifts and thioamide IV undergoes a radical change in appearance with bands at 750 and 730 cm^{-1} replacing the original bands.

In the low frequency region π(C–S) is negatively shifted from 530 to 500 cm^{-1} and the intensity of the δ(C–S) band, at 670 cm^{-1}, is considerably weakened. The general impression is one of major perturbation of the entire thioamide component of the molecule but with the major effects observed in the 'thione' region (800–500 cm^{-1}). A metal–ligand absorption at 340 cm^{-1} is also indicative of ν(Pd–S). The absence of ν(Pd–Cl) suggests ionic, rather than coordinated, chloride, in the complex. These observations suggest that MImt is S-donating in this complex and this has been confirmed by X-ray analysis.

The crystal structure of $Pd(MImt)_4Cl_2 \cdot 2H_2O$ consists of square-planar complexed cations, ionic chloride ions and water molecules which are held together by an extensive network of H-bonds. The overall arrangement is similar to that observed for the corresponding platinum complex [8, 9].

The palladium atom occupies a crystallographic centre of symmetry and is bonded by four thione sulphur atoms from monodentate MImt molecules in a strictly planar MS_4 arrangement with a S21–Pd–S22 angle of 92.9(1)°. Bond lengths and angles are in Table III. The Pd–S distances, 2.336(2) and 2.327(1) Å are comparable to values reported for other square-planar Pd(II) complexes involving thiourea and thiazolidine-2-thione respectively [15, 16]. Although the Pd–S distances in this complex are significantly different from one another librational correction of the data produced equivalent values of 2.363 Å which are close to the sum of the covalent radii (2.36 Å) [17]. The Pd–S–C angles (105.6(2) and 109.3(2)°) are close to the tetrahedral (sp^3) value previously observed for monodentate thione sulphur donating MImt molecules [4–9].

In addition, the ligands 'twist' around the Pd–S–C plane with angles of 24.8 and 41.1° and 'tilt' with respect to the PdS_4 plane with angles of 72.2 and 60.4° (Fig. 2, Table IV). This situation is comparable to the corresponding Pt(II) complex where the 'twist' angles are 35.2, 22.4° and the 'tilt' angles are 58.3 and 75.3° [8]. The effect of coordinating MImt with Pd(II) results in a lengthening of the C(2)–S(2) bond from 1.685(av) Å [3] to 1.703 (av) Å which corresponds to a reduction of π-SCF character [18] from 52.0 to 45.0%. There is also a concentration of π-density in the 'thioamide' portion of MImt similar to that in the free molecule [3].

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

Plane A
PdS$_4$
$6.8718X + 1.7947Y - 2.3006Z = 0.0$

Plane B
Pd, S21, C21
$3.9785X + 4.7982Y + 7.3809Z = 0.0$

Plane C
Pd, S22, C22
$8.7397X - 2.4485Y - 1.3456Z = 0.0$

Plane D
Ligand 1
$5.0056X + 1.4654Y + 7.7685Z - 0.9135 = 0.0$
[S21, 0.015; C21, −0.023; N11, −0.007; C11, 0.01; N31, −0.003; C41, 0.007; C51, 0.009]

Plane E
Ligand 2
$-6.4270X + 6.5372Y + 6.2642Z - 1.3917 = 0.0$
[S22, 0.025; C22, −0.030; N12, 0.009; C12, −0.013; N32, −0.017; C42, 0.011; C52, 0.014]

Dihedral Angles

Planes	Angle (°)
A/D	72.18
A/E	60.40
B/D	24.82
C/E	41.10
D/E	84.94

(e.s.d.'s are in the range 1.0–2.0°).

The chloride ion occupies an approximately axial position, relative to the PdS$_4$ plane (Cl–Pd–S(1), and S(2) 78.8° and 88.4° respectively) with a Pd····Cl distance of 3.907 Å.

Hydrogen-bonded distances are given in Table III and are illustrated in Fig. 3. The water molecules in the structure effectively bridge pairs of chloride ions which also bridge two N–H groups from different ligands.

Having previously demonstrated the ability of MImt to coordinate to platinum(II) in neutral media [8] this work has demonstrated that coordination to palladium(II) in highly acid media is also possible. More recently the reactivity of MImt towards palladium(II) has been extended by the production of complexes with stoichiometries (metal:ligand) of 1:1, 1:2, 1:3 as well as 1:4 in both acid and neutral media [19].

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