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The First Example of a *cis*-Platinum Analogue with Two Directly Bridged Imidazoles: $[Pt(mimim)Cl_2] \cdot Et_4NCl$

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Abstract

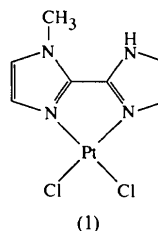
The crystal structure of the title compound, tetraethylammonium dichloro(1-methyl-2,2'-biimidazole- $N^3, N^{3'}$)-platinum(II) chloride, $(C_8H_{20}N)[PtCl_2(C_7H_8N_4)]Cl$, has been determined from single-crystal X-ray diffraction data. The square-planar coordination sphere of the platinum consists of two N atoms of the biimidazole ligand and two Cl atoms in a *cis* arrangement. The average Pt—N and Pt—Cl distances are 2.017 and 2.309 Å, respectively. One Et_4NCl molecule co-crystallizes in the asymmetric unit.

Comment

The chemistry of biimidazole (bi) compounds is of great interest since they are closely related to biological systems involving the histidine or purine residues. Another interesting aspect is the high antitumour activity, in combination with low toxicity, of some of the (biimidazole)-dichloroplatinum(II) complexes. The high antitumour activity is especially surprising in view of the lack of an NH moiety. These compounds react like *cis*-platinum with nucleobases and their analogues (Reusmann, Grehl, Reckordt & Krebs, 1994; Grehl & Krebs, 1994; Engelking, Karentzopoulos, Reusmann & Krebs, 1994). We were able to show that small changes in the ligands can evoke enormous changes in the cytostatic properties. Whereas the complex (2,2'-biimidazole)dichloroplatinum(II), $[Pt(bi)Cl_2]$, shows high cytostatic activity combined with low toxicity, (1,1'-dimethyl-2,2'-biimidazole)dichloroplatinum(II), $[Pt(dmibi)Cl_2]$, is inactive. Other examples of this as yet unexplained phenomenon are the two compounds [bis(1-methylimidazol-2-yl)carbinol]dichloroplatinum(II), $[Pt(bmic)Cl_2]$, and [bis(1-methylimidazol-2-yl)ketone]dichloroplatinum(II), $[Pt(bmik)Cl_2]$, where the former possesses greater antitumour properties than the latter (Bloemink, Engelking, Karentzopoulos, Krebs & Reedijk, 1996).

In the title complex, $[Pt(mimim)Cl_2] \cdot Et_4NCl$ [where mimim is 2-(1-methylimidazol-2-yl)imidazole], (1), the bidentate mimim ligand forms a five-membered chelate ring with the Pt atom (see Fig. 1). This was also

observed for related structures of dichloroplatinum(II) complexes with 2,2'-bipyridine (Osborn & Rogers, 1974; Canty, Skelton, Traill & White, 1992; Gund & Keppler, 1994) or *o*-phenanthroline derivatives (Anbei, Krüger & Pfeil, 1987; Fanizzi *et al.*, 1991). In addition to the two N atoms of the mimim ligand, the Pt atom is coordinated by two Cl atoms. The result is a square-planar PtN_2Cl_2 coordination sphere from which the displacement of the Pt atom amounts to 0.032 Å. The bond lengths are 2.021 (9) [Pt(1)—N(1)] and 2.013 (9) Å [Pt(1)—N(3)] for Pt—N, and 2.315 (3) [Pt(1)—Cl(1)] and 2.302 (3) Å [Pt(1)—Cl(2)] for Pt—Cl. These are in ranges comparable to reported structures (Bales *et al.*, 1983; Navarro-Ranninger, Martinez-Carrera & Garcia-Blanco, 1983*a,b*; Kuduk-Jaworska, Kubiak & Glowiak, 1988; Rochon, Kong, Melanson, Skov & Farrell, 1991; Rochon, Melanson & Farrell, 1993).



A small bite angle involving the two N atoms [N(3)—Pt(1)—N(1) 79.3 (4)°] is observed. The best least-squares fit for the two imidazole rings of the mimim ligand shows a dihedral angle of 2.6 (5)° between the rings. The ligand shows no unusual bond lengths and angles. The planar $[Pt(mimim)Cl_2]$ molecules are stacked into columns along the *x* axis, with a Pt(1)··Pt(1') distance of 4.686 (2) Å [symmetry code: (i) $-x, -y, -z$]. The

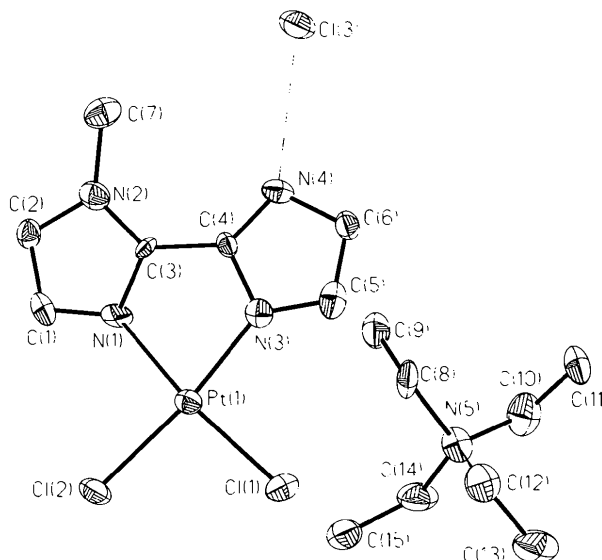


Fig. 1. Displacement ellipsoid plot of (1) at the 50% probability level [XP in SHELXTL (Sheldrick, 1990b)].

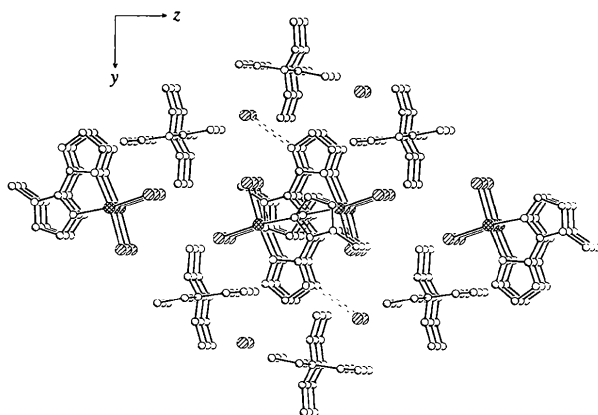


Fig. 2. Packing diagram viewed along the *x* axis [*XP* in *SHELXTL* (Sheldrick, 1990*b*)].

Et_4N^+ cations are aligned in an eclipsed arrangement along the *x* axis (Fig. 2).

A hydrogen bond between the NH group and the free Cl^- anion stabilizes the crystal packing (see Figs. 1 and 2). The $\text{Cl}(3)\cdots\text{N}(4)$ distance is 3.003 (10) Å.

Experimental

The mimim ligand was synthesized in accordance with published procedures (Tang, Davalian, Huang & Breslow, 1978). The synthesis of (1) was carried out by reacting $(\text{Et}_4\text{N})_2[\text{PtCl}_4]$ with one equivalent of mimim in acetonitrile for 2 h under reflux. Unreacted $(\text{Et}_4\text{N})_2[\text{PtCl}_4]$ was removed *via* ether diffusion into the solution and subsequent filtration. Crystallization of (1) was achieved by increasing the ether:acetonitrile ratio.

Crystal data

$(\text{C}_8\text{H}_{20}\text{N})[\text{PtCl}_2(\text{C}_7\text{H}_8\text{N}_4)]\text{Cl}$	Mo $K\alpha$ radiation
$M_r = 579.86$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 26 reflections
$P2_1/c$	$\theta = 3\text{--}13^\circ$
$a = 7.0470$ (10) Å	$\mu = 7.292$ mm $^{-1}$
$b = 23.973$ (5) Å	$T = 150$ (2) K
$c = 12.280$ (2) Å	Needle
$\beta = 101.00$ (3) $^\circ$	$0.35 \times 0.03 \times 0.02$ mm
$V = 2036.4$ (6) Å 3	Yellow
$Z = 4$	
$D_x = 1.891$ Mg m $^{-3}$	
D_m not measured	

Data collection

Synthex $P2_1$ diffractometer	2382 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.0386$
Absorption correction: empirical <i>via</i> ψ scans (North, Phillips & Mathews, 1968)	$\theta_{\text{max}} = 25^\circ$
$T_{\text{min}} = 0.732$, $T_{\text{max}} = 0.864$	$h = -8 \rightarrow 8$
3717 measured reflections	$k = -28 \rightarrow 19$
3545 independent reflections	$l = -14 \rightarrow 3$
	2 standard reflections every 98 reflections
	intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.0489$
 $wR(F^2) = 0.1050$
 $S = 1.018$
 3544 reflections
 222 parameters
 H atoms not refined; riding
 $w = 1/[\sigma^2(F_o^2) + (0.041P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.165$
 $\Delta\rho_{\text{max}} = 1.307$ e Å $^{-3}$
 $\Delta\rho_{\text{min}} = -0.927$ e Å $^{-3}$
 Extinction correction: none
 Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, $^\circ$)

Pt(1)—N(3)	2.013 (9)	N(4)—C(6)	1.400 (14)
Pt(1)—N(1)	2.021 (9)	C(1)—C(2)	1.38 (2)
Pt(1)—Cl(2)	2.302 (3)	C(3)—C(4)	1.467 (14)
Pt(1)—Cl(1)	2.315 (3)	C(5)—C(6)	1.36 (2)
N(1)—C(3)	1.315 (13)	N(5)—C(14)	1.488 (15)
N(1)—C(1)	1.353 (14)	N(5)—C(12)	1.51 (2)
N(2)—C(3)	1.339 (13)	N(5)—C(10)	1.52 (2)
N(2)—C(2)	1.372 (14)	N(5)—C(8)	1.527 (15)
N(2)—C(7)	1.470 (14)	C(8)—C(9)	1.51 (2)
N(3)—C(4)	1.353 (14)	C(10)—C(11)	1.50 (2)
N(3)—C(5)	1.358 (14)	C(12)—C(13)	1.48 (2)
N(4)—C(4)	1.322 (13)	C(14)—C(15)	1.60 (2)
N(3)—Pt(1)—N(1)	79.3 (4)	N(1)—C(3)—N(2)	111.2 (10)
N(3)—Pt(1)—Cl(2)	172.6 (3)	N(1)—C(3)—C(4)	115.6 (9)
N(1)—Pt(1)—Cl(2)	93.4 (3)	N(2)—C(3)—C(4)	133.1 (10)
N(3)—Pt(1)—Cl(1)	93.0 (3)	N(4)—C(4)—N(3)	110.7 (9)
N(1)—Pt(1)—Cl(1)	172.2 (3)	N(4)—C(4)—C(3)	135.9 (10)
Cl(2)—Pt(1)—Cl(1)	94.27 (11)	N(3)—C(4)—C(3)	113.4 (9)
C(3)—N(1)—C(1)	108.5 (9)	N(3)—C(5)—C(6)	110.2 (11)
C(3)—N(1)—Pt(1)	115.8 (7)	C(5)—C(6)—N(4)	105.2 (10)
C(1)—N(1)—Pt(1)	135.7 (8)	C(14)—N(5)—C(12)	112.4 (10)
C(3)—N(2)—C(2)	105.6 (9)	C(14)—N(5)—C(10)	105.4 (10)
C(3)—N(2)—C(7)	128.6 (10)	C(12)—N(5)—C(10)	111.5 (10)
C(2)—N(2)—C(7)	125.6 (10)	C(14)—N(5)—C(8)	112.7 (10)
C(4)—N(3)—C(5)	105.9 (10)	C(12)—N(5)—C(8)	105.6 (9)
C(4)—N(3)—Pt(1)	115.8 (7)	C(10)—N(5)—C(8)	109.3 (10)
C(5)—N(3)—Pt(1)	138.1 (8)	C(9)—C(8)—N(5)	115.6 (10)
C(4)—N(4)—C(6)	107.9 (9)	C(11)—C(10)—N(5)	115.6 (11)
N(1)—C(1)—C(2)	106.3 (10)	C(13)—C(12)—N(5)	114.1 (11)
N(2)—C(2)—C(1)	108.4 (10)	N(5)—C(14)—N(5)	112.7 (11)

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1120). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

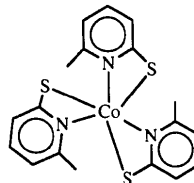
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Comment

Recent results from this laboratory have revealed the remarkable capacity of 6-substituted 2-pyridonate ligands to stabilize a structurally diverse array of polyoxo complexes of the later first-row transition metals, for example $[Fe_{17}O_{15}(OH)_6(chp)_{12}-(phen)_8(OMe)_3]$ (Parsons, Solan & Winpenny, 1995), $[Ni_{12}(O_2CMe)_{12}(H_2O)_6(thf)_6]$ (Blake, Grant, Parsons, Rawson & Winpenny, 1994) and $[Co_{13}(chp)_{20}(phth)_{2-(OH)_2}]$ (Brechin, Harris, Parsons & Winpenny, 1996) (ch is 6-chloro-2-pyridonate, phen is phenanthroline, thf is tetrahydrofuran and phth is phthalate). The synthesis and structural characterization of a chalcogenide-bridged complex containing 146 metal atoms (Krautscheid, Fenske, Baum & Semmelmann, 1993) encouraged us to extend our results in the coordination chemistry of 2-pyridone to the analogous sulfur system 2-mercaptopyridine. As part of this work we have prepared and isolated the complex *fac*-tris(6-methyl-2-mercaptopyridinato)cobalt(III), (1), and determined its crystal structure at 150 K.



(1)

The crystal structure of (1) consists of discrete distorted octahedral complexes containing three chelating mercaptopyridinate ligands (Fig. 1). Five tris(2-mercaptopyridinate) complexes of first-row transition metals have been structurally characterized previously [FeL_3^- (Rosenfield, Swedberg, Arora & Mascharak, 1986), NiL_3^- (Rosenfield, Berends, Gelmini, Stephan & Mascharak, 1987), CoL_3 and CoL'_3 (Block, Kang, Ofori-Okai & Zubieta, 1991), and VL_3^- (Henkel, Krebs & Schmidt, 1992), where L is 2-mercaptopyridinate and L' is 6-trimethylsilyl-2-mercaptopyridinate]. All have a similar distorted octahedral arrangement at the metal centre imposed by the narrow bite angle of the ligand (65 – 73°). The $M-N$ and $M-S$ bond lengths [shown for (1) in Table 2] are determined mostly by the oxidation state of the metal, with the $M-S$ distances spanning 2.52 – 2.58 Å for the divalent V, Fe and Ni systems, and 2.22 – 2.31 Å for the trivalent cobalt complexes; the ranges for the $M-N$ bond lengths are 2.13 – 2.18 and 1.90 – 1.99 Å, respectively. Longer metal–ligand bonds are associated with smaller bite angles at the metal centre and approximately linear correlations can be established between these three parameters when taken in pairs.

Burdett (1976) has suggested that low-spin d^6 complexes of general formula MA_3B_3 will preferentially

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fac-Tris(6-methyl-2-mercaptopyridinato)-cobalt(III) at 150 K

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Abstract

The title compound, tris(6-methylpyridine-2-thiolato-*N,S*)cobalt(III), $[Co(C_6H_6NS)_3]$, has been isolated and characterized as the *fac* isomer. However, several closely related cobalt and iron complexes which have been characterized previously all adopt the *mer* configuration.