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(1,1′-Dimethyl-2,2′-biimidazole-N^3,$N^{3'}$)diiodoplatinum(II)

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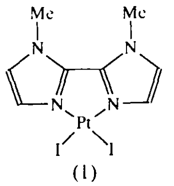
Abstract

The title compound, $[PtI_2(C_8H_{10}N_4)]$, exhibits square-planar *cis* coordination of the Pt atom to the two I atoms [mean Pt—I distance = 2.587 (6) Å] and the two unmethylated imidazole N atoms [mean Pt—N distance = 2.020 (6) Å]. Successively antiparallel near-planar $[PtI_2(C_8H_{10}N_4)]$ units form zigzag chains along the *b* axis, with Pt···Pt distances longer than the interplanar spacing.

Comment

In recent years, we have investigated the coordination chemistry of 2,2′-biimidazole derivatives, focusing on the structures and biological activities of their organotin compounds (Álvarez Boo *et al.*, 1997, and references therein). Prompted by reports (Karentzopoulos *et al.*, 1997, and references therein) that small differences between biimidazoles can be associated with significant differences in the cytotoxicity of their platinum complexes, a finding that heightens the interest of structural studies of these compounds, we have now synthesized and determined the crystal structure of (1,1′-dimethyl-2,2′-biimidazole)diiodoplatinum(II), $[Pt(Me_2bim)I_2]$, (1).



(1)

The molecular structure and atomic numbering scheme of (1) are shown in Fig. 1. The Pt atom is coordinated to the two unmethylated N atoms of the biimidazole ligand and to two I atoms in a square-planar PtN_2I_2 arrangement in which the Pt atom lies 0.0138 Å from the least-squares plane through four atoms (N_2I_2). The Pt—I and Pt—N bond distances (Table 1) are similar to those found in $[Pt(bipy)I_2]$ (bipy is bipyridyl) [Pt—I 2.589 (2) and Pt—N 2.029 (7) Å; Connick & Gray, 1994]. The N—Pt—N angle is just slightly narrower than in $[Pt(bipy)I_2]$ [79.3 (3) Å], but the I—Pt—I angle is wider than in the latter compound (87.7 Å), and is close to those found in complexes with monodentate *N*-donor ligands (Oksanen *et al.*, 1989; Raudaschl-Sieber *et al.*, 1986). The parameters of the PtN_2C_2 ring are very similar to those found in $[Pt(mimim)Cl_2].Et_4NCl$ (mimim is *N*-methyl-2,2′-biimidazole) (Karentzopoulos *et al.*, 1997); the Pt—N distances, in particular, are practically identical. The biggest difference is that the C3—C4 bond length is shorter in $[Pt(Me_2bim)I_2]$, which leads to the N—Pt—N angle being slightly narrower.

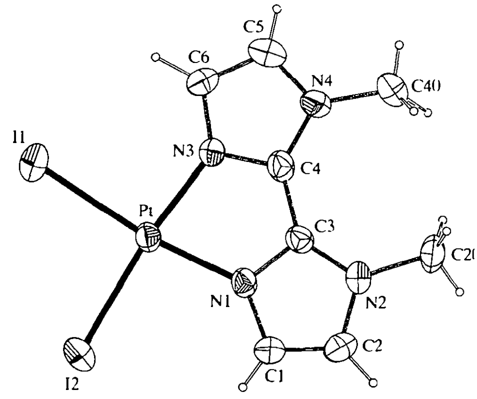


Fig. 1. The molecular structure of the title compound, showing the atom-labelling scheme. Ellipsoids are shown at the 50% probability level.

In the Me_2bim ligand, rings *A* (containing N1) and *B* (containing N3) are both planar and are almost coplanar, making angles of 2.6 (3) and 3.5 (3)°, respectively, with the PtN_2I_2 plane. This quasi-coplanarity of the two rings contrasts with the situation in $[SnMe_2Br_2(Me_2bim)]$ (23.8°; López *et al.*, 1992).

As in $[Pt(bipy)I_2]$, successively antiparallel monomer units form stacks, in this case along the *b* axis, with Pt···Pt distances [4.7388 (7) and 4.7731 (7) Å] longer than the distance between the planes of successive monomers (Fig. 2 and Table 1). The relative displacement of adjacent members of the stack gives it a zigzag structure.

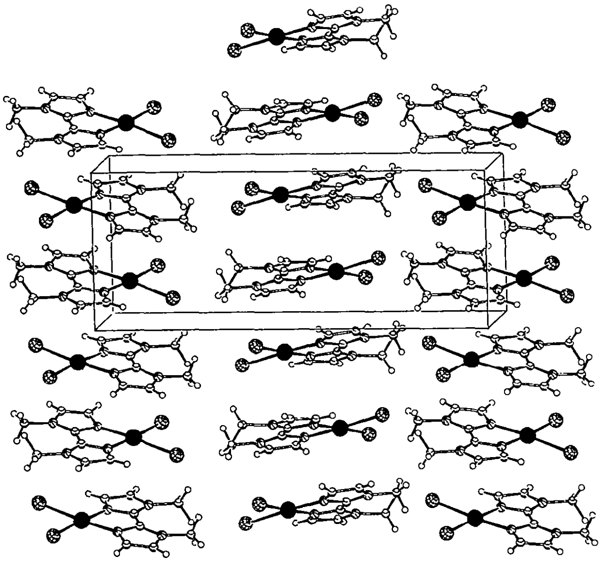


Fig. 2. The packing (*SCHAKAL*92; Keller, 1992) of the $[Pt(Me_2bim)I_2]$ molecules. The origin of the cell is in the lower left foreground with the *c* axis horizontal and the *b* axis vertical.

Experimental

Me_2bim was prepared as described in the literature (Melloni *et al.*, 1972). The title compound was prepared by treating an aqueous solution of K_2PtCl_4 (0.5 g, 1.2 mmol) with KI (4 g, 24 mmol), heating to 373 K for 5 min, adding Me_2bim (0.2 g, 1.2 mmol) and stirring for 24 h. The clear brown solid obtained was filtered out, washed with water, ethanol and ether, and dried *in vacuo* (yield 64%). Crystals suitable for X-ray analysis were obtained by slow concentration of a dimethylformamide solution.

Crystal data

$[PtI_2(C_8H_{10}N_4)]$
$M_r = 611.09$
Monoclinic
$P2_1/n$
$a = 8.4414\,(5)$ Å
$b = 7.7207\,(5)$ Å
$c = 19.4120\,(18)$ Å
$\beta = 90.342\,(6)°$
$V = 1265.13\,(16)$ Å^3
$Z = 4$
$D_x = 3.208$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9.00–18.18°$
$\mu = 15.95$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.25 \times 0.15 \times 0.10$ mm
Yellow

Data collection

Enraf–Nonius MACH3 diffractometer
ω scans
Absorption correction: ψ scan (Spek, 1997*b*)
$T_{min} = 0.113$, $T_{max} = 0.203$
2740 measured reflections
2562 independent reflections
1859 reflections with $I > 2\sigma(I)$

$R_{int} = 0.032$
$\theta_{max} = 26.29°$
$h = -10 \rightarrow 0$
$k = 0 \rightarrow 9$
$l = -24 \rightarrow 24$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.062$
$S = 1.046$
2562 reflections
177 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.056$

$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.76$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00223 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pt—N3	2.021 (6)	Pt—I2	2.5879 (6)
Pt—N1	2.020 (6)	Pt···Pt^i	4.7388 (7)
Pt—I1	2.5861 (6)	Pt···Pt^{ii}	4.7731 (7)
N3—Pt—N1	78.2 (2)	N1—Pt—I2	94.93 (17)
N3—Pt—I1	94.15 (18)	I1—Pt—I2	92.70 (2)
N1—Pt—I1	172.29 (17)	Pt^i···Pt···Pt^{ii}	108.522 (12)
N3—Pt—I2	173.15 (18)		

Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $1 - x, -y, -z$.

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from difference maps and refined isotropically [C—H 0.84 (8)–1.09 (9) Å and U_{iso} 0.13 (13)–0.08 (4) Å^2].

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *HELENA* (Spek, 1997*a*). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1997*b*) and *SCHAKAL*92 (Keller, 1992). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1137). Services for accessing these data are described at the back of the journal.

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Platinum(II) Complexes of Piperazine (and Derivatives): *cis*-Diiodo(*N*-methylpiperazine-*N*,*N*′)platinum(II)

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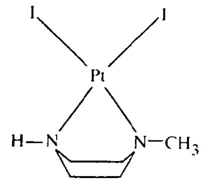
Abstract

The neutral chelate title complex, *cis*-[$PtI_2(C_5H_{12}N_2)$], has a distorted square-planar geometry around the Pt atom. The N and I atoms lie almost perfectly in a plane but the N—Pt—N angle is reduced to 70.1 (7)° while the I—Pt—I angle is 93.40 (5)°. The molecular structure, which resembles roughly that of the more symmetric *cis*-dichloro(*N*,*N*′-dimethylpiperazine-*N*,*N*′)platinum(II), shows some asymmetric distortions, for example, the two Pt—N distances of 2.05 (2) and 2.13 (1) Å. These distortions are mainly caused by steric hindrance between the bulky I atom and the methyl group of the *N*-methylpiperazine ligand.

Comment

Piperazine (H_2ppz), *N*-methylpiperazine (HMeppz) and *N*,*N*′-dimethylpiperazine (Me_2ppz) are extensively used by us as ligands towards metal ions, especially platinum(II) (Marzotto *et al.*, 1997, 1998; Ciccarese *et al.*, 1998*a*,*b*) and cobalt(II) (Visona', 1998). Moreover, piperazine and its derivatives possess pharmacological activity including antitumor properties (Hempel *et al.*, 1982). The literature reports metal complexes in which piperazine or its derivatives act as monodentate, bidentate or bidentate-chelate ligands. The chair conformation of the six-membered ring is always observed when monodentate coordination occurs, whereas the rare boat conformation is observed only when there is bidentate-chelate coordination.

We have recently synthesized and characterized, also through X-ray analysis, two platinum(II) complexes possessing the boat conformation, *i.e.* *cis*-dichloro(*N*,*N*′-dimethylpiperazine-*N*,*N*′)platinum(II), *cis*-[$PtCl_2(Me_2ppz)$] (Ciccarese *et al.*, 1998*a*), and *trans*-bis(*N*-methylpiperazine-*N*,*N*′)platinum(II) dichloride tetrahydrate, *trans*-[$Pt(HMeppz)_2]Cl_2\cdot4H_2O$ (Marzotto *et al.*, 1997). In addition, piperazine is forced to assume the boat conformation when it is incorporated into a macrocyclic ring for bonding to a metal atom in a bidentate fashion (Wade *et al.*, 1990; Kowallick *et al.*, 1997). This behaviour may be explained by the fact that the chair conformation of the hexa-atomic ring is 17.2 kJ mol^{-1} more stable than the boat one (Niemeyer, 1979). Since during the above-mentioned studies we have noticed strong steric hindrance between *N*-methylpiperazine and the groups bonded to platinum(II), we have synthesized the neutral complex *cis*-diiodo(*N*-methylpiperazine-*N*,*N*′)platinum(II), *cis*-[$PtI_2(HMeppz)$], in order to study the effect of the bulky I atoms on the Pt—N bond lengths.



cis-[$PtI_2(HMeppz)$]

The molecular structure of the title complex shows remarkable distortions due to unbalanced steric interactions, in fact, I2···CH_3 causes greater hindrance than I1···H1. For example, Pt—N2 [2.13 (1) Å] is longer than Pt—N1 [2.05 (2) Å], which is, on the contrary, close to the Pt—N distances [2.061 (10) and 2.065 (9) Å] found in *cis*-[$PtCl_2(Me_2ppz)$]. Furthermore, the I1···N1 distance, 3.45 (2) Å, could be explained by the presence of an intramolecular hydrogen bond which restricts the N1—Pt—I1 angle to 95.7 (5)°, while the N2—Pt—I2 angle is enlarged to 100.9 (4)° as a consequence of the requested planarity of platinum(II) coordination and steric hindrance between the I atom and the methyl group. This is confirmed by the average of the N—Pt—I angles, 98.3 (6)°, which is close to the N—Pt—Cl angle values, 98.5 (3) and 98.3 (3)°, found for the symmetrical *cis*-[$PtCl_2(Me_2ppz)$].

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