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Acta Cryst. (1998). C**54**, 27–29

Platinum(II) Complexes of Piperazine (and Derivatives): *trans*-Dichlorobis(*N*-methylpiperazine-*N'*)platinum(II)

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(Received 15 May 1997; accepted 18 September 1997)

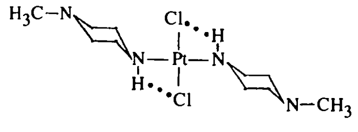
Abstract

The neutral title complex, *trans*-[$PtCl_2(C_5H_{12}N_2)_2$], has been synthesized in the course of our studies on piperazine derivative complexes with platinum(II). This complex is square planar and isomorphous with the analogous palladium(II) complex, and exhibits the same molecular, but not crystallographic, structure as *trans*-[$PtCl_2(C_5H_{13}N_2)_2$]Cl_2.$2H_2O$, [($C_5H_{13}N_2$) is *N*-methylpiperazinium(1+)]. The six-membered ring is in the chair conformation and binds platinum(II) through the unmethylated N1—H nitrogen, which is sterically less hindered than the methylated one. The molecule has a local pseudo-mirror plane nearly coincident with the square-planar coordination plane and nearly bisecting the piperazine ring.

Comment

The cyclic diamine piperazine (H_2ppz) contains a non-planar six-membered ring formed by four C and two basic N atoms. Piperazine and its derivatives, *N*-methylpiperazine (HMeppz) and *N,N'*-dimethylpiperazine (Me_2ppz), can act as monodentate, bidentate or bidentate chelate ligands. The six-membered ring commonly displays a chair and less frequently a boat conformation, the former conformation being 17.2 kJ mol^{-1} more stable (Niemeyer, 1979). However, the boat conformation occurs when *N*-methylpiperazine forms a bidentate chelate complex with one platinum(II) ion (Marzotto, Clemente & Valle, 1998), when *N,N'*-dimethylpiperazine forms a chelate complex with one palladium(II) ion (Hassel & Pedersen, 1959) or when the piperazine ring is forced to form a macrocyclic ligand capable of chelating selectively one metal ion (Wade *et al.*, 1990). Other interesting platinum(II) coordination compounds of *N*-methylpiperazine and *N,N'*-dimethylpiperazine, with potential antitumoral activity, will be published soon (Ciccarese *et al.*, 1998).

The X-ray analysis of the title complex, (I), shows that the platinum(II) ion has a distorted square-planar coordination geometry (Table 1), with the two Cl and the two *N*-methylpiperazine ligands each in *trans* positions, as found in *trans*-[$PdCl_2(HMeppz)_2$] (Ivanova *et al.*, 1991) and in *trans*-[$PtCl_2(H_2Meppz)_2$]Cl_2.$2H_2O$ (Ciccarese *et al.*, 1998) [H_2Meppz is *N*-methylpiperazinium(1+), *i.e.* a cationic ligand]. The piperazine ring possesses a chair conformation and is coordinated through the secondary amine N1 atom which is sterically less hindered than the methylated N2 atom. The Pt—N1 and N2—CH_3 bonds lie in equatorial positions, while the N1—H1 bond is in an axial position for steric reasons. In this way, N1 can form a strong intramolecular hydrogen bond with the Cl1 atom (Table 2). In fact, the decrease of the N1—Pt—Cl1 angle from 90 to 87.84 (11)° indicates that this hydrogen bond stabilizes the molecule. The angle between the Pt, Cl1, N1 plane and the C1, C2, C3, C4 plane is 89.06 (16)°, very near to 90°. This angle is very likely imposed by the abovementioned strong intramolecular N1—H1···Cl1 hydrogen bond. In fact, only if this angle is 90° does the H1 atom lie exactly in the square-planar coordination plane which favours the formation of a strong hydrogen bond. The entire molecule possess a pseudo-mirror plane, practically coincident with the square-planar coordination plane [the dihedral angle is 0.49 (7)°], and bisects the piperazine ring passing through the N1, N2 and C5 atoms.



(I)

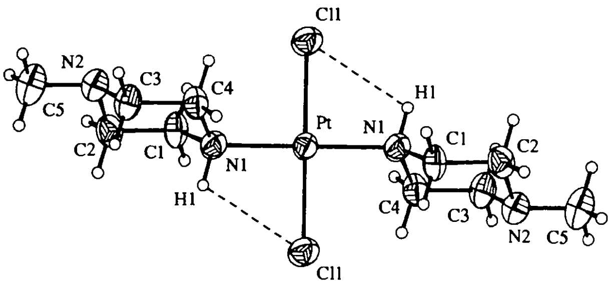


Fig. 1. View of compound (I) showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

Experimental

A solution of *N*-methylpiperazine (HMeppz, 98%, 0.028 ml, 0.25 mmol) in 2 ml of water was reacted with K_2PtCl_4 (0.104 g, 0.25 mmol) dissolved in 3 ml of water. To the resulting red solution, HCl (0.1 *N*) was added (0.050 ml, 0.5 mmol) and followed by free HMeppz (0.083 ml, 0.75 mmol) under stirring. The solution, at a final pH value near 11, was left to stand at room temperature to concentrate slowly. After 4 d, yellow crystals were obtained, filtered, washed with acetone–water (2:1 *v*/*v*) and dried under vacuum. Good quality single crystals suitable for the X-ray structure determination were obtained by slow recrystallization from an aqueous solution. Yield: 0.079 g (68%). Found: C 25.66, H 5.23, N 11.96, Cl 15.11%. Calculated for $C_{10}H_{24}Cl_2N_4Pt$: C 25.75, H 5.19, N 12.02, Cl 15.20%.

Crystal data

[$PtCl_2(C_5H_{12}N_2)_2$]
$M_r = 466.32$
Monoclinic
$P2_1/c$
$a = 6.451\ (2)$ Å
$b = 13.307\ (2)$ Å
$c = 8.885\ (2)$ Å
$\beta = 95.10\ (4)°$
$V = 759.7\ (3)$ Å^3
$Z = 2$
$D_x = 2.039$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71070$ Å
Cell parameters from 25 reflections
$\theta = 10$–$15°$
$\mu = 9.573$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.30 × 0.30 × 0.25 mm
Yellow

Data collection

Philips PW1100/20 diffractometer
$\theta/2\theta$ scans
Absorption correction: semi-empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.049$, $T_{max} = 0.091$
1942 measured reflections
1837 independent reflections

1289 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 27.99°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 90 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.071$
$S = 1.018$
1837 reflections
79 parameters
H atoms riding with fixed *U*
$w = 1/[\sigma^2(F_o^2) + (0.0439P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.218$ e Å^{-3}
$\Delta\rho_{min} = -1.869$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Pt—N1	2.058 (3)	N2—C5	1.462 (6)
Pt—Cl1	2.3005 (15)	N2—C3	1.464 (6)
N1—C4	1.479 (5)	C1—C2	1.513 (6)
N1—C1	1.486 (5)	C3—C4	1.517 (6)
N2—C2	1.457 (6)		
N1^i—Pt—Cl1	92.16 (11)	C2—N2—C3	108.2 (4)
N1—Pt—Cl1	87.84 (11)	C5—N2—C3	109.3 (4)
C4—N1—C1	108.9 (4)	N1—C1—C2	112.0 (4)
C4—N1—Pt	112.9 (3)	N2—C2—C1	110.6 (4)
C1—N1—Pt	115.1 (3)	N2—C3—C4	110.7 (4)
C2—N2—C5	110.3 (4)	N1—C4—C3	113.3 (4)
N1—C1—C2—N2	−59.7 (5)	N2—C3—C4—N1	56.5 (6)

Symmetry code: (i) $-x, -y, -z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	0.910 (5)	2.646 (3)	3.029 (4)	106.2 (3)

The intensities were corrected for Lorentz and polarization factors utilizing the program *RIFLUP*80 (Biagini Cingi *et al.*, 1980) and for absorption using the semi-empirical method of North, Phillips & Mathews (1968). The refinement started with the coordinates of the isomorphous palladium(II) complex and it was continued by introducing anisotropic displacement parameters for non-H atoms, while H atoms were refined isotropically fixing their distances as: N—H 0.91, methylene C—H 0.97 and methyl C—H 0.96 Å. The *U* displacement parameters of the amine and methylene H atoms were fixed at $1.2U_{eq}$ of the atom to which they are bonded, while the *U* displacement parameter of the methyl H atoms were fixed at $1.5U_{eq}$ of C5. The final difference electron-density map revealed a 1.218 e Å^{-3} positive peak and a −1.869 e Å^{-3} negative one at 0.94 and 0.85 Å, respectively, from the Pt atom. Most calculations were performed with the *SHELXL*93 package (Sheldrick, 1993); least-squares planes were calculated with *PARST* (Nardelli, 1983, 1995).

Data collection: Philips PW1100/20 software. Cell refinement: Philips PW1100/20 software. Data reduction: *RIFLUP*80. Molecular graphics: *ORTEP*II (Johnson, 1976).

The financial support given by MURST (40%) and in part by the Programma Finalizzato CNR–Rome is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1009). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 29–31

$(Tb_{0.9},Er_{0.1})_4TiO(O^iPr)_{14}$, a Novel Pentanuclear Oxo–Alkoxide

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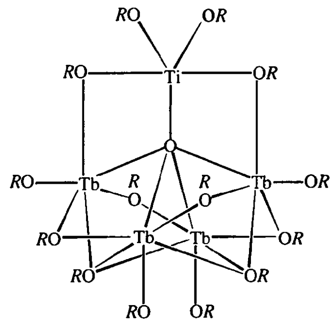
(*Received 3 April 1997; accepted 29 July 1997*)

Abstract

The new pentanuclear alkoxide μ_5-oxo-bis(μ_3-isopropoxo)hexakis(μ_2-isopropoxo)hexakis(isopropoxo)tetraterbium(III)titanium μ_5-oxo-bis(μ_3-isopropoxo)hexakis(μ_2-isopropoxo)hexakis(isopropoxo)tetraerbium(III)titanium, with the composition $[(Tb_{0.9}Er_{0.1})_4Ti(\mu_5\text{-}O)(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_6(OR)_6]$ (R = ^{i}Pr = C_3H_7O) has a metal–oxygen Ln_4TiO_{14} core which consists of five metal atoms arranged in approximately trigonal-bipyramidal geometry, with a μ_5-O atom in the centre of the polyhedron. The lanthanide atoms are sixfold coordinated and the Ti atom is fivefold coordinated, both by O atoms.

Comment

Metal alkoxides are important precursors in the organic sol–gel process for obtaining various types of fine ceramics (Chandler, Roger & Hampden-Smith, 1993). When using alkoxides containing different metal ions in the same molecule, *i.e.* heterometallic alkoxides, extremely good homogeneity of the constituents can be obtained both in gels and final ceramics. The present study is part of a program involving rare-earth alkoxides that are to be used as precursors for optical materials, *e.g.* laser amplifiers and frequency up-conversion devices, as well as for anionic conductor ceramics. The optical rare-earth-doped materials may contain one or more rare-earth metals (Desurvire, 1991). The present paper reports an investigation of a precursor containing Tb and Er in the ratio 9:1, together with an optically 'silent' Ti atom. The title compound, (I), is isostructural with the bimetallic alkoxide $[(Sm)_4Ti(\mu_5\text{-}O)(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_6(OR)_6]$ (R = ^{i}Pr) (Daniele *et al.*, 1994) and has a molecular metal-atom framework similar to that of the homometallic alkoxide $[Nd_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_2(\mu_2\text{-}OR)_6(OR)_5(HOR)_2]$ (R = ^{i}Pr) (Helgesson *et al.*, 1991).



(I)

The metal–oxygen framework of the novel termetallic alkoxide is formed by four hexacoordinated lanthanide atoms and a pentacoordinated Ti atom. The coordination sphere around the Ti atom constitutes a distorted trigonal bipyramid with two terminal O atoms, two μ_2-bridging O atoms and one μ_5-O atom. The angular distortions from ideal geometry are rather small. However, the two apical Ti—O bonds, involving μ_2-O atoms, are quite elongated compared with the equatorial Ti—O bonds involving terminal O atoms. These bond-length

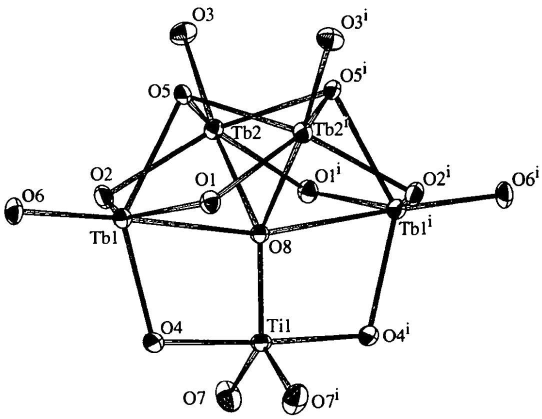


Fig. 1. The molecular structure showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity. [Symmetry code: (i) $1 - x, -y, z$.]

Acta Crystallographica Section C
ISSN 0108-2701 © 1998