tion of $NdCl_3$, 1,3,5-$^tBuC_6H_3$ and $AlCl_3$ (molar ratio 1:1:3) in toluene for 30 min at 353 K, followed by crystallization at 268 K.

Crystal data

[$Al_3NdCl_{12}(C_7H_8)$]
$M_r = 742.761$
Monoclinic
$P2_1/n$
$a = 9.728\ (3)$ Å
$b = 19.856\ (11)$ Å
$c = 12.939\ (4)$ Å
$\beta = 103.75\ (3)°$
$V = 2427.7\ (14)$ Å^3
$Z = 4$
$D_x = 2.032$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 2.62–12.63°$
$\mu = 3.580$ mm^{-1}
$T = 298$ K
Needle
0.44 × 0.28 × 0.24 mm
Yellow

Data collection

Nicolet $R3m/E$ diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ scans (*SHELXTL*; Sheldrick, 1984)
$T_{\min} = 0.265$, $T_{\max} = 0.642$
5982 measured reflections
5837 independent reflections

4236 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 28.0°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 27$
$l = 0 \rightarrow 18$
2 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F
$R = 0.039$
$wR = 0.038$
$S = 1.464$
4236 reflections
208 parameters
H atoms not refined
$w = 1/[\sigma^2(F) + 0.0002F^2]$

$(\Delta/\sigma)_{\max} = 0.051$
$\Delta\rho_{\max} = 0.46$ e Å^{-3}
$\Delta\rho_{\min} = -1.33$ e Å^{-3} (near the Nd atom)
Extinction correction: none
Scattering factors from *SHELXTL*

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

Nd—Cl1	2.864 (1)	Nd—C1	2.999 (6)
Nd—Cl2	2.902 (1)	Nd—C2	2.910 (5)
Nd—Cl3	2.857 (1)	Nd—C3	2.879 (5)
Nd—Cl4	2.846 (1)	Nd—C4	2.871 (5)
Nd—Cl5	2.875 (1)	Nd—C5	2.923 (5)
Nd—Cl6	2.799 (1)	Nd—C6	2.976 (6)
Cl1—Nd—Cl4	69.8 (1)	Cl2—Nd—Cl4	69.4 (1)
Cl1—Nd—Cl5	69.4 (1)	Cl3—Nd—Cl5	71.7 (1)
Cl1—Nd—Cl6	81.2 (1)	Cl3—Nd—Cl6	72.2 (1)
Cl2—Nd—Cl3	73.7 (1)		

The main program used was *SHELXTL* (Sheldrick, 1984). The structure was solved by the Patterson method and refined by least-squares calculations, initially with isotropic and finally with anisotropic displacement parameters for the non-H atoms. H atoms were not observed in difference maps but were placed in the calculated positions and assigned an isotropic displacement parameter $U_{\rm iso}$ of 0.08 Å^2.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1314). Services for accessing these data are described at the back of the journal.

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Piperazine (and Derivatives) Platinum(II) Complexes: *trans*-Bis(*N*-methylpiperazine-*N*,*N*′)platinum(II) Dichloride Tetrahydrate

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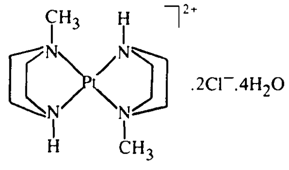
Abstract

The title compound, *trans*-$[L_2\mathrm{Pt^{II}}]^{2+}.2\mathrm{Cl}^-.4\mathrm{H_2O}$, ($L$ = *N*-methylpiperazine), $[\mathrm{Pt(C_5H_{12}N_2)_2}]\mathrm{Cl_2.4H_2O}$, has been synthesized in the course of our work on complexes formed by the Pt^{2+} ion with piperazine derivatives. X-ray diffraction analysis showed that two *N*-methylpiperazine molecules bind one Pt^{2+} ion in such a way that the two methyl groups lie in opposite directions with respect to the Pt atom. The coordination around the Pt atom is square planar with four N atoms occupying the coordination sites, and the coordination plane is perfectly planar because the Pt atom lies on a centre of symmetry. This type of coordination imposes a boat conformation on the six-membered *N*-methylpiperazine ring. As found in other *N*-methylpiperazine complexes, the molecule has a local mirror plane coincident with the square-planar coordination plane and nearly bisecting the piperazine six-membered ring.

Comment

Piperazine (H_2ppz) is a cyclic diamine that possesses a non-planar six-membered ring containing four C and two N atoms. Owing to the presence of two basic N atoms, piperazine and its derivatives [*N*-methylpiperazine (HMeppz) and *N*,*N*′-dimethylpiperazine (Me_2ppz)] may be used as monodentate, bidentate or bidentate-chelate ligands. The six-membered ring may possess a chair or a boat conformation depending on the chemical situation which in turn depends on synthesis features. In fact, the reaction conditions, in particular pH, must be perfectly controlled since at acidic pH values, monoprotonated *N*-methylpiperazinium(1+) or diprotonated *N*-methylpiperazinium(2+) cations are obtained. The former is still able, even if it is positively charged, to coordinate the Pt^{2+} ion, forming complexes such as $[PtCl_3(H_2Meppz)]$ and *trans*-$[PtCl_2(H_2Meppz)_2]^{2+}.2Cl^-.2H_2O$. Further details of the coordination chemistry of piperazine derivatives are reported in papers under preparation (Ciccarese, Clemente, Fanizzi, Marzotto & Valle, 1997; Marzotto, Clemente & Valle, 1997) where both neutral and ionic complexes are described. The structural analysis indicates the presence of a monoclinic *C*-centered unit cell containing four $[Pt(HMeppz)_2]^{2+}$ cations, eight Cl^- anions and sixteen water molecules; thus, one molecular unit can be formulated as *trans*-$[Pt(HMeppz)_2]^{2+}.2Cl^-.4H_2O$, (I). The metal complex cations are placed in the Wyckoff position 4*c*, *i.e.* with the Pt atom on the centre of symmetry at $(\frac{1}{4},\frac{1}{4},0)$, and the two *N*-methylpiperazine molecules are constrained to coordinate the Pt^{2+} ion with the methyl groups in *trans* positions with respect to each other. Although there are eight Cl^- anions in the unit cell, with space group *C*2/*c*, they are not all equivalent because they are on Wyckoff position 4*e*, *i.e.* on the twofold axis, and not in the general position 8*f*. The *N*-methylpiperazine molecule is bonded to the Pt atom through N1 and N2 in a boat conformation as we have already found in $[PtCl_2(Me_2ppz)]$ (Ciccarese, Clemente, Fanizzi, Marzotto & Valle, 1997). This very rare boat conformation is imposed by the coordination to the Pt atom; in fact, previous studies (Niemeyer, 1979) have shown that the chair conformation of the piperazine ring is more stable by 17.2 kJ mol^{-1} than the boat conformation. The dihedral angle between the N1, C1, C4 and C1–C4 planes is 118.1 (7)°, while the angle between the N2, C2, C3 and C1–C4 planes is 120.0 (7)°. The distances and angles are quite normal, in particular, the Pt—N1 [2.041 (7) Å] and [Pt—N2 2.060 (7) Å] distances are close to those observed for a Pt—N_{amine} distance without strain. This finding is surprising as the low 'bite' of the piperazine ligand [2.52 Å in free piperazine and 2.37 (1) Å in the present complex] reduces the N1—Pt—N2 angle from 90 to 70.7 (3)°. As is usual for these piperazine-containing molecules, the coordination plane (*i.e.* Pt, N1, N2) almost exactly bisects the piperazine molecule, in fact, the deviations (Å) from this plane are C1 1.18 (1), C2 1.21 (1), C3 −1.18 (2), C4 −1.23 (1), C5 −0.01 (1) and H1N2 0.04 (8), and the dihedral angle formed by this plane and the C1–C4 plane is 90.1 (3)°, very near to 90°. Two interconnected systems of hydrogen bonds are present in the crystal: the first runs along the *a* axis and connects the two Cl^- ions, Cl1 and Cl2, and the water molecule H1*W*1—O1*W*—H2*W*1 in an infinite chain of the type ···Cl2···H1*W*1—O1*W*—H2*W*1···Cl1···H2*W*1—O1*W*—H1*W*1···Cl2··· with the following geometrical parameters: O1*W*···Cl1 3.094 (9) Å and O1*W*—H2*W*1···Cl1 162 (6)°; O1*W*···Cl2 3.063 (9) Å and O1*W*—H1*W*1···Cl2 167 (6)°.



(I)

The second system of hydrogen bonds connects the $[Pt(HMeppz)_2]^{2+}$ cations to the previous hydrogen-bond system using three water molecules. In fact, the H1*W*2—O2*W*—H2*W*2 molecule, which is strongly bonded to the cation through an N2—H1N2···O2*W* hydrogen bond [H1N2···O2*W* 2.09 (5), N2···O2*W* 2.94 (1) Å and N2—H1N2···O2*W* 155 (4)°], is also bonded to two other O1*W* water molecules [O2*W*···O1*W*^{i} 2.86 (1) Å and O2*W*—H1*W*2···O1*W*^{i} 118 (11)°; O2*W*···O1*W*^{ii} 2.83 (1) Å and O2*W*—H2*W*2···O1*W*^{ii} 155 (6)°; symmetry codes: (i) $-x, y, \frac{1}{2}-z$; (ii) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$]. All other contacts are near to the normal van der Waals values and the atoms most involved in short contacts are the H atoms of the six-membered ring: Cl1···H4*A*—C4

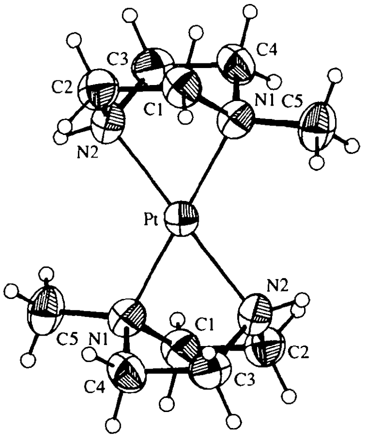


Fig. 1. View of the $[Pt(C_5H_{12}N_2)_2]^{2+}$ cation showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels and H atoms are drawn as small circles of arbitrary radii.

2.90 (2), Cl2···H3*B*—C3 2.82 (2), O1*W*···H1*B*—C1^{iii} 2.76 (1) and O1*W*···H4*B*—C4^{iv} 2.76 (2) Å; symmetry codes: (iii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (iv) $x, -y, \frac{1}{2}+z$.

Experimental

For the synthesis of *trans*-$[Pt(HMeppz)_2]^{2+}.2Cl^-.4H_2O$, a solution of free *N*-methylpiperazine (HMeppz, 98%, 0.113 ml, 1.0 mmol) in 5 ml water was reacted with $K_2[PtCl_6]$ (0.122 g, 0.25 mmol) dissolved in 5 ml water under stirring at 328 K. To the resulting yellow–orange solution, an aqueous solution containing HMeppz (0.028 ml, 0.25 mmol) and 10 *M* HCl (0.050 ml, 0.5 mmol) was added under stirring. The final golden yellow solution, at pH near 11, was cooled and left to stand at room temperature to concentrate slowly. After a week, yellow–brown crystals were obtained, filtered, washed with acetone–water (2:1 *v*/*v*) and dried under vacuum. Good quality single crystals for X-ray structure determination were obtained by slow recrystallization from a water solution. Yield 0.098 g, 73% (found: C 22.25, H 6.03, N 10.36, Cl 13.09%; calculated for $C_{10}H_{32}Cl_2N_4O_4Pt$: C 22.31, H 5.99. N 10.41, Cl 13.17%). The same synthesis using *N*,*N*′-dimethylpiperazine (Me_2ppz) in place of *N*-methylpiperazine did not give the expected $[Pt(Me_2ppz)_2]^{2+}$ cationic complex but the *cis*-$[PtCl_2(Me_2ppz)]$ complex already synthesized using the method of Mann & Watson (1958) and characterized by us using X-ray diffraction (Ciccarese, Clemente, Fanizzi, Marzotto & Valle, 1997). In fact, the elemental analysis, IR spectra and, in particular, the unit-cell determination by X-ray diffraction evidenced that, even if the Me_2ppz diamine is present with a large stoichiometric excess with respect to $K_2[PtCl_6]$, the *cis*-$[PtCl_2(Me_2ppz)]$ complex is always obtained. The formation of the $[Pt(Me_2ppz)_2]^{2+}$ cationic complex proved to be impossible probably because it is inhibited by steric hindrance between the two pairs of methyl groups that should be constrained to lie on the same side (Mann & Watson, 1958).

Crystal data

$[Pt(C_5H_{12}N_2)_2]Cl_2.4H_2O$
$M_r = 538.39$
Monoclinic
$C2/c$
$a = 10.501\ (2)$ Å
$b = 14.235\ (3)$ Å
$c = 12.485\ (2)$ Å
$\beta = 91.10\ (10)°$
$V = 1865.9\ (6)$ Å^3
$Z = 4$
$D_x = 1.916$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54180$ Å
Cell parameters from 25 reflections
$\theta = 14–18°$
$\mu = 16.873$ mm^{-1}
$T = 293\ (2)$ K
Irregular
0.5 × 0.1 × 0.1 mm
Yellow–brown

Data collection

Philips PW1100/20 diffractometer
ω–2θ scans
Absorption correction: refined from ΔF (*XABS*2; Parkin, Moezzi & Hope, 1995)
$T_{min} = 0.111$, $T_{max} = 0.185$
1384 measured reflections
1384 independent reflections

1092 reflections with $I > 2\sigma(I)$
$\theta_{max} = 60.01°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 14$
3 standard reflections every 60 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.073$
$wR(F^2) = 0.213$
$S = 1.055$
1384 reflections
118 parameters
Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.1731P)^2 + 4.749P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.032$
$\Delta\rho_{max} = 3.202$ e Å^{-3}
$\Delta\rho_{min} = -2.384$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Pt	1/4	1/4	0	0.0349 (5)
N1	0.3477 (7)	0.1438 (5)	−0.0713 (6)	0.040 (2)
N2	0.1229 (7)	0.1516 (5)	−0.0586 (6)	0.044 (2)
C1	0.2964 (9)	0.1389 (7)	−0.1828 (7)	0.047 (2)
C2	0.1488 (10)	0.1473 (7)	−0.1733 (8)	0.050 (2)
C3	0.1620 (14)	0.0640 (11)	−0.0079 (13)	0.056 (4)
C4	0.3060 (14)	0.0573 (10)	−0.0122 (12)	0.052 (3)
C5	0.4896 (9)	0.1489 (7)	−0.0724 (9)	0.053 (3)

Table 2. *Selected geometric parameters (Å, °)*

Pt—N1	2.041 (7)	N2—C2	1.464 (13)
Pt—N2	2.060 (7)	N2—C3	1.45 (2)
N1—C1	1.484 (12)	C1—C2	1.561 (14)
N1—C5	1.492 (12)	C3—C4	1.52 (2)
N1—C4	1.50 (2)		
N1—Pt—N2	70.7 (3)	C2—N2—C3	109.5 (9)
N1^i—Pt—N2	109.3 (3)	C2—N2—Pt	104.2 (6)
C1—N1—C5	109.8 (8)	C3—N2—Pt	104.6 (7)
C1—N1—C4	108.5 (8)	N1—C1—C2	105.6 (8)
C5—N1—C4	110.2 (8)	N2—C2—C1	106.3 (7)
C1—N1—Pt	105.5 (5)	N2—C3—C4	108.2 (11)
C5—N1—Pt	118.6 (6)	N1—C4—C3	105.4 (8)
C4—N1—Pt	103.8 (7)		

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$.

The intensities were corrected for Lorentz and polarization factors using *RIFLUP* (Biagini Cingi, Bandoli, Clemente & Tiripicchio, 1980). The structure was solved by the usual Fourier and Patterson method and several refinement cycles with isotropic displacement parameters for all the non-H atoms lowered the usual *R* factor to 0.11. At this point, an empirical absorption correction was performed. The refinement then continued with anisotropic displacement parameters for all the heavy atoms, while H atoms were refined isotropically with *U* fixed at $1.2U_{eq}$ of the N or C atom to which they are bonded, and at $1.5U_{eq}$ for the C5 methyl H atoms. The U_{iso} values of the H atoms bonded to O1*W* and O2*W* were refined.

Data collection: Philips PW1100/20 software. Cell refinement: Philips–Pavia University software. Data reduction: *RIFLUP*80. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1302). Services for accessing these data are described at the back of the journal.

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4-Methylpyridinium Pentachloro(4-methylpyridine-*N*)titanate(IV) Acetonitrile Solvate at 143 K

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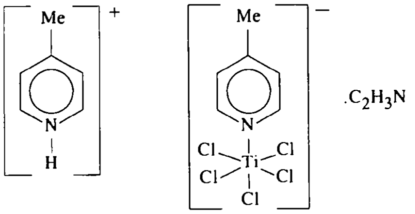
Abstract

The structure of the title compound, $(C_6H_8N)[TiCl_5(C_6H_7N)].C_2H_3N$, consists of discrete complexes in which the Ti atom has a distorted pseudo-octahedral coordination with a 4-methylpyridinium cation as counterion. The 4-methylpyridine ligand and one chloro ligand occupy axial positions with the other four chloro ligands in the equatorial plane. The acetonitrile solvent molecule occupies a cavity in the structure.

Comment

Our group has been investigating the interactions of organic nitrogen bases with halogensilanes and methylhalogensilanes for a long time (Hensen & Wagner, 1976; Hensen, Zengerly, Pickel & Klebe, 1983; Hensen, Zengerly, Müller & Pickel, 1988; Hensen, Roßmann & Bensch, 1992; Fleischer, Hensen & Stumpf, 1996). Silicon and titanium tetrahalides are strong Lewis acids and form Lewis acid–Lewis base adducts with electron-pair donors (Emeléus & Rao, 1958; Rao, 1960; Mazo, Bobilev & Troyanov, 1987; Lemke, 1996). Thus, titanium tetrachloride forms complexes with pyridine and 4-methylpyridine in a 1:2 ratio. The structure of the title compound, (I), has been determined as part of our studies on the structure and properties of adducts of titanium tetrahalides and tertiary amines.



(I)

The three molecules lie on a crystallographic mirror plane perpendicular to the *a* axis forming layers parallel to the (100) plane. The distance between the layers is 3.59 Å, that is *a*/2. The Ti atom in the $[TiCl_5(4\text{-}Mepy)]^-$ anion is pseudo-octahedrally coordinated with a 4-methylpyridinium cation as a counterion. This is the first structure of a pseudo-octahedral titanium complex consisting of one nitrogen and five halogeno ligands. The Ti atom deviates by 0.132 (1) Å from the plane of the equatorial Cl atoms towards the axial Cl atom, so that all N—Ti—Cl_{eq} angles are smaller and all Cl_{ax}—Ti—Cl_{eq} angles are wider than 90°. While the bond lengths between Ti and the two equatorial Cl atoms differ significantly, 2.349 (1) and 2.291 (1) Å for Ti1—Cl2 and Ti1—Cl3, respectively, the axial Ti1—Cl1 bond [2.309 (2) Å] is in the same range as the Ti1—Cl2 bond. The torsion angles Cl2—Ti1—N1—C2 and Cl3—Ti1—N1—C2, with values of −136.23 (3) and −45.68 (3)°, respectively, show that the aromatic plane almost exactly bisects the equatorial Cl—Ti—Cl angle. There are two short N—H···Cl contacts: H11···Cl1 2.567 (5) Å and N11—H11···Cl1 140.9 (1)°, and H11···Cl2 2.730 (5) Å and N11—H11···Cl1 130.34 (8)°.

Our original aim was to determine the structure of the compound which is formed by titanium tetrachloride and 4-methylpyridine in a 1:2 ratio. However, slight moisture in the solvent, even though it was dried through a molecular sieve, causes part hydrolyzation of $TiCl_4(4\text{-}Mepy)_2$ which leads to the title compound, (I). The only structure that is similar to the title compound is the $[TiCl_5(thf)]^-$ anion (Sobota, Utko & Lis, 1984). In this structure, the Ti atom deviates by 0.174 Å from the plane of the equatorial Cl atoms towards the axial Cl atom, but in contrast to the title compound, the bonds from the Ti atom to the equatorial Cl atoms are significantly longer (2.296 to 2.318 Å) than the axial Ti—Cl bond (2.249 Å).