(Enraf–Nonius, 1985*b*). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SDP OMEGA*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: FG1063). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1186–1188

Diammine(dimethylmalonato)platinum(II) Monohydrate

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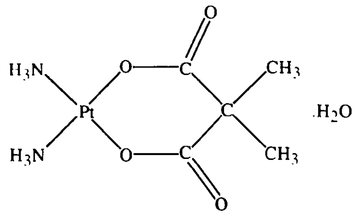
(*Received 22 June 1994; accepted 27 October 1995*)

Abstract

The complex molecule of the title compound, $[Pt(C_5H_6O_4)(NH_3)_2].H_2O$, assumes a boat conformation that is more planar than expected from an optimization of bond lengths and angles. Likely origins of this extra flattening are the repulsion between the Pt centre and the methyl group in the axial position, and hydrogen bonding with the water of crystallization.

Comment

Fig. 1 shows an *ORTEP*II (Johnson, 1976) drawing of the complex molecule, and Fig. 2 shows the crystal packing. The complex of the title compound, (I), possesses a mirror plane which contains the Pt, C(2), C(3) and C(4) atoms, and is perpendicular to the Pt coordination plane. The Pt atom exhibits usual square-planar coordination. The Pt—N and Pt—O bond distances are as expected for the *cis*-PtN_2O_2 chromophore (Rochon, Melanson, Macquet, Bellanger-Gariepy & Beauchamp, 1985, and references therein). There is one water molecule present in the lattice (Fig. 2), which is connected by hydrogen bonding to both ammine ligands of one molecule and to one carbonyl O atom [O(2)] of each of two other molecules. The compound is isostructural with the recently determined cyclopropylmalonato derivative (Dong *et al.*, 1990).



(I)

The molecule adopts a boat conformation, with the Pt and C(2) atoms at the bow and the stern, respectively, similar to that found in other malonato complexes of platinum(II) (Rochon, Melanson, Macquet, Bellanger-Gariepy & Beauchamp, 1985; Dong *et al.*, 1990). As in these complexes, the boat is flattened at the Pt end, with O—Pt—O—C torsion angles of ±41° (instead of ±60° if all the bond angles were tetrahedral) (Table 4). The C2 end of the boat is flattened as well, with C—C—C—O torsion angles of ±44° (Table 4). In order to find out whether this flattening is simply due to the strain introduced to the six-membered ring by the two perpendicular Pt—O bonds of 2.00 (6) Å, we have constructed energy-minimized models using the program *AMBER* (Weiner & Kollman, 1981). The energy function contained only bond and bond angle terms. The energy minimization resulted in a completely relaxed boat structure, with the bond lengths and bond angles having exactly the required values. The torsion angles of the relaxed model are given in Table 4. Their comparison with the experimental values shows that the boat is flattened at both ends more than expected for

Acta Crystallographica Section C
ISSN 0108-2701 ©1996

a strain-minimized structure. The extra flattening could result from the hydrogen-bonding network connecting the complex molecule with the water of crystallization. Specifically, the two hydrogen bonds connecting both NH_3 ligands of one Pt atom and a water molecule (Fig. 2) are likely to cause a flattening of the boat at the Pt end. In addition, the repulsion between the methyl H atom lying in the mirror plane and the Pt atom [H(4*b*)···Pt 2.51 (15) Å] could cause a flattening on the carboxylate side.

The C(1)—C(2)—C(1$^{\rm i}$) angle of 114.5 (6)° corresponds to a mean value found in platinum malonate complexes (Rochon, Melanson, Macquet, Bellanger-Gariepy & Beauchamp, 1985) and probably represents the best compromise between the sp^3 hybridization at C(2) and the mutual repulsion of the carboxylate groups.

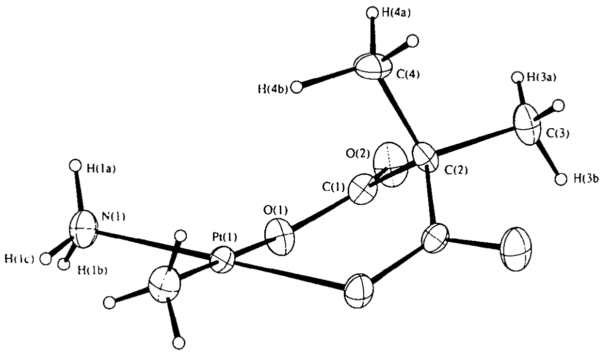


Fig. 1. *ORTEP*II (Johnson, 1976) drawing (30% probability ellipsoids) of the complex molecule of the title compound with the atom numbering.

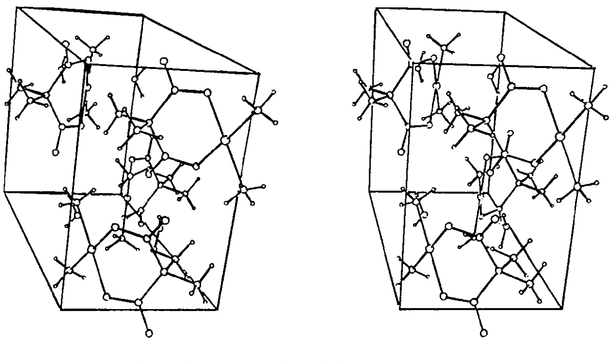


Fig. 2. Stereoview of the crystal packing.

Experimental

The title compound was prepared following the procedure outlined by Harrison & McAuliffe (1980) from equimolar amounts of *cis*-$[Pt(NH_3)_2(H_2O)_2](NO_3)_2$ and sodium dimethylmalonate, with a yield of 60%. Monocrystals were grown from an aqueous ethanol solution kept in a closed round-bottomed flask.

Crystal data

$[Pt(C_5H_6O_4)(NH_3)_2].H_2O$
$M_r = 377.27$
Orthorhombic
Pnma
$a = 6.5901$ (8) Å
$b = 9.4434$ (9) Å
$c = 14.983$ (2) Å
$V = 932.4$ (3) Å^3
$Z = 4$
$D_x = 2.69$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 18$–22°
$\mu = 15.84$ mm^{-1}
$T = 291$ K
Prism
0.35 × 0.35 × 0.20 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\rm min} = 0.07$, $T_{\rm max} = 0.25$
994 measured reflections
872 independent reflections

772 observed reflections $[I > 3\sigma(I)]$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 17$
2 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F
$R = 0.029$
$wR = 0.037$
$S = 1.05$
772 reflections
91 parameters
H atoms refined isotropically with an overall U
$w = [\Sigma_{r=1,3}A_rT_r(X)]^{-1} \times [1-\{(F_o-F_c)/6\sigma(F_o)\}^2]^2$ with three coefficients for the Chebyshev polynomial $T_r(X)$; $X = F_o/F_o(\max)$

$(\Delta/\sigma)_{\rm max} = 0.47$
$\Delta\rho_{\rm max} = 1.2$ e Å^{-3} (in proximity of Pt)
$\Delta\rho_{\rm min} = -1.3$ e Å^{-3} (in proximity of Pt)
Extinction correction: Larson (1970)
Extinction coefficient: 7.34×10^{-8}
Atomic scattering factors from *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985)

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

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

	x	y	z	$U_{\rm eq}$
Pt(1)	0.16835 (4)	1/4	0.03218 (2)	0.020 (2)
N(1)	0.1016 (9)	0.4024 (6)	0.1229 (3)	0.030 (2)
O(1)	0.2338 (6)	0.3997 (4)	−0.0583 (3)	0.027 (2)
O(2)	0.4412 (6)	0.4871 (4)	−0.1588 (3)	0.036 (2)
C(1)	0.3878 (8)	0.3874 (5)	−0.1116 (3)	0.022 (2)
C(2)	0.514 (1)	1/4	−0.1130 (5)	0.020 (2)
C(3)	0.652 (1)	1/4	−0.1932 (7)	0.031 (2)
C(4)	0.645 (2)	1/4	−0.0286 (6)	0.034 (2)
O(3)	0.221 (1)	1/4	0.2967 (4)	0.037 (2)

Table 2. *Selected bond lengths (Å) and angles (°)*

Pt(1)—N(1)	2.027 (5)	C(1)—C(2)	1.543 (6)
Pt(1)—O(1)	2.006 (4)	C(2)—C(3)	1.51 (1)
O(1)—C(1)	1.296 (7)	C(2)—C(4)	1.53 (1)
O(2)—C(1)	1.229 (6)		
N(1)—Pt(1)—N(1$^{\rm i}$)	90.4 (3)	C(2)—C(1)—O(2)	118.8 (5)
O(1)—Pt(1)—N(1)	90.0 (2)	C(2)—C(1)—O(1)	120.5 (4)
O(1)—Pt(1)—N(1$^{\rm i}$)	179.5 (2)	C(1)—C(2)—C(1$^{\rm i}$)	114.5 (6)

O(1)—Pt(1)—O(1^i)	89.6 (2)	C(3)—C(2)—C(1)	109.7 (4)
C(1)—O(1)—Pt(1)	121.4 (3)	C(4)—C(2)—C(3)	108.6 (7)
O(2)—C(1)—O(1)	120.7 (5)	C(4)—C(2)—C(1)	107.0 (4)

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
O3—H3···O2^i	2.0 (1)	2.784 (7)	145 (4)
N1—H1c···O3^{ii}	2.38 (9)	3.133 (7)	159 (4)

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (ii) $x - \frac{1}{2}, y, \frac{1}{2} - z$.

Table 4. *Torsion angles within the six-membered chelate ring (°)*

	Experimental	Model*
Pt(1)—O(1)—C(1)—C(2)	6	14
O(1)—C(1)—C(2)—C(1^i)	44	48
C(1)—C(2)—C(1^i)—O(1^i)	−44	48
C(2)—C(1^i)—O(1^i)—Pt(1)	−6	−14
C(1^i)—O(1^i)—Pt(1)—O(1)	41	59
O(1^i)—Pt(1)—O(1)—C(1)	−41	−59

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

* Values from model structure with bond lengths Pt—O 2.00, C—O 1.30 and C—C 1.52 Å, and bond angles O—Pt—O 90.0, Pt—O—C 109.5, O—C—C 109.5 and C—C—C 114.5°.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques. All H atoms could be located from the difference Fourier maps and were refined with an overall isotropic displacement parameter.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXS*86. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1135). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1188–1190

Tetrahydrogen 1,2-Bis(1,4,7-triaza-1-cyclononyl)ethane Tetrachlorocadmate

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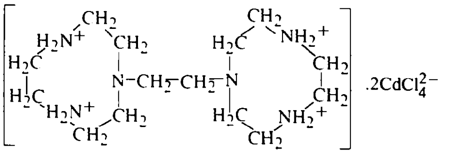
(*Received 1 September 1995; accepted 10 November 1995*)

Abstract

The title salt, $C_{14}H_{36}N_6^{4+}.2CdCl_4^{2-}$ [1,2-bis(1-aza-4,7-diazonia-1-cyclononyl)ethane tetrachlorocadmate], has been structurally characterized. Hydrogen bonds are formed from protons of the secondary amine N atoms to the $CdCl_4^{2-}$ anions and the tertiary amine N atoms. This suggests that the secondary amines of the tetraprotonated cation are protonated in the crystal as they appear to be in aqueous solution.

Comment

Hexaprotonated salts of α,ω-bis(1,4,7-triaza-1-cyclononyl)alkanes are strong diprotic acids in aqueous solution. Trends in acidity within the series indicate that protons attached to the tertiary amines are most acidic (Zhang, Hsieh, Margulis & Zompa, 1995). In the course of metal complexation studies with 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane, the title compound, (I), was isolated (see *Experimenatal*).



(I)

The crystal is composed of discrete ions linked by hydrogen bonds between the secondary-amine groups and the tetrachlorocadmate ion. The closest nonbonded distances of the secondary-amine N atoms include: N2···Cl2($-x, 1 - y, 2 - z$) 3.202 (6), N2···Cl1 ($x - 1, y + 1, z$) 3.253 (6), and N3···Cl2 ($x, y + 1, z$) 3.293 (6) Å. The shortest nonbonded contact to the tertiary amine N atom is N1···Cl2($-x, 1 - y, 2 - z$) 3.448 (6) Å. This indicates that the protons of the tetracation are likely to be associated with the secondary amines. The Cd—Cl bond distances range from 2.429 (1) to 2.504 (1) Å. The Cl—Cd—Cl bond angles range from 99.48 (5) to 114.77 (5)°, indicating considerable distortion probably