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Structure of *cis*-Dichloro[methylphosphinylidenebis(methylamine-*N*,*N'*)]platinum(II) Hemihydrate

BY JOSEF MACÍČEK

Institute of Applied Mineralogy, Bulgarian Academy of Sciences, Rakovski Str. 92, 1000 *Sofia, Bulgaria*

OLYANA ANGELOVA

Department of Chemistry, University of Sofia, A. Ivanov 1, 1126 *Sofia, Bulgaria*

AND NICOLAY DODOFF

Institute of Molecular Biology, Bulgarian Academy of Sciences, Acad. G. Bontchev Str., BL. 21, 1113 *Sofia, Bulgaria*

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Abstract. $[PtCl_2(C_3H_{11}N_2OP)].\frac{1}{2}H_2O$, M_r = 397·11, monoclinic, $C2/c$, a = 18·177 (3), b = 7·175 (4), c = 17·155 (1) Å, β = 119·97 (1)°, V = 1938 (1) Å^3, Z = 8, D_x = 2·722 g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 76·525 cm^{-1}, $F(000)$ = 1464, T = 292 K, R = 0·019 for 1514 observed reflections with $I > 3\sigma(I)$. Molecules of the complex placed in general positions are linked *via* hydrogen bonds to water molecules on twofold axes. The Pt atom is planar coordinated by two *cis* Cl atoms [Pt—Cl 2·311 (2), 2·300 (2) Å, Cl—Pt—Cl 91·53 (7)°] and two amino N atoms from the chelating ligand [Pt—N 2·048 (6), 2·038 (6) Å, N—Pt—N 93·9 (2)°]. The conformation of the six-membered chelate ring is a slightly distorted chair; Pt and P atoms deviate from the least-squares plane of the N_2C_2 fragment by −0·915 and 0·922 Å respectively. The phosphonyl O atom takes an axial position with respect to the ring.

Introduction. Since the establishment of the antitumor activity of *cis*-$[PtCl_2(NH_3)_2]$ by Rosenberg, van Camp, Trosko & Mansour (1969), various analogues of the parent compound have been synthesized and tested in order to find alternative drugs with lower toxicity and better solubility (Hacker, Douple & Krakoff, 1984). In this respect, special attention has been drawn to the platinum complexes of functionalized amines (Hydes & Russell, 1988). Recently Dodoff, Varbanov, Borisov & Spassovska (1990) reported the preparation, characterization and *in vivo* antitumor activity of a series of Pt^{II}, Pt^{IV} and Pd^{II} complexes of amine-containing phosphine oxide ligands, $(CH_2)_2P(O)CH_2NH_2$ and $CH_3P(O)(CH_2NH_2)_2$ (L). One of the compounds previously formulated as $[PtCl_2L].H_2O$ on the basis of elemental analysis and spectral data has been re-examined in the present X-ray structure analysis, which shows that the correct formula is $[PtCl_2L].\frac{1}{2}H_2O$.

Experimental. The title complex was prepared as described by Dodoff *et al.* (1990). Yellow crystals, suitable for X-ray analysis, were grown from a saturated aqueous solution. An irregularly shaped crystal with approximate dimensions 0·15 × 0·15 × 0·1 mm was examined. D_m was not determined. Intensity data were collected with an Enraf–Nonius CAD-4 diffractometer (graphite monochromator, Mo $K\alpha$ radiation); ω–2θ scan, scan speed 1–7° min^{-1}, $\Delta\omega$ = (0·8 + 0·4tanθ)°. Cell constants were determined

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Table 1. *Positional and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq} (Å^2)
Pt	0·13023 (1)	0·44223 (3)	0·38183 (1)	0·01980 (6)
Cl(1)	0·19063 (9)	0·7205 (3)	0·3746 (1)	0·0340 (5)
Cl(1)	0·1260 (1)	0·3350 (3)	0·2533 (1)	0·0416 (5)
P	0·09586 (9)	0·2166 (2)	0·5499 (1)	0·0229 (4)
O	0·0041 (2)	0·2629 (6)	0·5114 (3)	0·030 (1)
N(1)	0·1323 (3)	0·5427 (7)	0·4947 (3)	0·024 (1)
N(2)	0·0723 (3)	0·1989 (8)	0·3818 (3)	0·027 (1)
C(1)	0·1611 (4)	0·4202 (9)	0·5747 (4)	0·027 (2)
C(2)	0·1092 (4)	0·0883 (9)	0·4671 (4)	0·027 (2)
C(3)	0·1403 (4)	0·079 (1)	0·6480 (4)	0·042 (2)
O(*W*)	0·000	−0·121 (1)	0·250	0·060 (3)

Table 2. *Interatomic distances* (Å), *angles* (°) *and hydrogen-bond geometry* (Å,°) *with e.s.d.'s in parentheses*

Pt—Cl(1)	2·311 (2)	P—C(1)	1·793 (7)
Pt—Cl(2)	2·300 (2)	P—C(2)	1·808 (8)
Pt—N(1)	2·048 (6)	P—C(3)	1·759 (7)
Pt—N(2)	2·038 (6)	N(1)—C(1)	1·489 (8)
P—O	1·493 (4)	N(2)—C(2)	1·496 (8)
Cl(1)—Pt—Cl(2)	91·53 (7)	O—P—C(3)	115·2 (4)
Cl(1)—Pt—N(1)	87·8 (2)	C(1)—P—C(2)	105·6 (3)
Cl(1)—Pt—N(2)	177·2 (1)	C(1)—P—C(3)	107·2 (3)
Cl(2)—Pt—N(1)	178·7 (1)	C(2)—P—C(3)	106·8 (3)
Cl(2)—Pt—N(2)	86·8 (2)	Pt—N(1)—C(1)	119·7 (4)
N(1)—Pt—N(2)	93·9 (2)	Pt—N(2)—C(2)	118·3 (3)
O—P—C(1)	112·6 (3)	P—C(1)—N(1)	112·1 (3)
O—P—C(2)	108·9 (3)	P—C(2)—N(2)	109·1 (4)

D—H···*A*	*D*···*A*	*D*—H···*A*
O(*W*)—H(*W*)···Cl(1^{i})	3·235 (5)	140 (9)
N(1)—H(11N)···O^{ii}	2·801 (7)	153*
N(1)—H(12N)···Cl(1^{iii})	3·326 (3)	147*
N(2)—H(21N)···O(*W*)	3·024 (8)	139*
N(2)—H(22N)···Cl(2^{iv})	3·312 (5)	147*

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, 1-y, 1-z$; (iii) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$; (iv) $-x, y, \frac{1}{2}-z$.

* Angle illustrating the directionality of the hydrogen bond based on the calculated H-atom position.

from a least-squares fit of 22 reflections with $20·4 < \theta < 21·2°$. 3908 reflections were measured with $(\sin\theta)/\lambda < 0·616$ Å^{-1} (h 0 to 21, k −8 to 8, l −21 to 18). Three standard reflections were monitored every 2 h. As the intensity variation was less than 1% no decay correction was applied. The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on ψ scans of five reflections (transmission factors 68·930–99·875%) was used. 2052 unique reflections ($R_{int} = 0·019$) were measured, 653 of which were considered unobserved [$I < 3\sigma(I)$]. The structure was solved by the heavy-atom method and refined by full-matrix least squares on F. H atoms [calculated positions for tetrahedral NH_2, CH_2 and CH_3 (staggered) groups; H_2O localized from difference Fourier synthesis] were included in the refinement as riding atoms with fixed U's. The refinement converged at $R = 0·019$, $wR = 0·029$ and $S = 1·034$ with weights defined as $w = 4(F_o)^2/[\sigma(F_o)^2]^2$; $(\Delta/\sigma)_{max} = 0·22$. The maximum and minimum residual densities were 0·56 and −1·29 e Å^{-3} in the vicinity of Pt. No correction was applied for secondary extinction. Atomic scattering factors and anomalous-dispersion coefficients were taken from the *SDP/PDP* package (Enraf–Nonius, 1985) operating on a PDP11/44 computer. The conformational analysis of the chelate ring was performed with the program *CONPUC* (Boeyens & Evans, 1989; Evans & Boeyens, 1989) adapted by one of us (JM).

Discussion. Final fractional coordinates are given in Table 1.* The atomic labelling scheme is depicted in Fig. 1 and the molecular packing is shown in Fig. 2. The interatomic distances and angles are summarized in Table 2.

Pt is planar *cis*-coordinated by two Cl atoms and two chelating amino-N atoms. The Pt—Cl(1) distance of 2·311 (2) Å is longer than the Pt—Cl(2) distance [2·300 (2) Å], probably due to the participation of Cl(1) in hydrogen bonding with the water molecule. In the *A* form of *cis*-$Pt(CH_3NH_2)_2Cl_2$ (Wimmer, Wimmer, Jaud, Johnson & Castan, 1988),

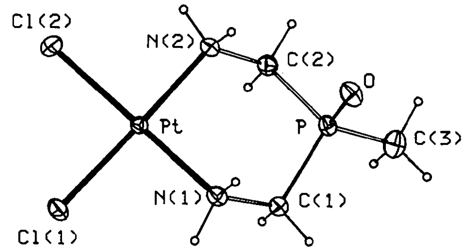

Fig. 1. *ORTEP* plot of the $[PtCl_2\{CH_3PO(CH_2NH_2)_2\}]$ molecule and the atom labelling. 30% probability thermal ellipsoids are shown. H atoms are arbitrarily reduced.

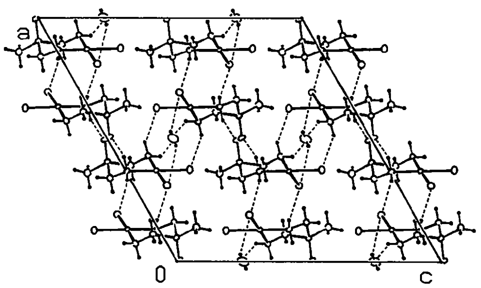

Fig. 2. Projection of the structure down the b axis. Dashed lines denote hydrogen bonds.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53740 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the Pt—Cl distances are similar [2·306 (2) and 2·308 (2) Å] but vary significantly [from 2·284 (2) to 2·334 (2) Å] in the three independent molecules of the *B* form of the complex. In *cis*-[$PtCl_2(NH_3)_2$] (Milburn & Truter, 1966) these distances are equally elongated [2·328 (9) and 2·333 (9) Å], whereas in the two independent molecules of the *cis*-Pt[$(CH_3)_2NH]_2Cl_2$ complex (Arpalahti, Lippert, Schollhorn & Thewalt, 1988), the Pt—Cl bond lengths have values ranging from 2·294 (5) to 2·312 (5) Å.

The Pt—N(1) and Pt—N(2) distances [2·048 (6) and 2·038 (6) Å respectively] are slightly longer than the analogous distances in the *A* form of *cis*-Pt$(CH_3NH_2)_2Cl_2$ (Wimmer *et al.*, 1989) [2·027 (7), 2·040 (7) Å] and lie within the interval of 2·034 (6)–2·084 (6) Å for bond lengths in the alternative *B* form. In *cis*-[$PtCl_2(NH_3)_2$] (Milburn & Truter, 1966), the less accurate values are 1·95 (3) and 2·05 (4) Å and in *cis*-Pt[$(CH_3)_2NH]_2Cl_2$ (Arpalahti *et al.*, 1988) these distances range from 2·05 (1) to 2·06 (2) Å.

The C—N distances have normal lengths. The endocyclic P—C bonds [average 1·801 (8) Å] are slightly longer than the exocyclic bond [1·759 (7) Å]. The P—O distance of 1·493 (4) Å corresponds to the P═O double bond which participates in hydrogen bonding (Blessing, 1988). The conformation of the six-membered chelate is a slightly distorted chair (Boeyens, 1978), which follows from the values of the ring-puckering parameters (Cremer & Pople, 1975), $q = 0{\cdot}701$ Å, $\theta = 10{\cdot}6°$, $\varphi = 203{\cdot}1°$.

The shortest Pt···Pt distances are between the complex molecules related by the centre of symmetry at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ [4·634 (1) Å] and the twofold axis at $\frac{1}{4},y,0$ [5·037 (1) Å]. In *cis*-[$PtCl_2(NH_3)_2$] the Pt···Pt distances are much shorter [3·372 (2) and 3·409 (2) Å] and Milburn & Truter (1966) suggested that there was an interaction between the orbitals of the Pt atoms. In *cis*-Pt[$(CH_3)_2NH]_2Cl_2$ (Arpalahti *et al.*, 1988), the Pt separation distances are 5·514 and 5·576 Å.

The complex molecules are linked by a system of hydrogen bonds. Both amino groups and the water molecule perform a hydrogen-donating function and all electron-rich sites (the Cl, phosphoryl and water O atoms) act as hydrogen-bond acceptors.

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Structure of (4*α*)-Kaura-9(11),16-dien-18-oic Acid (Grandiflorenic Acid), an Active Ingredient of the Mexican Medicinal Plant Zoapatle

By William F. Reynolds, Alan J. Lough and Jeffery F. Sawyer

Department of Chemistry, University of Toronto, 80 *St George Street, Toronto, Ontario M*5*S* 1*A*1, *Canada*

and Raul G. Enriquez, Benjamin Ortiz and Fernando Walls

Instituto de Quimica, Universidad Autonoma de Mexico, Circuito Interior, Ciudad Universitaria Mexico,
DF Mexico 04510

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Abstract. Grandiflorenic acid, $C_{20}H_{28}O_2$, $M_r = 300{\cdot}44$, monoclinic, $P2_1$, $a = 10{\cdot}697\,(1)$, $b = 11{\cdot}476\,(2)$, $c = 14{\cdot}229\,(2)$ Å, $\beta = 98{\cdot}86\,(1)°$, $V = 1725{\cdot}8$ Å^3, $Z = 4$, $D_x = 1{\cdot}159$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}7$ cm^{-1}, $F(000) = 656$, $T = 298$ K, $R(wR) = 0{\cdot}0478\ (0{\cdot}0576)$ for 2007 reflections with $I \geq$

0108-2701/91/050973-05$03.00