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Structure of Trichloro(7-8- η -morphinium)platinum(II) Hemihydrate Acetone Solvate, $[\text{PtCl}_3(\text{C}_{17}\text{H}_{20}\text{NO}_3)] \cdot \text{C}_3\text{H}_6\text{O} \cdot 0.5\text{H}_2\text{O}$

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Abstract. $M_r = 654.9$, tetragonal, $P4_2,2$, $a = 9.468$ (4), $c = 52.30$ (1) Å, $V = 4688.3$ Å³, $Z = 8$, $D_m = 1.85$ (1), $D_x = 1.855$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å (graphite monochromator), $\mu(\text{Mo } K\alpha) = 6.42$ mm⁻¹, $F(000) = 2552$, $T = 293$ K, $R = 0.039$, 1537 nonzero reflections [$I > 3\sigma(I)$]. Pt forms a square-planar complex with three Cl atoms [Pt–Cl 2.320 (4), 2.291 (5), 2.313 (5) Å] and the middle of the C(7)–C(8) double bond [Pt–C(7) 2.168 (13), Pt–C(8) 2.132 (14) Å]. The PtCl_3 units stand on the top of the horizontal arms of the T-shaped morphine moiety.

Introduction. In a previous paper (Macquet & Beauchamp, 1984), we reported the preparation of the title compound and briefly commented on its crystal structure. A detailed account of the crystallographic work is given in the present paper.

Experimental. Crystals obtained as described earlier (Macquet & Beauchamp, 1984). Density measured by flotation in $\text{CCl}_4\text{-CHBr}_3$. Yellow prism, 0.15 mm (102–102) \times 0.18 mm (001–001) \times 0.42 mm (012–012). Cell parameters derived from least-squares fit on angles for 24 reflections ($12 < \theta < 16^\circ$) centered on Enraf–Nonius CAD-4 diffractometer. Laue symmetry (4/ mmm) and systematic absences (00 l , $l \neq 4n$; $h00$, $h \neq 2n$; $0k0$, $k \neq 2n$) derived from precession and

cone-axis photographs were consistent with space groups $P4_2,2$ and $P4_3,2,2$.

Data collected as described elsewhere (Bélanger-Gariépy & Beauchamp, 1980). Reflection sphere: $2\theta \leq 50^\circ$, $0 \leq h \leq 11$, $k \leq h$, $0 \leq l \leq 61$. Fluctuations of 3 standards $< \pm 2\%$. 2531 unique reflections measured, 994 unobserved [$I < 3\sigma(I)$], 1537 observed. Data corrected for the Lorentz effect, polarization and absorption (Gaussian integration, grid $10 \times 10 \times 10$, transmission range 0.34–0.44).

Structure solved by the heavy-atom method and refined on $|F|$ by full-matrix least squares. H atoms whose positions were predictable from C skeleton fixed at calculated positions ($B = 5.0$ Å²). Remaining H atoms neglected. Refinement of scale factor, coordinates and anisotropic temperature factors of non-hydrogen atoms. H atoms not refined, but repositioned after each cycle. $R = 0.039$, $wR = 0.044$, $S = 1.46$ for $m = 1537$ and $n = 271$. w based on counting statistics (Authier-Martin & Beauchamp, 1977). Δ/σ in last cycle, max. 0.12, av. 0.04. Background in final difference Fourier map 0.55 e Å⁻³, 6 peaks within ± 10.6 – 1.1 e Å⁻³ near Pt or Cl.

No attempt was made to refine the enantiomorphic structure (in $P4_2,2$), since torsion angles corresponded to the known absolute configuration of morphine (Bye, 1976; Gylbert, 1973).

Scattering curves from Cromer & Waber (1965) and Stewart, Davidson & Simpson (1965). Anomalous-dispersion terms for Pt and Cl from Cromer (1965). Computer programs listed elsewhere (Authier-Martin & Beauchamp, 1977).

Table 1. Refined coordinates ($\times 10^4$, Pt $\times 10^5$) and equivalent isotropic temperature factors ($\times 10^3$)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Pt	7408 (7)	-917 (8)	11103 (1)	31
Cl(1)	-397 (5)	-44 (6)	1503 (1)	56
Cl(2)	366 (5)	-2480 (5)	1092 (1)	50
Cl(3)	952 (5)	2338 (5)	1135 (1)	43
O(1)	2808 (14)	-2074 (15)	-169 (2)	59
O(2)	-273 (10)	978 (12)	394 (2)	38
O(3)	2297 (12)	400 (12)	151 (2)	40
O(4)†	930 (31)	930	5000	84
O(5)‡	5660 (26)	1829 (26)	2119 (4)	187
N(1)	5976 (14)	1537 (16)	888 (2)	37
C(1)	5282 (24)	-2521 (20)	358 (4)	62
C(2)	4568 (21)	-2745 (21)	135 (3)	61
C(3)	3545 (21)	-1750 (20)	39 (3)	52
C(4)	3385 (17)	-578 (18)	185 (3)	33
C(5)	2317 (17)	1367 (18)	380 (3)	29
C(6)	973 (14)	1067 (17)	538 (3)	27
C(7)	1206 (16)	-220 (16)	705 (3)	26
C(8)	2434 (14)	-388 (16)	847 (3)	22
C(9)	4988 (18)	281 (17)	911 (3)	29
C(10)	5639 (17)	-1031 (19)	777 (3)	35
C(11)	5081 (22)	-1247 (18)	501 (3)	46
C(12)	4127 (17)	-306 (17)	401 (3)	33
C(13)	3691 (17)	1070 (17)	528 (3)	30
C(14)	3506 (16)	744 (18)	819 (3)	28
C(15)	4766 (18)	2242 (18)	489 (3)	35
C(16)	6151 (19)	1996 (21)	615 (3)	48
C(17)	7343 (17)	1359 (21)	1016 (3)	45
C(18)‡	5078 (41)	876 (32)	2016 (9)	242
C(19)‡	3578 (45)	686 (42)	2056 (8)	239
C(20)‡	5991 (31)	111 (33)	1873 (5)	139

† Water.

‡ Acetone.

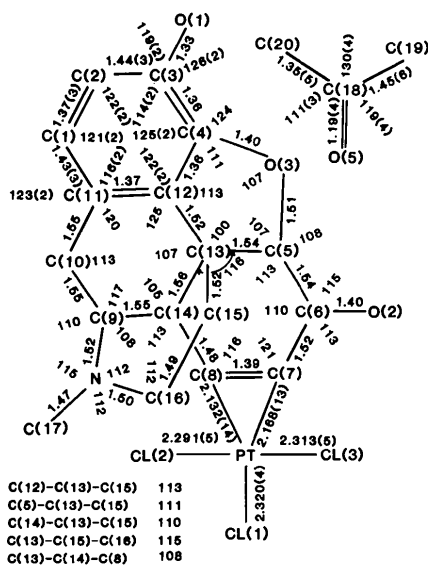


Fig. 1. Numbering scheme, interatomic distances (\AA) and bond angles ($^\circ$) in the $\text{PtCl}_3(\text{morphinium})$ molecule. Unless otherwise stated, the e.s.d.'s are 0.02 \AA and 1 $^\circ$.

Table 2. Bond angles ($^\circ$) around platinum and hydrogen-bond distances (\AA)

Cl(1)-Pt-Cl(2)	89.1 (2)	Cl(3)-Pt-C(7)	95.3 (4)
Cl(1)-Pt-Cl(3)	88.4 (2)	Cl(3)-Pt-C(8)	95.9 (4)
Cl(1)-Pt-C(7)	163.9 (4)	C(7)-Pt-C(8)	37.7 (6)
Cl(1)-Pt-C(8)	157.5 (4)	Pt-C(7)-C(8)	69.7 (8)
Cl(2)-Pt-Cl(3)	176.0 (2)	Pt-C(7)-C(6)	119.3 (10)
Cl(2)-Pt-C(7)	86.3 (4)	Pt-C(8)-C(7)	72.6 (9)
Cl(2)-Pt-C(8)	87.7 (4)	Pt-C(8)-C(14)	118.9 (10)
O(1)-H...O(2 ^b)	2.70 (2)	O(4)-H...O(5 ^b)	2.92 (3)
O(2)...H-O(1 ^b)	2.70 (2)	O(4)-H...O(5 ^b)	2.92 (3)
O(4)...H-O(2 ^b)	2.81 (2)	N(1)-H(163)...Cl(1 ^b)	3.33 (2)
O(4)...H-O(2 ^b)	2.81 (2)	N(1)-H(163)...Cl(2 ^b)	3.14 (1)

Symmetry code: (i) $y, x, -z$; (ii) $-x, -y, \frac{1}{2}+z$; (iii) $-y, -x, \frac{1}{2}-z$; (iv) $\frac{1}{2}-y, -\frac{1}{2}+x, \frac{1}{2}+z$; (v) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; (vi) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Discussion. Refined coordinates are listed in Table 1.* The $[\text{PtCl}_3(\text{morphinium})]$ zwitterion is schematically represented in Fig. 1 where interatomic distances and bond angles are also given.

The morphinium moiety is π -bonded to the PtCl_3 unit via the C(7)-C(8) double bond, as in Zeise's salt (Love, Koetzle, Williams, Andrews & Bau, 1975). An ORTEP drawing of the molecule is provided in our previous paper (Macquet & Beauchamp, 1984). The Pt-Cl and Pt-olefin distances are similar to those found in Zeise's salt and the coordination of Pt is roughly square planar (Table 2) as expected.

The morphine ligand retains the overall T shape found in the free molecule (Bye, 1976; Gylbert, 1973), an angle of 88 $^\circ$ being found between the top (olefinic ring and N-containing ring) and the vertical portion (aromatic ring, oxide ring and third ring attached to both of them). Our torsion angles (deposited) agree well with those reported by Bye (1976) for neutral morphine and by Gylbert (1973) for its hydrochloride. The interatomic distances and bond angles in the morphine unit (Fig. 1) have not been appreciably affected by complexation. The only exception is the coordinated C(7)-C(8) double bond [1.39 (3) \AA] which appears to be longer than in the free state (av. 1.33 \AA) (Bye, 1976; Gylbert, 1973; Kartha, Ahmed & Barnes, 1962; Arzeno, Barton, Davies, Lusinchi, Meunier & Pascard, 1980). The nearby C(5)-C(6)-C(7) and C(7)-C(8)-C(14) angles have also decreased by $\sim 3^\circ$ in the complex.

The crystal is stabilized by two systems of H bonds involving water and acetone molecules, as well as two regions of the $\text{PtCl}_3(\text{morphinium})$ complex (Fig. 2). Two molecules related by a twofold axis along the ab diagonal are paired by means of two strong

* Lists of structure factors, anisotropic temperature factors, coordinates of the fixed hydrogen atoms, torsion angles, the geometry of the hydrogen bonds, and details on weighted least-squares plane calculations, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42030 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

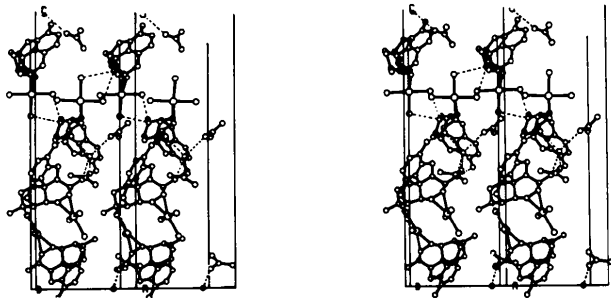


Fig. 2. Stereoview of the unit cell of PtCl₃(morphinium) hemihydrate acetone solvate. Only the 0–c/2 portion is shown. The atoms are represented by spheres of arbitrary sizes. The H bonds are represented by dashed lines.

O(1)–H...O(2) hydrogen bonds [O(1)–O(2) = 2.70 (2) Å, Table 2]. At the same time, the H attached to O(2) forms an additional H bond with the water molecule O(4). As for the H atoms of water, they act as donors in H bonds with the carbonyl groups O(5) of two acetone molecules. The interactions surrounding O(4) are, however, weaker than those responsible for molecular pairing. The second system of H bonds links these pairs into a helical chain running roughly along the *c* direction. They involve the ammonium N–H bond and the coordinated Cl atoms, which are the presumed sites of charge concentration in the zwitterion. The N–H bond is pointing roughly halfway between Cl(1) and Cl(2). The N–Cl distances [3.14 (1) and 3.33 (2) Å, respectively] lie well below the upper limit of 3.54 Å proposed by Stout & Jensen (1968) for this type of H bond.

In summary, this structure shows that the PtCl₃ group forms a normal olefinic complex with the morphinium moiety, without direct participation of other potential donor sites, such as the hydroxyl groups, the exocyclic O or the aromatic system.

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Structure of Tetraphenylphosphonium Bis(benzenethiolato)aurate(I), [P(C₆H₅)₄][Au(C₆H₅S)₂]

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Abstract. *M_r* = 754.7, hexagonal, *P*6₁, *a* = 9.746 (3), *c* = 56.552 (11) Å, *U* = 4652 Å³, *Z* = 6, *D_m* = 1.63, *D_x* = 1.617 g cm⁻³, Mo *K*α, λ = 0.71073 Å, μ =

50.7 cm⁻¹, *F*(000) = 2232, room temperature, *R* = 0.034 using 882 data. The coordination about the gold atom is found to be linear with Au–S bond lengths of 2.271 (8) and 2.262 (8) Å. The two S–C bond lengths are 1.79 (1) and 1.80 (1) Å suggesting purely σ nature. The two Au–S–C angles are consistent with tetrahedral S atoms.

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