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Structure of (1,3,6,8,10,13,16,19-Octaazabicyclo[6.6.6]icosane)platinum(IV) Dithionate 2½ Hydrate

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Abstract. [Pt(C₁₂H₃₀N₈)](S₂O₆)₂·2½H₂O, C₁₂H₃₀N₈·Pt⁴⁺·2S₂O₆²⁻·2½H₂O, FW = 846.78, monoclinic, *P*2₁/*c*, *a* = 18.250 (3), *b* = 9.264 (1), *c* = 17.461 (3) Å, β = 121.50 (1)°, *U* = 2614.8 (5) Å³, *Z* = 4, μ = 6.04 mm⁻¹, *D*_x = 2.151 Mg m⁻³. The cage-shaped ligand in which the metal ion is encapsulated is sexidentate in this complex. The geometry of the cage structure depends on the nature of the central metal atom. The three non-equivalent N–C bonds differ significantly from each other [1.498 (7), 1.421 (8) and 1.532 (8) Å]. The tris(ethylenediamine)Pt^{IV} moiety of the complex has a *le*₃ conformation. The complex is hydrogen bonded to dithionate ions and water molecules to form a network in the *c* and *b* directions.

Introduction. The macrocyclic title complex offers interesting prospects for the study of intramolecular rearrangements, electron transfer and spectroscopic properties. With this ligand, a metal ion could be in different oxidation states without seriously changing its coordination number or the structure. Moreover, cage complexes are usually mononuclear (Creaser, Harrowfield, Herlt, Sargeson, Springborg, Geue & Snow, 1977). In this connection, the crystal structure of the title complex, trivially represented as [Pt(sepulchrate)](S₂O₆)₂·2½H₂O, was determined. The [Pt(sepulchrate)]⁴⁺ was prepared by condensation of a

formaldehyde and an ammonia with an ethylenediamine complex of Pt. The prismatic transparent crystals were kindly supplied by A. Sargeson of the Australian National University. The crystal used for the intensity measurements was bounded by ±(110), (1̄10), (001) and (111), with interplanar spacings of 0.10, 0.16, 0.15 and 0.25 mm respectively. X-ray diffraction data were collected within the range 2θ < 65° on an automated four-circle diffractometer, using graphite-monochromated Mo *K*α radiation (λ = 0.7107 Å). Four standard reflections counted at 50-reflection intervals indicated considerable decay (5–15%) during the two weeks of data collection. The intensity measurements were completed by employing six different sets of setting parameters based on the same 18 reflections in order to obtain the average structure.

Structure determination was carried out on 6305 independent reflections with |*F*_o| ≥ 3σ(|*F*|). Corrections were applied to the net intensities to account for Lorentz and polarization effects and for absorption. The lattice constants showed 0.08 Å elongations in *a* and *c*, while that of *b* showed a shrinkage of 0.06 Å during the period of data collection. The coordinates of the Pt and S atoms, derived from the sharpened Patterson maps, were used for a structure factor calculation which gave an *R* value of 0.382. Successive Fourier and difference syntheses revealed the remaining

non-hydrogen and H atoms. The structure was refined by block-diagonal least squares and the final *R* became 0.057. The data were divided into six blocks according to different settings, and the six scale factors employed for the six blocks were also refined. Water molecules were added as indicated by difference density maps. Anisotropic thermal parameters were used for the non-hydrogen atoms and anomalous dispersion was taken into account. The H atoms could be located on the difference Fourier maps and their coordinates and isotropic thermal parameters were fixed during the refinement. Atomic scattering factors for the non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974), and those for H from Stewart, Davidson & Simpson (1965). The atomic fractional coordinates are listed in Table 1. At

Table 1. Fractional atomic coordinates for the non-hydrogen atoms ($\times 10^4$, for Pt $\times 10^5$) with corresponding e.s.d.'s

	<i>x</i>	<i>y</i>	<i>z</i>
Pt	24677 (2)	22157 (4)	26752 (2)
N(1)	3445 (5)	3236 (10)	3780 (6)
N(2)	1592 (5)	3685 (9)	2571 (6)
N(3)	2691 (5)	3354 (10)	1800 (6)
N(4)	3401 (5)	746 (10)	2950 (6)
N(5)	2106 (5)	1119 (9)	3441 (6)
N(6)	1568 (5)	1186 (10)	1517 (6)
N(7)	2747 (5)	5224 (11)	2770 (6)
N(8)	2159 (5)	-810 (10)	2523 (7)
C(1)	3431 (8)	4820 (13)	3636 (9)
C(2)	1895 (8)	5182 (12)	2601 (9)
C(3)	2840 (7)	4895 (13)	2036 (8)
C(4)	4276 (6)	2592 (13)	3986 (7)
C(5)	1407 (7)	3356 (12)	3287 (7)
C(6)	1943 (7)	3103 (12)	868 (7)
C(7)	4149 (6)	1060 (13)	3867 (8)
C(8)	1714 (7)	1585 (14)	775 (7)
C(9)	1305 (7)	1800 (13)	3303 (8)
C(10)	1595 (8)	-398 (13)	1636 (9)
C(11)	3067 (7)	-730 (13)	2863 (9)
C(12)	1960 (8)	-426 (14)	3185 (9)
S(1)	4017 (2)	882 (3)	1051 (2)
S(2)	4863 (2)	2470 (3)	1890 (2)
S(3)	725 (2)	8445 (3)	4628 (2)
S(4)	890 (2)	6618 (3)	4062 (2)
O(1)	3763 (6)	188 (10)	1604 (6)
O(2)	3304 (5)	1634 (9)	311 (5)
O(3)	4486 (6)	53 (11)	772 (6)
O(4)	4342 (6)	3179 (11)	2144 (8)
O(5)	5613 (7)	1841 (12)	2598 (8)
O(6)	4990 (8)	3281 (14)	1282 (8)
O(7)	1193 (8)	9485 (11)	4481 (9)
O(8)	1062 (7)	8165 (11)	5552 (6)
O(9)	-197 (6)	8607 (13)	4125 (7)
O(10)	257 (6)	5677 (11)	4025 (8)
O(11)	1758 (6)	6158 (10)	4653 (7)
O(12)	720 (6)	7046 (11)	3187 (6)
OW(1)	3287 (7)	4688 (11)	185 (7)
OW(2)	3314 (7)	7390 (15)	329 (11)
OW(3)	73 (17)	7394 (31)	1265 (18)

the final stage of the refinement,* the positional shifts were all less than one eighth of the corresponding standard deviations. The six scale factors converged within the range 1.2522–1.3797.

Discussion. Fig. 1 shows the complex ion with average bond lengths and angles. The complex ion has approximate *D*₃ symmetry with a pseudo threefold axis along N(7)–N(8) which is about 8° from the *b* axis. The cage-shaped ligand is sexidentate, and encapsulates the metal ion. The six N atoms coordinated to the central Pt^{IV} ion form a distorted octahedron, the [PtN₆] cluster being contracted along the pseudo threefold axis. The [PtN₆] exhibits distortion from trigonal-prismatic coordination with a twist angle between two triangular faces of 16(3)° (Fleischer, Gebala & Tasker, 1970; Donaldson, Tasker & Alcock, 1977). The average bite angle of the five-membered chelate ring is 84.5(4)° and other N–Pt–N angles range from 90.2 to 94.4°. The geometry of the complex ion can be most conveniently described as having a tris(methylene)amino cap attached to each end of a tris(ethylenediamine) complex. The three ethylenediamine chelate rings take the *lel* conformation. The average N–C bond length of the ethylenediamine chelate ring, 1.498(7) Å, is a typical value. However, the N–C_{cage} bonds are longer and the N_{cap}–C_{cage} bonds are shorter than this, with average lengths of 1.532(7) and 1.421(8) Å, respectively. Consequently the capped part is farther from the

* Lists of structure factors, anisotropic thermal parameters and H atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34740 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

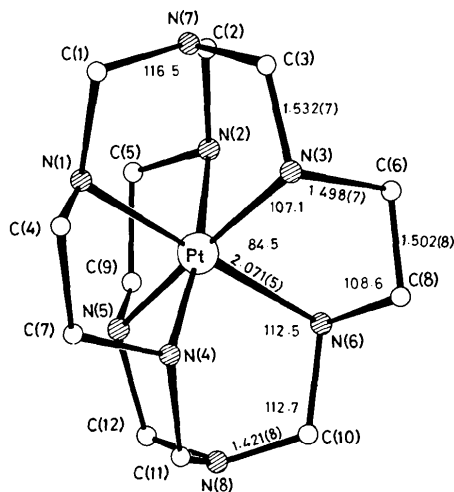


Fig. 1. The complex cation with average bond lengths (Å) and angles (°). The e.s.d.'s given for average bond lengths are the root mean square errors, and the average e.s.d. for angles is 0.7°.

Pt atom, and the complex appears to be elongated in that direction. This effect is more pronounced in the Pt complex than in the analogous Co complex. In [Co(sepulchrates)]³⁺, average distances are for N—C_{cage} 1.523 (7) Å and for N_{cap}—C_{cage} 1.443 (8) Å, and the difference between them is much smaller (Creaser *et al.*, 1977). The bond angles inside the cage are larger than tetrahedral and the N—C—N angles range from 111.7 to 114.0°. The N_{cap} atoms deviate by about 0.26 (2) Å from the planes defined by the three C_{cage} atoms.

Figs. 2 and 3 illustrate the packing features of the structure along the *b* and *a* axes respectively. The

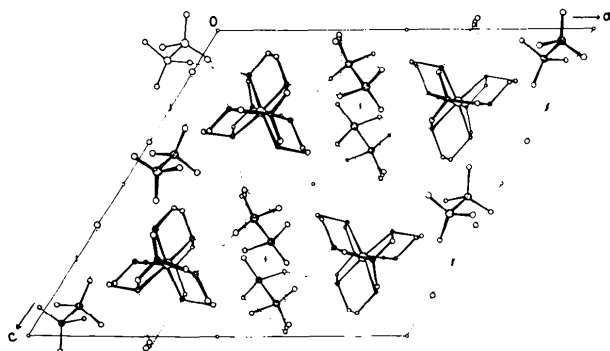


Fig. 2. *b*-Axis projection of the structure.

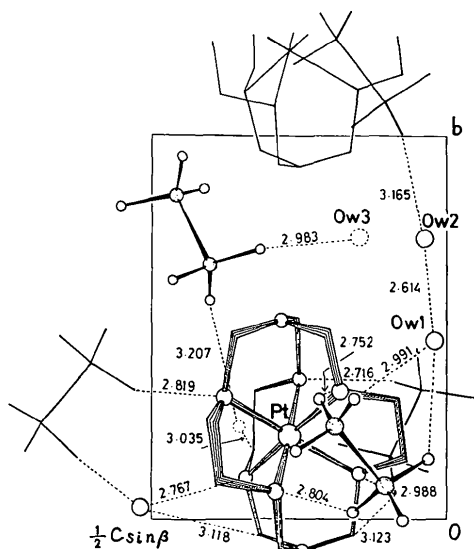


Fig. 3. The structure viewed along the *a* axis with intermolecular distances shorter than 3.20 Å indicated by broken lines. The corresponding e.s.d.'s range from 0.09 to 0.19 Å.

complex ion is hydrogen bonded to five O atoms of the dithionate ions and a water molecule in three directions. The *lel* conformation of the complex seems to be stabilized by these hydrogen bonds. The complex, dithionate ions and water molecules are linked by the hydrogen bonds forming a network in the *c* and *b* directions. These hydrogen-bond distances range from 2.752 (14) to 3.165 (16) Å. The dithionate ion has a staggered conformation. The average S—S—O and O—S—O angles are 113.7 (7) and 104.7 (5)° respectively. The average bond lengths are 2.117 (4) for S—S and 1.434 (12) Å for S—O. From a study of the difference Fourier syntheses it was clear that there are two distinct water molecules of crystallization, and one disordered water [OW(3)] with a smaller population in the asymmetric unit. The population of the disordered water was estimated to be 0.25–0.50 from the peak heights and its thermal parameters. The two regularly arranged water molecules are hydrogen bonded to each other at 2.61 (1) Å, and the disordered OW(3) is located between the two N_{cap}'s of adjacent complex cations related by a unit translation along *b*, being slightly closer to the complex in the +*b* direction.

The considerable changes in the lattice constants observed during the two weeks of X-ray exposure may be interpreted as follows. If the water molecules OW(3) are partly dehydrated or displaced by X-ray irradiation or by other means, the distance between the complexes in the *b* direction is expected to be shortened, resulting in the expansion of the layers of hydrogen-bonded complexes and counter anions. This may give rise to contraction in *b* and expansion in *a* and *c*; these were actually observed in the experiment. Thus the changes in the lattice constants may be reasonably accounted for by the behavior of the disordered water molecules and the resulting structural changes.

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