

Dichloro(7,16-dimethyl-1,4,10,13-tetrathia-7,16-diazacyclooctadecane)diplatinum Bis(hexafluorophosphate)

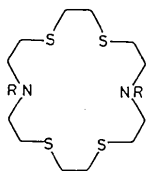
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Abstract. $[\text{Pt}_2\text{Cl}_2(\text{C}_{14}\text{H}_{30}\text{N}_2\text{S}_4)]^{2+} \cdot 2\text{PF}_6^-$, $M_r = 1105.5$, triclinic, $P\bar{1}$, $a = 6.7536$ (15), $b = 9.5719$ (15), $c = 11.9510$ (28) Å, $\alpha = 105.736$ (12), $\beta = 91.722$ (12), $\gamma = 101.516$ (10)°, $V = 725.7$ Å³, $Z = 1$, $D_x = 2.529$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 10.39$ mm⁻¹, $F(000) = 520$, $T = 298$ K, $R = 0.0372$ for 1752 unique observed reflections. The 18-membered ring macrocycle acts as a binucleating agent, coordinating each Pt^{II} centre *via* one aza and two thia donors [Pt—S = 2.288 (3), 2.296 (3); Pt—N = 2.048 (9) Å] with the two SCH₂CH₂NCH₂CH₂S moieties bound meridionally to the Pt^{II} centres. Square planar geometry is completed by a terminal chloro ligand [Pt—Cl = 2.296 (3) Å]. The dimeric cation lies across a crystallographic inversion centre, with an intramolecular Pt...Pt separation of 4.2807 (6) Å.

Introduction. As part of a continuing study of the coordination chemistry of the potentially hexadentate macrocycles [18]aneN₂S₄ and Me₂[18]aneN₂S₄ with transition metal centres, we have shown that these ligands can alter their mode of coordination to meet the stereochemical requirements of the d^n configuration of the metal ion (Blake, Hyde, Reid & Schröder, 1988; Blake, Reid & Schröder, 1990; Atkinson, Blake, Drew, Forsyth, Lavery, Reid & Schröder, 1989). In view of this coordinative flexibility, we were interested in studying the binucleating properties of these ligands. To this end we have determined the structure of $[\text{Pt}_2\text{Cl}_2(\text{Me}_2[18]\text{aneN}_2\text{S}_4)]^{2+} \cdot 2\text{PF}_6^-$.



[18]aneN₂S₄: R = H
Me₂[18]aneN₂S₄: R = Me

Experimental. Compound prepared by reaction of Me₂[18]aneN₂S₄ with two molar equivalents of PtCl₂ in refluxing MeCN/H₂O followed by addition of excess NH₄PF₆. Crystals obtained by slow evaporation from a solution of the complex in H₂O. Colourless plate, 0.32 × 0.31 × 0.13 mm, Stoe STADI-4 four-circle diffractometer, graphite-monochromated Mo K α X-radiation, cell parameters from 2 θ values of 32 reflections measured at $\pm \omega$ ($31 < 2\theta < 32^\circ$). For data collection, ω -2 θ scans with ω -scan width $(0.99 + 0.35 \tan \theta)^\circ$, $2\theta_{\text{max}} = 45^\circ$, $h - 7 \rightarrow 7$, $k - 10 \rightarrow 9$, $l 0 \rightarrow 12$, 3 standard reflections, no significant crystal movement or decay, initial absorption correction using ψ scans (min. and max. transmission factors 0.0928, 0.3697, respectively), 1900 unique reflections, giving 1732 with $F > 6\sigma(F)$ for structure solution [from a Patterson synthesis (Pt) followed by iterative cycles of least-squares refinement and difference Fourier synthesis] and refinement [using full-matrix least-squares on F (Sheldrick, 1976)]. At isotropic convergence, final absorption corrections (min. 0.843, max. 1.190) applied empirically using DIFABS (Walker & Stuart, 1983). Anisotropic thermal parameters for all non-H atoms, H atoms in fixed, calculated positions. At final convergence, $R = 0.0372$, $wR = 0.0467$, $S = 0.980$ for 172 parameters, $(\Delta/\sigma)_{\text{max}}$ in final cycle 0.006, max. peak and min. trough in final ΔF synthesis 1.16, -1.12 e Å⁻³, respectively. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000124F^2$ gave satisfactory agreement analyses. Scattering factors were inlaid (Sheldrick, 1976) except for Pt (Cromer & Mann, 1968). Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, and selected bond lengths, angles and torsion angles in Table 2.† The atom-numbering scheme for the molecule is shown in Fig. 1, which was generated using ORTEP (Mallinson & Muir, 1985). Molecular geometry cal-

† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53334 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atomic coordinates with *e.s.d.*'s

	x	y	z	U_{iso} (Å ²)
Pt	0.10930 (6)	0.17453 (4)	0.15702 (4)	0.0289 (3)
S(1)	0.0043 (4)	-0.3436 (3)	-0.0815 (3)	0.0408 (18)
S(4)	0.1936 (4)	0.0030 (3)	0.2403 (3)	0.0412 (18)
N(7)	-0.0782 (13)	0.2196 (9)	0.2875 (8)	0.036 (6)
Cl	0.3311 (4)	0.1327 (4)	0.0159 (3)	0.0498 (20)
C(2)	0.1780 (16)	-0.2272 (13)	0.0458 (10)	0.042 (7)
C(3)	0.0608 (17)	-0.1782 (12)	0.1488 (10)	0.043 (7)
C(5)	0.0300 (21)	0.0261 (14)	0.3589 (10)	0.053 (8)
C(6)	-0.1502 (20)	0.0845 (13)	0.3273 (11)	0.053 (8)
C(8)	-0.2580 (19)	0.2624 (14)	0.2409 (12)	0.056 (9)
C(9)	-0.1918 (18)	0.3871 (13)	0.1848 (12)	0.050 (8)
C(7N)	0.0273 (22)	0.3436 (15)	0.3904 (12)	0.061 (9)
P(1)	0.5147 (5)	0.3065 (3)	0.6409 (3)	0.0469 (20)
F(1)	0.2808 (13)	0.3051 (11)	0.6321 (9)	0.095 (8)
F(2)	0.7483 (12)	0.3063 (12)	0.6461 (10)	0.108 (8)
F(3)	0.5422 (18)	0.3350 (15)	0.5200 (10)	0.135 (11)
F(4)	0.4892 (20)	0.2658 (21)	0.7551 (12)	0.186 (15)
F(5)	0.5604 (18)	0.4732 (10)	0.6980 (14)	0.156 (12)
F(6)	0.4647 (20)	0.1403 (11)	0.5759 (14)	0.149 (12)

Table 2. Bond lengths (Å), angles (°) and torsion angles (°) with *e.s.d.*'s

Pt—S(4)	2.288 (3)	N(7)—C(6)	1.494 (16)
Pt—N(7)	2.048 (9)	N(7)—C(8)	1.495 (17)
Pt—Cl	2.296 (3)	N(7)—C(7N)	1.499 (17)
Pt—S(1')	2.296 (3)	C(2)—C(3)	1.501 (17)
S(1)—C(2)	1.839 (12)	C(5)—C(6)	1.515 (19)
S(4)—C(3)	1.817 (12)	C(8)—C(9)	1.520 (19)
S(4)—C(5)	1.817 (14)	C(9)—S(1')	1.824 (13)
S(4)—Pt—N(7)	87.0 (3)	C(6)—N(7)—C(8)	108.7 (9)
S(4)—Pt—Cl	93.16 (11)	C(6)—N(7)—C(7N)	108.5 (9)
S(4)—Pt—S(1')	174.49 (11)	C(8)—N(7)—C(7N)	109.2 (10)
N(7)—Pt—Cl	177.3 (3)	S(1)—C(2)—C(3)	110.3 (8)
N(7)—Pt—S(1')	88.0 (3)	S(4)—C(3)—C(2)	109.6 (8)
Cl—Pt—S(1')	91.92 (11)	S(4)—C(5)—C(6)	110.3 (9)
Pt—S(4)—C(3)	106.5 (4)	N(7)—C(6)—C(5)	109.7 (10)
Pt—S(4)—C(5)	98.5 (4)	N(7)—C(8)—C(9)	110.9 (11)
C(3)—S(4)—C(5)	99.6 (6)	C(8)—C(9)—S(1')	111.1 (9)
Pt—N(7)—C(6)	110.0 (7)	Pt—S(1')—C(9)	97.6 (4)
Pt—N(7)—C(8)	108.7 (7)	Pt—S(1')—C(2')	103.8 (4)
Pt—N(7)—C(7N)	111.7 (7)	C(9)—S(1')—C(2')	98.7 (6)
C(3)—S(4)—C(5)—C(6)	-83.0 (10)	C(9)—S(1')—C(2')—C(3')	178.0 (8)
C(8)—N(7)—C(6)—C(5)	172.0 (10)	C(7N)—N(7)—C(8)—C(9)	69.1 (13)
C(5)—S(4)—C(3)—C(2)	-176.3 (9)	S(1)—C(2)—C(3)—S(4)	-148.9 (6)
C(7N)—N(7)—C(6)—C(5)	-69.3 (12)	S(4)—C(5)—C(6)—N(7)	-51.7 (12)
C(6)—N(7)—C(8)—C(9)	-172.7 (10)	N(7)—C(8)—C(9)—S(1')	50.1 (12)
C(8)—C(9)—S(1')—C(2')	82.8 (10)		

culations were performed using *CALC* (Gould & Taylor, 1985).

Discussion. The $[\text{Pt}_2\text{Cl}_2(\text{Me}_2[18]\text{janeN}_2\text{S}_4)]^{2+}$ cation (Fig. 1) lies across a crystallographic inversion centre. Each Pt centre is bound by a square-planar arrangement of two thioether S donors and one N donor of the macrocycle and one terminal chloride $[\text{Pt}-\text{S} = 2.288$ (3), 2.296 (3); $\text{Pt}-\text{N} = 2.048$ (9); $\text{Pt}-\text{Cl} = 2.296$ (3) Å]. The two $\text{SCH}_2\text{CH}_2\text{NCH}_2\text{-CH}_2\text{S}$ segments of the macrocycle are bound *meridionally* to the Pt^{II} ions and their small bite angle is reflected in the angles around the metal [$\angle\text{SPtS} = 87.0$ (3), 88.0 (3)°]. Similar meridional coordination

has been observed previously in mono- and binuclear transition-metal complexes of $[18]\text{janeN}_2\text{S}_4$ (Blake, Hyde, Reid & Schröder, 1988; Blake, Reid & Schröder, 1990). However, this structure represents the first example of meridional coordination of $\text{Me}_2[18]\text{janeN}_2\text{S}_4$; binding of $\text{Me}_2[18]\text{janeN}_2\text{S}_4$ to tetrahedral Cu^{I} centres in the binuclear species $[\text{Cu}_2(\text{Me}_2[18]\text{janeN}_2\text{S}_4)(\text{NCMe})_2]^{2+}$ has been reported previously (Atkinson *et al.*, 1989).

Interestingly, in $[\text{Pt}_2\text{Cl}_2(\text{Me}_2[18]\text{janeN}_2\text{S}_4)]^{2+}$ the Cl^- ligands are displaced by 0.172 Å from the mean Pt_2N plane in the direction opposite to that of the methylene groups linking adjacent thia donors: this presumably minimizes the steric interactions between the Cl^- and methylene groups. The closest $\text{Pt}\cdots\text{Pt}$ non-bonded distance of 4.2807 (6) Å is intramolecular, involving the metals in the two halves of the cation related by the inversion centre: this indicates that the metal centres are non-interacting. A comparable intramolecular $\text{Pd}\cdots\text{Pd}$ separation of 4.196 (2) Å has been observed in the binuclear Pd^{II} complex $[\text{Pd}_2\text{Cl}_2([18]\text{janeN}_2\text{S}_4)]^{2+}$ (Blake, Hyde, Reid & Schröder, 1988; Blake, Reid & Schröder, 1990): however, in this case the closest metal-metal distance of 3.406 (2) Å occurs between Pd ions in adjacent

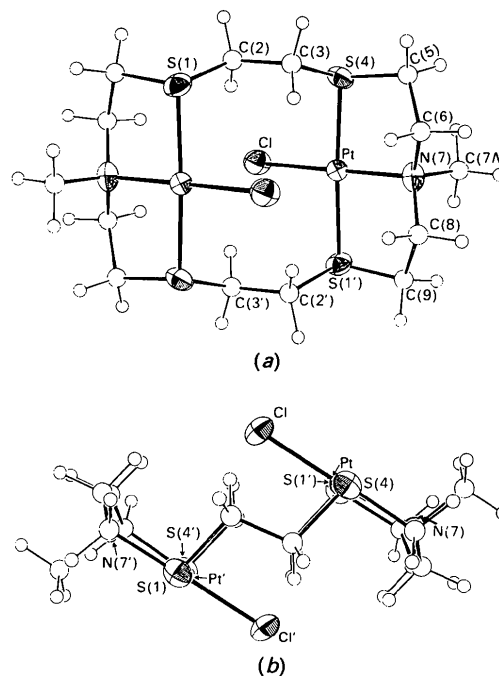


Fig. 1. (a) A general view of the dimeric cation showing atom-numbering scheme: primed atoms are related to their unprimed equivalents by inversion through (0,0,0). Thermal ellipsoids are drawn at the 30% probability level, excepting those of H which have artificial radii of 0.10 Å for clarity. (b) An orthogonal view showing the conformation of the macrocycle.

molecules which are related by a crystallographic twofold axis. A related NS₂Cl donor set has been reported for a series of binuclear macrocyclic complexes of Pd^{II} (Lehn, Parker & Rimmer, 1985).

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16-Crown-5 Derivative of 1,6-Anhydro-β-D-glucopyranose: Structure of [1,6-Anhydro-2,4-di-O-(3,6,9-trioxaundecane-1,11-diyl)- β-D-glucopyranose]sodium Tetraphenylborate

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Abstract. [Na(C₁₄H₂₄O₈)] [B(C₆H₅)₄], *M_r* = 662.56, orthorhombic, *P*2₁2₁2₁, *a* = 29.865 (5), *b* = 12.163 (3), *c* = 9.499 (2) Å, *V* = 3450.5 Å³, *Z* = 4, *D_x* = 1.275 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 8.29 cm⁻¹, *F*(000) = 1408, *T* = 295 K, final *R* = 0.049 and *wR* = 0.068 for 3195 reflections having *I* > 2σ(*I*). In the 1:1 complex of the Na⁺ 16-crown-5 cation and the tetraphenylborate anion the sodium ion is 0.77 Å above the crown center and is coordinated to the five oxygen atoms of the crown and to O(1) of the sugar moiety belonging to a symmetry-related molecule *via* the screw axis in the *z* direction. The integration of the 1,6-anhydro sugar fragment into the 16-crown-5 ether does not affect the rather rigid conformation of this fused ring system but causes certain changes in the crown ether geometry when compared to a previously determined 16-crown-5 complex.

Introduction. A great number of chiral crown ethers so far described in the literature (Stoddart, 1987) contain a sugar molecule as a chiral component, usually a modified sugar alcohol or a hexose, the polyether part being 15-crown-5 or 18-crown-6. The complexing ability of these compounds is sensitive to

the configuration of the sugar moiety and to geometrical changes of the polyether ring. It has been shown that the presence of an additional hydroxyl group in the polyether ring may modify the formation of complexes and makes the introduction of a pendant arm possible (Pugia, Knudsen, Cason & Bartsch, 1987). These aspects were taken into account in our effort to prepare a new type of crown ether containing 1,6-anhydro-β-D-glucopyranose as a chiral component.

The starting compound used in our synthesis was 1,6:3,4-dianhydro-2-*O*-toluene-*p*-sulfonyl-β-D-galactopyranose (Černý, Gut & Pacák, 1961) which was converted into the title compound by reaction with tetraethylene glycol followed by intramolecular cyclization and complex formation with sodium tetraphenylborate (Jindřich, 1987). This paper describes the results of the crystallographic analysis of the complex and gives evidence for its previously suggested structure.

Experimental. Crystallization from acetone/water; colorless plate-shaped single crystals; crystal size 0.2 × 0.4 × 0.5 mm. Stoe four-circle diffractometer controlled by a DEC Micro PDP-11 computer. Lattice