

quantitative transformation of the experimental difference Fourier map into a dynamic deformation density map is precluded, because at room temperature thermal movements give rise to uncertainties in bond lengths of about 0.01 Å, as demonstrated in the corresponding Mg salt (Gupta, Geise & Lenstra, 1984; Vanhouteghem, Lenstra & Schweiss, 1987). Such bond-length uncertainties cause uncertainties in atomic positions too large for a meaningful multipole analysis.

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Structure of (2-Ammonioethyl methyl sulfoxide)trichloroplatinum(II)

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Abstract. [Pt{CH₃(SO)CH₂CH₂NH₃}Cl₃], $M_r = 409.61$, monoclinic, $P2_1/n$, $a = 7.063$ (2), $b = 13.000$ (2), $c = 10.628$ (3) Å, $\beta = 96.86$ (1)°, $V = 969.0$ (4) Å³, $D_x = 2.81$ g cm⁻³, $Z = 4$, $Mo K\alpha$, $\lambda = 0.71069$ Å, $\mu = 161.8$ cm⁻¹, $F(000) = 752$, $T = 294$ K, final $R = 0.029$ for 2218 reflections. The amine-sulfoxide ligand is coordinated to the Pt centre *via* the S donor atom only, the Pt–S bond length being 2.205 (1) Å. The Pt–Cl bond lengths range from 2.286 (2) to 2.325 (2) Å. The geometry about Pt is approximately square planar.

Introduction. On the basis of molecular mechanics studies, it has been proposed that destabilizing interactions prevent the chemotherapeutic drug cisplatin {[Pt(NH₃)Cl₂]} from binding intrastrand to GpA sequences of DNA (Hambley, 1991). We have designed and synthesized a series of platinum sulfoxide complexes including [Pt{CH₃(SO)CH₂CH₂NH₂}Cl₂], which avoid these unfavourable interactions and thereby target such DNA sequences (Ling, Allen & Hambley, 1991). Unlike closely

related compounds, [Pt{CH₃(SO)CH₂CH₂NH₂}Cl₂] proved difficult to synthesize as the sulfoxide ligand readily coordinated to the Pt centre in a monodentate fashion *via* the S donor atom. A mixture of both [Pt{CH₃(SO)CH₂CH₂NH₂}Cl₂] and [Pt{CH₃(SO)CH₂CH₂NH₃}Cl₃] was usually produced upon reaction of the protonated or basic forms of the CH₃(SO)CH₂CH₂NH₂ ligand with K₂[PtCl₄], acidic conditions (pH ≤ 3) favouring formation of the trichloro complex. We have structurally characterized both of these complexes and herein report the results for the latter.

Experimental. Solutions of K₂[PtCl₄] and CH₃(SO)CH₂CH₂NH₂.HCl were combined, yielding orange crystals of the title compound and pale yellow crystals of [Pt{CH₃(SO)CH₂CH₂NH₂}Cl₂] in a ratio of *ca* 4:1. A crystal was mounted on a glass fibre with epoxy resin and data collected using an Enraf-Nonius CAD-4 diffractometer, graphite-monochromated radiation. 25 independent reflections with $20 \leq 2\theta \leq 30^\circ$ were used for least-squares

Table 1. Summary of data collection and processing parameters

Crystal dimensions	0.10 × 0.11 × 0.24 mm
Crystal faces	{100}, {142}, {011}, {142}, {011}
Data collection range	2 ≤ 2θ ≤ 55°
Scan width	(1.10 + 0.34 tan θ)°
Horizontal counter aperture	(2.70 + 1.05 tan θ) mm
Scan type	ω-θ
Absorption correction*	
number of sampling points	10 × 10 × 12
maximum correction	0.292
minimum correction	0.193
Range of hkl	-9 → 9, 0 → 16, 0 → 13
R _{int}	0.049
Total data collected	2445
Number of unique reflections	2112
Data with I ≥ 2.5σ(I)	1913
Total variables	96
R	0.0292
wR	0.0330
S	1.385
Weighting constants†	g = 1.25, k = 0.00063

* Coppens, Leiserowitz & Rabinovich (1965).

† Weight w = g/[σ²(F_o) + kF_o²], g and k refined.Table 2. Final atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters B_{eq} (Å²)

$$B_{eq} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	B _{eq}
Pt(1)	0.0996 (1)	0.1353 (1)	0.1684 (1)	1.93
Cl(1)	-0.0352 (3)	0.2591 (1)	0.0273 (2)	3.28
Cl(2)	0.3092 (3)	0.0949 (2)	0.0263 (2)	4.69
Cl(3)	-0.1154 (3)	0.1814 (2)	0.3028 (2)	4.65
S(1)	0.2301 (2)	0.0186 (1)	0.3024 (1)	2.05
O(1)	0.1863 (7)	0.0212 (3)	0.4346 (4)	2.75
N(1)	-0.0372 (9)	-0.1751 (5)	0.4002 (5)	3.21
C(1)	0.1652 (10)	-0.1060 (5)	0.2404 (6)	2.74
C(2)	-0.0316 (10)	-0.1353 (5)	0.2691 (7)	3.07
C(3)	0.4825 (9)	0.0160 (6)	0.3079 (7)	3.28

Table 3. Bond lengths (Å) and angles (°)

Cl—Pt(1)	2.325 (2)	Cl(2)—Pt(1)	2.298 (2)
Cl(3)—Pt(1)	2.286 (2)	S(1)—Pt(1)	2.205 (1)
O(1)—S(1)	1.476 (4)	C(1)—S(1)	1.788 (7)
C(3)—S(1)	1.777 (6)	C(2)—N(1)	1.492 (9)
C(2)—C(1)	1.507 (10)		
Cl(2)—Pt(1)—Cl(1)	88.9 (1)	Cl(3)—Pt(1)—Cl(1)	88.3 (1)
Cl(3)—Pt(1)—Cl(2)	177.2 (1)	S(1)—Pt(1)—Cl(1)	179.4 (1)
S(1)—Pt(1)—Cl(2)	90.8 (1)	S(1)—Pt(1)—Cl(3)	92.0 (1)
O(1)—S(1)—Pt(1)	118.7 (2)	C(1)—S(1)—Pt(1)	108.5 (2)
C(1)—S(1)—O(1)	107.3 (3)	C(3)—S(1)—Pt(1)	112.0 (2)
C(3)—S(1)—O(1)	107.0 (3)	C(3)—S(1)—C(1)	102.0 (3)
C(2)—C(1)—S(1)	110.9 (5)	C(1)—C(2)—N(1)	113.8 (6)

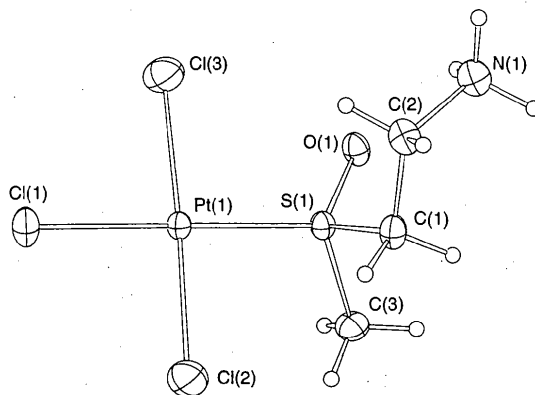
determination of cell constants. The intensities of three reference reflections were monitored and indicated less than 2% decomposition. The structure was solved by heavy-atom methods and all non-H atoms were refined with anisotropic thermal parameters. Positions of the H atoms were calculated by applying geometric constraints so that they occupied tetrahedral sites about the N and C atoms with N—H and C—H bond lengths of 0.91 and 0.97 Å, respectively. The H atoms were refined with group

isotropic thermal parameters. Full-matrix least-squares refinement converged with all shifts less than 0.4σ. The maximum excursions in the final difference map were 2.1 and -1.4 e Å⁻³. All calculations were performed using SHELX76 (Sheldrick, 1976) and drawings were produced using ORTEP (Johnson, 1965). Scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Data collection and refinement parameters, atomic coordinates and bond lengths and angles are listed in Tables 1, 2 and 3, respectively.* The atom numbering is shown in Fig. 1.

Discussion. [Pt{CH₃(SO)CH₂CH₂NH₃}Cl₃] is a square-planar complex, in which the sulfoxide ligand is coordinated to the metal centre via the S atom only. The least-squares plane through the first coordination sphere shows that the *trans* Cl(1) and S atoms are below Cl(2) and Cl(3), and that the Pt lies above all these atoms. Comparisons have indicated that this is a common feature in Pt complexes with chelated sulfoxide or thioether ligands (Ling, Allen & Hambley, 1991).

The Pt—S bond length, 2.205 (1) Å, is slightly longer than those observed for Pt complexes with chelated sulfoxide ligands (Allain, Kubiak, Jezowska-Trebatowska, Kozłowski & Glowiak, 1980; Freeman, 1977; Ling, Allen & Hambley, 1991), Pt—S bond lengths having been reported to range from 2.182 (3) Å in dichloro{(SR)-S-methylcysteine sulfoxide}platinum(II) (Allain *et al.*, 1980) to 2.198 (2) Å to 2.198 (2) Å in dichloro{(SR)-

* Structure amplitudes, anisotropic thermal parameters of non-H atoms, positional and thermal parameters of H atoms and close contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54894 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1. ORTEP plot of [Pt{CH₃(SO)CH₂CH₂NH₃}Cl₃] showing atom numbering and 30% probability ellipsoids.

methionine sulfoxide}platinum(II) (Freeman, 1977). Although the longer Pt—Cl bond length being *trans* to S suggests a possible *trans* effect, a trend was not observed when *cis* and *trans* Pt—Cl bond lengths for a series of compounds were compared.

[Pt{CH₃(SO)CH₂CH₂NH₂}Cl₂] is designed to specifically target GpA sequences in DNA (Ling, Allen & Hambley, 1991) with a hydrogen bond between the sulfoxide oxygen and the —NH₂ group of the adenine promoting the binding. Thus, the hydrogen bonding of the sulfoxide O is of some relevance. In the present structure, the sulfoxide O makes two hydrogen bonds with N(1), one of which is intramolecular [O(1)···N(1) 3.000, O(1)···H(1B) 2.28, O(1)···N(1) 2.938, O(1)···H(1B) 2.30 Å], con-

firmed its propensity to hydrogen bond to amine groups.

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Structure of [ThCl(OH)(OH₂)₆]₂Cl₄·18-Crown-6·2H₂O

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Abstract. Bis[hexaqua(chloro)hydroxothorium(IV)] tetrachloride–18-crown-6–water (1/1/2), [ThCl(OH)(OH₂)₆]₂Cl₄·C₁₂H₂₄O₆·2H₂O, *M_r* = 1227.3, triclinic, *P* $\bar{1}$, *a* = 9.227 (3), *b* = 10.599 (3), *c* = 11.089 (2) Å, α = 74.01 (2), β = 67.36 (2), γ = 77.02 (2)°, *V* = 953.6 Å³, *Z* = 1, *D_x* = 2.14 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 85.5 cm⁻¹, *F*(000) = 584, *T* = 295 K, final *R* = 0.044 for 2552 observed [*F_o* ≥ 5σ(*F_o*)] reflections. The structure consists of hydroxide bridged thorium dimers hydrogen bonded to uncoordinated chloride ions and water molecules and to 18-crown-6 molecules. Each Th is nine-coordinate tricapped trigonal prismatic which includes two hydroxide bridges, one terminal chloride ion, and six water molecules. The 18-crown-6 molecules reside around centers of inversion and accept eight hydrogen bonds.

Introduction. Reaction of hydrated thorium salts with crown ethers in nonaqueous solvents has led to a variety of compounds with one common feature: the crown ether resides in the thorium ion's second coordination sphere, hydrogen bonded to coordinated solvent or water molecules. Structurally characterized complexes include [Th(NO₃)₄(OH₂)₃]₂·18-crown-6 (Rogers, Kurihara & Benning,

1987), [ThCl₂(OH₂)₇]₂Cl₂·18-crown-6·2H₂O (Rogers, 1989), [ThCl₄(OHEt)₃(OH₂)₂]₂·18-crown-6·H₂O (Rogers, Kurihara & Benning, 1988), and [ThCl₄(OHMe)₂(OH₂)₂]₂·15-crown-5·CH₃CN (Rogers & Benning, 1988). The title complex is the first we have isolated of this type in which hydrolysis has taken place and this allows us to compare the hydrogen-bonding environment of a larger dimer to the previously characterized monomeric cations.

Experimental. The title complex was isolated from the same reaction scheme that led to the isolation of [ThCl₂(OH₂)₇]₂Cl₂·18-crown-6·2H₂O (Rogers, 1989). Clear parallelepipeds grown from THF. *D_m* not determined. Crystal 0.08 × 0.15 × 0.15 mm. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo *K* α radiation, ω –2 θ scans. Cell constants from setting angles of 25 reflections ($\theta > 15^\circ$). Corrections for Lorentz–polarization effect and for absorption (empirical, ψ scans), range of relative transmission factors 45/100%. θ_{\max} = 25°; *h* 0 to 10, *k* –12 to 12, *l* –13 to 13. Standard reflections 500, 060, 003 measured every 3600s of data collection time, variation ± 1.5%. 3361 reflections measured, 2552 independent observed reflections [*F_o* ≥ 5σ(*F_o*)], *R_{int}* = 0.0015. Structure solved via *SHELXS* (Sheldrick, 1985). Crown ether H atoms placed 0.95 Å from the bonded C atom with a fixed isotropic

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