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trans-Dichloro(dimethyl sulfoxide)(isopropylamine)platinum(II), C₅H₁₅Cl₂NOPtS

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Abstract. $M_r = 403.24$, triclinic, $P\bar{1}$, $a = 7.789$ (4), $b = 8.781$ (5), $c = 8.874$ (7) Å, $\alpha = 108.23$ (5), $\beta = 101.67$ (5), $\gamma = 93.05$ (4)°, $V = 560.1$ (6) Å³, $Z = 2$, $D_x = 2.390$, $D_m = 2.38$ (2) Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 13.778$ mm⁻¹, $F(000) = 376$, $T = 295$ K. Final $R = 0.035$ for 2829 unique observed reflections. The coordination around the Pt atom is square-planar. The compound which was synthesized in our laboratory is the *trans*-isomer. The Pt–Cl bond distances are 2.290 (2) and 2.315 (2) Å, the Pt–N bond is 2.067 (6) Å while the Pt–S bond is 2.220 (2) Å. The crystal is stabilized by intermolecular hydrogen bonds.

Introduction. Continuing our studies on (Me₂SO)(amine)platinum compounds, we have synthesized *trans*-[Pt(Me₂SO)(isopropylamine)Cl₂] and determined its molecular and crystal structure. It was prepared from the aqueous reaction of K[Pt(Me₂SO)Cl₃] with isopropylamine. In these conditions, only the *trans*-isomer is produced.

Experimental. Crystals recrystallized from water; density by flotation in a thallos malonate aqueous solution; hexagonal plate 0.6 mm by 0.08 mm thick; precession photographs indicated triclinic system; Syntex $P\bar{1}$ diffractometer; graphite-monochromatized Mo $K\alpha$ radiation; cell parameters from setting angles of 15 centered reflections ($10 < 2\theta < 25^\circ$); 3626 independent reflections measured up to $2\theta < 60^\circ$ by θ - 2θ scan technique; range of hkl : $h -10 \rightarrow 10$, $k -12 \rightarrow 12$, $l -12 \rightarrow 11$; standard reflections 130, 410 and 014; variations <3%; reflections with $I_{\text{net}} < 2.5\sigma(I)$ unobserved, $\sigma(I)$ calculated as in Melanson & Rochon (1975); absorption correction based on equations of crystal

faces, transmission factors: 0.031 to 0.309; data corrected for Lorentz and polarization effects; 2829 unique observed reflections. Patterson map indicated space group $P\bar{1}$ and position of Pt; positions of other atoms (except H) obtained by structure-factor and Fourier-map calculations; H, except those in CH₃, fixed at calculated positions (C–H = 0.95 and N–H = 0.85 Å) with isotropic $\beta = 6.0$ Å². $R = 0.035$, $R_w = 0.049$; $w = 1/\sigma^2(F)$; $(\Delta/\sigma)_{\text{max}}$ in final refinement cycle <0.008; $\rho_{\text{max}} = 1.6$ (close to Pt), $\rho_{\text{min}} = -0.5$ e Å⁻³ in final difference Fourier synthesis. Isotropic secondary-extinction correction (Coppens & Hamilton, 1970). Atomic scattering factors of Cromer & Waber (1965) for Pt, Cl, S, O, N and of Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion terms of Pt, Cl and S from Cromer (1965). Calculations on a Cyber 171 with programs of Melanson & Rochon (1975).

Discussion. The refined atomic parameters are listed in Table 1.* A labeled diagram of the molecule is shown in Fig. 1. The coordination around the Pt atom is square-planar. The deviations from the weighted co-ordination plane are: Pt, 0.0007 (3); Cl(1), -0.017 (2); Cl(2), -0.013 (2); S, -0.007 (2); and N, -0.076 (6) Å. The bond lengths and angles are given in Table 2. The angles around the Pt atom are close to the expected values of 90 and 180°.

* Lists of structure factors, anisotropic thermal parameters and coordinates of the H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39166 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters (with their e.s.d.'s) and equivalent isotropic temperature factors ($\times 10^4$)

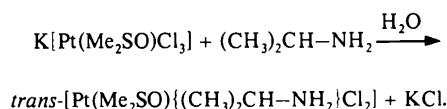
	x	y	z	$U_{eq}^*(\text{\AA}^2)$
Pt	1651.4 (3)	2084.3 (3)	453.7 (3)	268
Cl(1)	4540 (3)	2274 (3)	1872 (3)	545
Cl(2)	-1160 (3)	1749 (3)	-1104 (3)	438
S	874 (2)	3644 (2)	2647 (2)	312
N	2294 (8)	546 (7)	-1591 (8)	312
C(1)	2505 (10)	1230 (9)	-2918 (10)	335
C(2)	4053 (12)	2542 (12)	-2338 (16)	552
C(3)	2625 (14)	-121 (12)	-4447 (12)	528
C(4)	-908 (14)	4728 (11)	2150 (13)	525
C(5)	2523 (14)	5303 (12)	3832 (15)	636
O	367 (10)	2800 (7)	3709 (8)	473

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

Table 2. Bond distances (\AA) and angles ($^\circ$)

Pt—Cl(1)	2.315 (2)	S—C(4)	1.784 (11)
Pt—Cl(2)	2.290 (2)	S—C(5)	1.782 (12)
Pt—S	2.220 (2)	N—C(1)	1.512 (10)
Pt—N	2.067 (6)	C(1)—C(2)	1.508 (14)
S—O	1.466 (7)	C(1)—C(3)	1.521 (13)
Cl(1)—Pt—Cl(2)	175.80 (9)	Pt—S—C(5)	112.3 (4)
Cl(1)—Pt—S	92.40 (8)	Pt—N—C(1)	117.2 (5)
Cl(1)—Pt—N	88.8 (2)	N—C(1)—C(2)	111.4 (7)
Cl(2)—Pt—S	91.73 (8)	N—C(1)—C(3)	110.2 (7)
Cl(2)—Pt—N	87.0 (2)	C(2)—C(1)—C(3)	112.6 (8)
S—Pt—N	177.4 (2)	O—S—C(4)	107.0 (5)
Pt—S—O	115.1 (3)	O—S—C(5)	109.2 (5)
Pt—S—C(4)	112.6 (4)	C(4)—S—C(5)	99.4 (5)

As expected, the compound is the *trans*-isomer. It was synthesized by the following reaction:



Since the *trans*-effect of Me_2SO is much larger than that of chloride, only the *trans*-isomer is produced. In these experimental conditions, the compound does not isomerize. The IR spectrum of the compound showed one Pt—Cl vibration at 343 cm^{-1} .

The Pt—Cl(1) bond [$2.315(2) \text{ \AA}$] seems slightly longer than the Pt—Cl(2) bond [$2.290(2) \text{ \AA}$] probably because Cl(1) appears to be involved in intermolecular hydrogen bonds with the amine group.

The Pt—S bond [$2.220(2) \text{ \AA}$] is of normal length and compares well with the values already reported for Pt— Me_2SO complexes (Melanson, Hubert & Rochon, 1976; Melanson & Rochon, 1978*a,b*). The S atom in the Me_2SO molecule is in approximate tetrahedral environment with angles ranging from 99.4 to 115.1° . The structure of the coordinated Me_2SO molecule is very similar to the structure of Me_2SO itself (Thomas, Shoemaker & Eriks, 1966; Viswamitra & Kannan, 1966). The S—O and S—C distances agree well with the published results.

The Pt—N bond distance of $2.067(6) \text{ \AA}$ is of about the expected value, and agrees well with the value of $2.046(10) \text{ \AA}$ found in *trans*-[Pt(Me_2SO)(2-picoline) Cl_2] (Melanson & Rochon, 1978*a*), the value of $2.058(7) \text{ \AA}$ found in *trans*-[Pt(diisopropyl sulfoxide)(1-methylcytosine) Cl_2] (Lock, Speranzini & Powell, 1976) and the value of $2.034(13) \text{ \AA}$ found in *trans*-[Pt(Me_2SO)(cytidine) Cl_2] (Melanson & Rochon, 1978*b*). Me_2SO has a high *trans*-effect but its *trans*-influence is probably not very high. No obvious lengthening of the Pt—N bond in the *trans* position to Me_2SO has been observed yet in the literature. Our value of $2.067(6) \text{ \AA}$ might be at the higher end of the range, but it is probably not significant. Furthermore, the N atom is involved in hydrogen bonds, which might have a slight influence on its bond lengths.

Fig. 2 illustrates the packing in the *trans*-[Pt(Me_2SO){ $(\text{CH}_3)_2\text{CH-NH}_2$ }] Cl_2 crystal which consists of layers of molecules parallel to the a^*c^* plane. The layers are held together in pairs by hydrogen bonds with the $-\text{NH}_2$ groups. The N atom forms two intermolecular hydrogen bonds with Cl(1) and O. The $\text{N}\cdots\text{Cl}(1)$ distance is $3.576(7) \text{ \AA}$ and the angles are favorable [$\text{C}(1)-\text{N}\cdots\text{Cl}(1) = 101.9(4)$ and $\text{Pt}-\text{N}\cdots\text{Cl}(1) = 129.4(3)^\circ$]. The $\text{N}\cdots\text{O}$ distance is $3.284(9) \text{ \AA}$ and the angles $\text{C}(1)-\text{N}\cdots\text{O}$ and $\text{Pt}-\text{N}\cdots\text{O}$ are $101.2(4)$ and $118.5(3)^\circ$ respectively. The paired layers seem to be held together only by van der Waals forces.

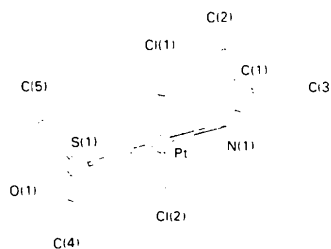


Fig. 1. Labeled diagram of the *trans*-[Pt(Me_2SO)(isopropylamine) Cl_2] molecule. The ellipsoids correspond to 50% probability.

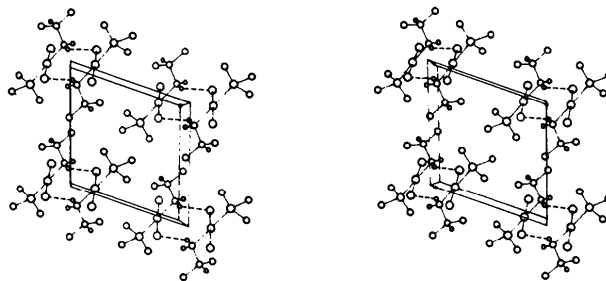


Fig. 2. Stereoscopic diagram of the packing in the *trans*-[Pt(Me_2SO)(isopropylamine) Cl_2] crystal. The large face is the bc plane with c vertical.

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Trinitrato-(*O, O'*)(triethylene glycol)europium(III), $\text{Eu}(\text{NO}_3)_3(\text{C}_6\text{H}_{14}\text{O}_4)^*$

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Abstract. $M_r = 488$, monoclinic, $P2_1/c$, $a = 12.342$ (5), $b = 9.305$ (4), $c = 14.201$ (5) Å, $\beta = 110.88$ (5)°, $V = 1524$ (1) Å³, $Z = 4$, $D_m(\text{floatation}) = 2.12$ (1), $D_x = 2.13$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 4.55$ mm⁻¹, $F(000) = 952$, room temperature, $R = 3.16\%$ for 2286 observed reflections. The Eu atom is ten-coordinated being directly bonded to the oxygen atoms of the glycol and of three bidentate nitrates. The glycol molecule forms a ring-like structure around the metal together with a nitrate ion; two other nitrates are axial above and below the ring plane. Eu–O bond distances are in the range 2.433 (4)–2.508 (4) Å for the glycol and 2.488 (5)–2.522 (5) Å for the nitrate oxygen atoms.

Introduction. Coordination compounds of rare earths with macrocyclic ligands such as crown ethers and cryptands have been increasingly studied in recent years, whereas relatively little attention has been devoted to the coordination behaviour of lanthanoids towards acyclic polyethers and their derivatives with various chain lengths. Recently, structural investigations on complexes of lanthanoid ions with some polyethylene glycols have shown that the etheric chain wraps the metal ion achieving a ring-like structure,

similar to those of the crown ethers, and the possibility of separation of lanthanoids by fractional crystallization by using polyoxyethylene derivatives has been suggested (Hirashima & Shiokawa, 1979; Hirashima, Tsutsui & Shiokawa, 1980), as a consequence of the decreasing stability of the complexes with the decrease of the cationic radius. These properties, together with the high flexibility of the etheric chain, make the polyoxyethylene derivatives attractive ligands for cations with different ionic radii such as the lanthanoids. We report here the crystal and molecular structure of the complex of europium nitrate with triethylene glycol.

Experimental. Very stable crystals obtained by adding a solution of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in methyl cyanide to an equimolecular solution of the ligand in the same solvent; the mixture was refluxed for 1–2 h, crystals were obtained after addition of CH_2Cl_2 . Crystal 0.12 × 0.16 × 0.18 mm, Philips PW 1100 four-circle diffractometer; lattice parameters by least-squares refinement of 25 medium-angle settings; integrated intensities up to $\theta = 25^\circ$, $h_{\text{max}} = \pm 13$, $k_{\text{max}} = 10$, $l_{\text{max}} = 14$, $\theta/2\theta$ scan, graphite-monochromated Mo $K\alpha$ radiation; 2 standard reflections: no variation; 2686 unique reflections measured, 2286 with $I > 3\sigma(I)$ used; intensities corrected for Lorentz, polarization and for

* Triethylene glycol is 2,2'-(ethylenedioxy)diethanol.