

where C-coordination has been confirmed (Bailey, Higson & McKenzie, 1971), and the Pt complex of $C(CN)_3^-$ where C-coordination has been assigned spectroscopically, the coordination sphere about the metal is not as crowded (fewer ligands) and thus may permit a different ligand coordination scheme.

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trans-Dichlorobis(di-*n*-propyl sulfoxide)platinum(II)

BY R. MELANSON AND F. D. ROCHON

Département de Chimie, Université du Québec à Montréal, CP 8888, succ. A, Montréal, Canada H3C 3P8

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Abstract. $[PtCl_2(C_6H_{14}OS)_2]$, $M_r = 534.48$, monoclinic, $P2_1/c$, $a = 9.092$ (2), $b = 5.696$ (2), $c = 19.749$ (7) Å, $\beta = 110.63$ (3)°, $V = 957.2$ (6) Å³, $Z = 2$, $D_x = 1.854$ Mg m⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu(Mo K\alpha) = 7.894$ mm⁻¹, $F(000) = 520$, room temperature, $R = 0.047$ for 1842 unique observed reflections. The Pt atom is located on a center of symmetry. Pt has *trans* square-planar coordination and the sulfoxide ligands are bonded through their S atoms. The Pt–Cl bond distances are 2.292 (3) Å. The Pt–S bond lengths [2.292 (2) Å] are significantly longer than the corresponding distances in the *cis* isomer. The packing consists of layers of molecules parallel to the *ab* plane.

Introduction. When K_2PtCl_4 reacts with sulfoxide ligands (*L*) in water, *trans*-[Pt(*L*)₂Cl₂] is first formed

because of the large *trans* effect of sulfoxides. The compound is then isomerized to the *cis*-isomer since the enhanced $\pi(d-d)$ bonding seems to be quite efficient in *cis* Pt compounds (Price, Williamson, Schramm & Wayland, 1972; Price, Birk & Wayland, 1978). *cis* structures have been reported for all the Pt^{II} disubstituted complexes except with a very sterically demanding ligand, diisoamyl sulfoxide, which gave only the *trans* isomer (Price *et al.*, 1972). With Me₂SO the *trans* compound cannot be isolated. But with more bulky ligands like benzyl methyl sulfoxide (bmso) the *trans* compound has been isolated (Rochon, Kong & Girard, 1986). The two isomers can be identified by their stretching $\nu(Pt-Cl)$. For example *cis*-[Pt(bmso)₂Cl₂] absorbs at 331 and 311 cm⁻¹ while the *trans* isomer shows only one band at 349 cm⁻¹. The colors of the two isomers are also quite different. The *cis*

Table 1. Positional parameters ($\times 10^4$) with their e.s.d.'s and 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	0	0	0	25
Cl	-898 (3)	2881 (5)	-858 (1)	45
S	2467 (2)	335 (4)	-56 (1)	27
O	3484 (7)	-1753 (11)	148 (4)	35
C(1)	2433 (10)	1286 (19)	-930 (4)	37
C(2)	1684 (13)	-554 (26)	-1514 (6)	72
C(3)	1753 (17)	281 (32)	-2246 (6)	91
C(4)	3443 (9)	2782 (15)	491 (4)	31
C(5)	3810 (11)	2303 (20)	1287 (5)	46
C(6)	4819 (13)	4325 (20)	1739 (6)	61

compounds are white or very pale yellow while the *trans* compounds are yellow. With intermediate ligands like di-*n*-propyl sulfoxide (dpsu), yellow *trans*-[Pt(dpsu)₂Cl₂] can be observed in the first few minutes of reaction, but it is difficult to obtain it pure.

The crystal structures of several *cis* dichloro compounds with Me₂SO (Melanson & Rochon, 1975), tetramethylene sulfoxide (Melanson, de la Chevrotière & Rochon, 1985), di-*n*-propyl sulfoxide and ethyl methyl sulfoxide (Melanson & Rochon, 1987) have been published. But no crystal structure of *trans* disubstituted compounds has been reported yet. We were able to isolate a crystal of *trans*-[Pt(dpsu)₂Cl₂] which was analyzed by X-ray diffraction. The results are reported below.

Experimental. 1 mmol of K₂PtCl₄ and 2.2 mmol of dpsu were dissolved in 20 mL of water and stirred for 15 min. The yellow precipitate was filtered, dried and recrystallized from acetone. The compound contained a small quantity of the *cis* isomers which are very pale yellow in colour. Therefore a bright yellow crystal was chosen for crystallographic measurements.

Yellow platelet, dimensions (mm): 0.058 × 0.404 × 0.25; Syntex P1 diffractometer; graphite-monochromatized Mo K α radiation; cell parameters from refined angles of 15 centered reflections; 2804 independent reflections measured up to $2\theta \leq 60^\circ$ by θ - 2θ scan technique; range of hkl : $h = 0 \rightarrow 12$, $k = 0 \rightarrow 8$, $l = -27 \rightarrow 26$; standard reflections 300, 0,0,10 and 031, variations $\leq 2.0\%$; reflections with $I_{net} \leq 2.5\sigma(I)$ unobserved, $\sigma(I)$ calculated as in Melanson, Hubert & Rochon (1975); absorption correction based on equations of crystal faces, transmission factors from 0.074 to 0.631; data corrected for Lorentz and polarization effects; 1842 unique observed reflections; atomic scattering factors of Cromer & Waber (1965) for Pt, S, Cl, O, C and of Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion terms of Pt, Cl and S from Cromer (1965); isotropic secondary-extinction corrections (Coppens & Hamilton, 1970).

Patterson map showed position of Pt; other non-H atoms located by structure factors and Fourier-map

calculations; refinement by full-matrix least-squares calculations; H atoms fixed at calculated positions (C-H = 0.95 Å) with isotropic $B = 6.0 \text{ \AA}^2$; individual weights = $1/\sigma^2(F)$; ratio of maximum least-squares shift to e.s.d. in final refinement cycle (on F) 0.085; $\rho(\text{max}) = 0.9 \text{ e \AA}^{-3}$ (close to Pt) in final Fourier synthesis; $R = 0.047$ and $wR = 0.050$.

Discussion. The refined atomic parameters are listed in Table 1.* A labeled diagram of the molecule is shown in Fig. 1. As expected, the coordination around the Pt^{II} atom is square planar and the angles around Pt are close to 90 and 180°. As predicted from IR spectroscopy [one $\nu(\text{Pt}-\text{Cl})$ at 340 cm^{-1}], the compound is the *trans* isomer and the sulfoxide ligands are bonded to Pt through their S atoms. The bond distances and angles are listed in Table 2.

The Pt-Cl bond distances are normal [2.292 (3) Å] and are very similar to the distances [2.289 (3) and 2.302 (3) Å] found in the corresponding *cis* isomer (Melanson & Rochon, 1987). The *trans* influence of sulfoxides is not larger than the *trans* influence of chlorides. But the Pt-S bond lengths [2.292 (2) Å] are significantly longer than those observed for the *cis* isomers with Me₂SO [2.244 (2) and 2.229 (2) Å], tetramethylene sulfoxide [2.228 (2) and 2.248 (3) Å], ethyl methyl sulfoxide [2.257 (5) and 2.272 (5) Å] and di-*n*-propyl sulfoxide [2.263 (3) and 2.247 (3) Å] from the references mentioned above. This crystal structure analysis is the first example of a *trans* disubstituted compound. These results indicate that the Pt-S bonds are longer in the *trans* compound than in the *cis* isomer. The stronger *cis* Pt-S bonds could be explained by the enhanced $\pi(d-d)$ bonding which is more effective in the *cis* compound than in the *trans* isomer. Therefore the

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51147 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

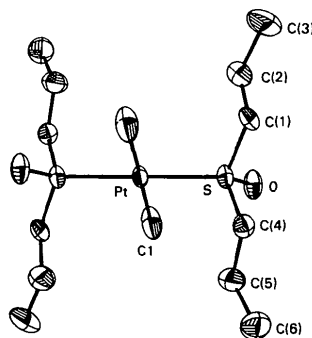
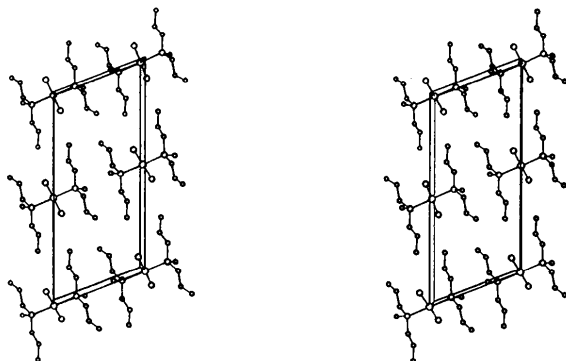


Fig. 1. Labeled diagram of the *trans*-[Pt(dpsu)₂Cl₂] molecule. The ellipsoids correspond to 50% probability.

Table 2. Bond distances (Å) and angles (°)

Pt—Cl	2.292 (3)	C(1)—C(2)	1.53 (2)
Pt—S	2.292 (2)	C(2)—C(3)	1.54 (2)
S—C(1)	1.799 (9)	C(4)—C(5)	1.51 (1)
S—C(4)	1.795 (9)	C(5)—C(6)	1.55 (1)
S—O	1.473 (7)		
Cl—Pt—S	90.3 (1)	O—S—C(4)	109.4 (4)
S—Pt—Cl'	89.7 (1)	C(1)—S—C(4)	100.4 (4)
Pt—S—C(1)	112.7 (3)	S—C(1)—C(2)	111.7 (7)
Pt—S—C(4)	108.7 (3)	S—C(4)—C(5)	111.5 (6)
Pt—S—O	116.7 (3)	C(1)—C(2)—C(3)	109.9 (10)
O—S—C(1)	107.6 (4)	C(4)—C(5)—C(6)	109.6 (8)

Fig. 2. Stereoscopic drawing of the packing in the *trans*-[Pt(dps)₂Cl₂] crystal (*c* axis vertical, view down *b* axis).

multiple-bond character of the Pt—S bonds in the *cis* compounds would be more important than in the corresponding *trans* isomers. The stronger Pt—S bonds in the *cis* isomer would explain the rapid isomerization of *trans* disulfoxide compounds (if the sulfoxide ligand is not too bulky).

The S atoms in the sulfoxide ligands are in approximate tetrahedral environment. The Pt—S—O

angle [116.7 (3)°] is larger than the tetrahedral value while the C(1)—S—C(4) [100.4 (4)°] is smaller, as observed in the Pt-sulfoxide structures described above. The S—O, S—C and C—C bond distances agree well with published values.

The packing of the molecules is shown in Fig. 2. It consists of layers of molecules parallel to the *ab* plane and centered at $z = 0$ and $\frac{1}{2}$. No strong hydrogen bonds are expected in this compound, but one intermolecular distance is slightly shorter than the sum of the van der Waals radii. The C(4)···O distance is 3.19 (1) Å and the angles S—C(4)···O = 132.1 (4) and C(5)—C(4)···O = 112.4 (6)°.

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The Structure of Bis(acetonitrile)bis(*cis*-1,2-diphenylphosphinoethene)iron(II) Diperchlorate

BY ALAN F. WILLIAMS

Department of Inorganic, Analytical and Applied Chemistry, University of Geneva,
30 quai Ernest Ansermet, CH-1211 Geneva 4, Switzerland

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Abstract. [Fe(CH₃CN)₂{(C₆H₅)₂PCHCHP(C₆H₅)₂}₂](ClO₄)₂ (1), $M_r = 1129.7$, tetragonal, $P4_2/m$, $a = 13.183$ (2), $c = 16.040$ (3) Å, $V = 2788$ (1) Å³, $Z = 2$,

$D_m = 1.38$ (2), $D_x = 1.35$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.531$ mm⁻¹, $F(000) = 1168$, room temperature, $R = 0.070$ for 1092 reflections. The cation

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