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## Structure of *cis*-Dichloro(dimethyl sulfoxide)(pyridine)platinum(II)

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**Abstract.** [PtCl<sub>2</sub>(C<sub>2</sub>H<sub>6</sub>OS)(C<sub>5</sub>H<sub>5</sub>N)],  $M_r = 423.22$ , monoclinic,  $P2_1/b$ ,  $a = 8.884(1)$ ,  $b = 8.784(1)$ ,  $c = 16.355(3)$  Å,  $\gamma = 113.96(2)^\circ$ ,  $V = 1166.3(7)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.41$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 127.56$  cm<sup>-1</sup>,  $F(000) = 784$ ,  $T = 298$  K,  $R = 0.050$  for 1500 unique observed reflections. Pt<sup>II</sup> exhibits a slightly distorted *cis* square-planar coordination to two Cl and one N atom of the pyridine (py) moiety and to one S atom of the dimethyl sulfoxide (dmsO) moiety. The Pt—S distance is 2.209(4) Å. The observed variations in the Pt—S bond lengths in *cis*-[Pt(dmsO)LCl<sub>2</sub>] ( $L = \text{dmsO, MeCN, PhCH}_2\text{CN, py, 2Me-C}_5\text{H}_4\text{N, NH}_3$ ) complexes provide a rare example of the *cis* influence of the ligands.

**Introduction.** The pyridine *cis* effect in Pt<sup>II</sup> complexes has been widely discussed in the literature (Kukushkin, 1985). But py's position in the sequence of the *cis* influence of the ligands is unknown. Earlier we found (Moiseev, Kukushkin, Simanova, Belsky & Kononov, 1989) that the value of the Pt—S bond length in *cis*-[Pt(dmsO)LCl<sub>2</sub>] ( $L = \text{dmsO, MeCN, 2Me-C}_5\text{H}_4\text{N, NH}_3$ ) complexes is affected mainly by the *L cis* influence. In this work we have prepared single crystals of the *cis*-[Pt(dmsO)pyCl<sub>2</sub>] complex

suitable for X-ray analysis and determined the py *cis* influence.

**Experimental.** The title compound was prepared by solid-state thermal isomerization of *trans*-[Pt(dmsO)pyCl<sub>2</sub>] at 420 K (Kukushkin, Moiseev & Sidorov, 1989). Anal. Calc.: Cl, 16.75; Pt, 46.1. IR (KBr pellet, Perkin-Elmer model 983G spectrometer), cm<sup>-1</sup>: 1608 *s* ( $\nu_{\text{C}=\text{C}, \text{C}=\text{N}}$ ), 1150 and 1141 *s* ( $\nu_{\text{SO}}$ ), 443 *m* ( $\nu_{\text{PtS}}$ ), 376 *m* ( $\gamma_{\text{CSO}}$ ), 345 and 318 *m* ( $\nu_{\text{PtCl}}$ ). The colourless rod-like crystals were obtained by recrystallization from boiling acetonitrile by slow cooling of the saturated solution.

Diffraction data collected on a Nicolet P3 diffractometer, using Mo  $K\alpha$  radiation,  $\beta$ -filter; cell parameters from refined angles of 12 centered reflections with  $2\theta$  between 20 and 24°. 1599 independent reflections of which 1500 with  $I \geq 3\sigma(I)$  measured up to  $2\theta \leq 50^\circ$  by the  $\theta/2\theta$  scan technique. Scan speed 3.4–12° min<sup>-1</sup>, range of  $hkl$ :  $h = 0$  to 12,  $k = -12$  to 12,  $l = 0$  to 20. Standard reflections 300, 040, 006 measured every 100 reflections showed no change with time. Structure solved by means of Fourier synthesis based on the Pt-atom coordinates obtained from Patterson synthesis and refined by full-matrix

least squares based on  $F$  with weights  $w = 1/\sigma^2(F) + 0.002F^2$ . All non-H atoms were treated anisotropically. H atoms not refined.  $R = 0.050$ ,  $wR = 0.049$ ,  $S = 1.31$ ,  $(\Delta/\sigma)_{\max} = 0.41$ , in the final  $\Delta F$  map,  $(\Delta\rho)_{\max} = 2.9 \text{ e } \text{Å}^{-3}$  near Pt atom,  $(\Delta\rho)_{\min} = -4.6 \text{ e } \text{Å}^{-3}$ . Lorentz, polarization and absorption corrections were made [crystal size:  $0.186 \times 0.071 \times 0.071 \text{ mm}$ , crystal faces (100), (011), (0 $\bar{1}$ 1)]. Calculation carried out with *SHELXTL* (Sheldrick, 1984) on Nova-3 computer. Scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

**Discussion.** The final atomic coordinates are listed in Table 1 and bond lengths and angles in Table 2.\* Fig. 1 shows a view of the molecule with the atomic numbering scheme.

The coordination around the Pt atom is slightly distorted square planar. The atom deviations from the best least-squares plane calculated through Pt, N, S, Cl(1) and Cl(2) atoms are:  $-0.006$ ,  $0.009$ ,  $-0.008$ ,  $0.008$  and  $-0.008 \text{ Å}$ , respectively. The angles around the Pt atom are close to  $90$  and  $180^\circ$ .

The compound has the *cis* configuration as earlier expected (Kukushkin, Moiseev & Sidorov, 1989). Dimethyl sulfoxide is bonded to Pt through sulfur. The presence of the S coordination of dmsO in the complex studied is in agreement with other results of the X-ray structure analyses of the dimethyl sulfoxide Pt<sup>II</sup> complexes (Sotman, Fundamensky, Kukushkin & Pankova, 1988; Davies, 1981). Only one structural study has resulted in an O-bonded dmsO molecule in a Pt<sup>II</sup> complex (Elding & Oskarsson, 1987).

The S atom in the dmsO ligand is in an approximately tetrahedral environment. The O—S—C bond angles [ $107.8$  (8) and  $109.2$  (7) $^\circ$ ] and the C—S—C bond angle [ $102.2$  (7) $^\circ$ ] are consistent with O—S—C (*ca*  $107^\circ$ ) and C—S—C ( $97.4^\circ$ ) in the dmsO free molecule (Davies, 1981).

In dmsO—Pt<sup>II</sup> complexes, the coordination most strongly influences the S=O bond (Sotman *et al.*, 1988). The S=O distance in free dmsO is known to be  $1.531$  (5) Å (Davies, 1981) and in the title complex it is  $1.476$  (12) Å. The latter value agrees well with those found in *cis*-[Pt(dmsO)(2Me-C<sub>5</sub>H<sub>4</sub>N)Cl<sub>2</sub>] [ $1.470$  (9) Å (Melanson & Rochon, 1977)], *trans*-[Pt(dmsO)(2Me-C<sub>5</sub>H<sub>4</sub>N)Cl<sub>2</sub>] [ $1.440$  (10) Å (Melanson & Rochon, 1978*b*)] and *trans*-[Pt(dmsO)pyCl<sub>2</sub>] [ $1.458$  (8),  $1.469$  (7) Å for two crystallographically independent molecules (Caruso, Spagna & Zambonelli, 1980)].

\* 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 53416 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{Å}^2 \times 10^3$ ) with *e.s.d.*'s in parentheses

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
Pt	6553 (1)	6220 (1)	6148 (1)	31 (1)
Cl(1)	9255 (4)	7239 (4)	5711 (2)	49 (1)
Cl(2)	6693 (5)	3737 (4)	6520 (3)	58 (2)
S	6440 (4)	8595 (4)	5788 (2)	38 (1)
O	4874 (12)	8753 (13)	5944 (6)	53 (4)
N	4195 (12)	5284 (12)	6556 (6)	36 (4)
C(1)	3867 (18)	4758 (20)	7336 (8)	49 (6)
C(2)	2331 (21)	4112 (22)	7637 (9)	57 (7)
C(3)	998 (17)	4021 (20)	7141 (9)	55 (6)
C(4)	1309 (18)	4538 (20)	6350 (9)	52 (6)
C(5)	2911 (17)	5172 (17)	6058 (7)	40 (5)
C(6)	8045 (22)	10311 (18)	6265 (11)	60 (7)
C(7)	6949 (18)	8970 (21)	4737 (8)	53 (7)

Table 2. Bond lengths (Å) and angles ( $^\circ$ )

Pt—Cl(1)	2.309 (3)	Pt—Cl(2)	2.316 (4)
Pt—S	2.209 (4)	Pt—N	2.027 (10)
S—O	1.476 (12)	S—C(6)	1.780 (15)
S—C(7)	1.775 (14)	N—C(1)	1.348 (17)
N—C(5)	1.373 (18)	C(1)—C(2)	1.340 (22)
C(2)—C(3)	1.411 (24)	C(3)—C(4)	1.361 (20)
C(4)—C(5)	1.386 (20)		
Cl(1)—Pt—Cl(2)	90.1 (1)	Cl(1)—Pt—S	89.4 (1)
Cl(2)—Pt—S	179.5 (1)	Cl(1)—Pt—N	178.4 (3)
Cl(2)—Pt—N	88.5 (3)	S—Pt—N	92.0 (3)
Pt—S—O	116.7 (4)	Pt—S—C(6)	110.8 (7)
O—S—C(6)	107.8 (8)	Pt—S—C(7)	109.1 (7)
O—S—C(7)	109.2 (7)	C(6)—S—C(7)	102.2 (7)
Pt—N—C(1)	119.6 (9)	Pt—N—C(5)	121.7 (8)
C(1)—N—C(5)	118.6 (11)	N—C(1)—C(2)	122.3 (15)
C(1)—C(2)—C(3)	119.9 (14)	C(2)—C(3)—C(4)	118.4 (13)
C(3)—C(4)—C(5)	119.8 (14)	N—C(5)—C(4)	120.8 (11)

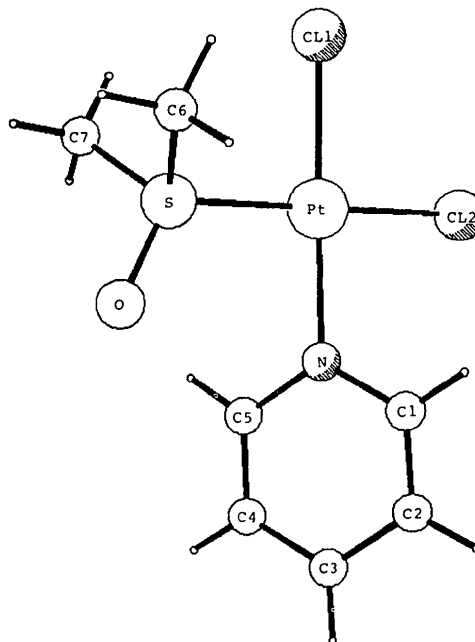


Fig. 1. Labelled diagram of the *cis*-[PtCl<sub>2</sub>(C<sub>2</sub>H<sub>6</sub>OS)(C<sub>5</sub>H<sub>5</sub>N)] molecule.

The Pt—Cl bond lengths [2.316 (4) *trans* to S and 2.309 (3) Å *trans* to N] are normal for this type of complex (Sotman *et al.*, 1988). The Pt—S distance is 2.209 (4) Å. The results of X-ray structure determinations of the *cis*-[Pt(dmsO)LCl<sub>2</sub>] complexes show that Pt—S bond lengths decrease following the ligand *L* sequence: dmsO [av. 2.234 (6) Å (Melanson & Rochon, 1975) and 2.248 (5) Å (Shibaeva, 1985)] > MeCN [av. 2.220 (6) Å for two crystallographically independent molecules (Moiseev *et al.*, 1989)] > PhCH<sub>2</sub>CN [2.215 (1) Å (Belsky, Kononov & Kukushkin, 1990)] > py [2.209 (4) Å] > 2Me—C<sub>5</sub>H<sub>4</sub>N [2.200 (3) Å (Melanson & Rochon, 1977)] > NH<sub>3</sub> [2.186 (4) Å (Melanson & Rochon, 1978a)]. The observed variations in the Pt—S bond lengths provide a rare example of the *cis* influence of the ligands.

The Pt—N distance [2.027 (10) Å] is normal and agrees with Pt—N bond lengths in (Ph<sub>3</sub>PCH<sub>2</sub>Ph)[PtPyCl<sub>3</sub>] [2.028 (6) Å (Belsky, Kukushkin, Kononov, Moiseev & Yakovlev, 1990)] and (Et<sub>4</sub>N)[PtPyCl<sub>3</sub>] [2.018 (6) Å (Kukushkin *et al.*, 1990)]. The pyridine ring is planar. The dihedral angle between the py plane and the PtNSCl(1)Cl(2) plane is 56.8°. The value of the dihedral angle in *cis*-[Pt(dmsO)(2Me—C<sub>5</sub>H<sub>4</sub>N)Cl<sub>2</sub>] with the more sterically hindered 2-methylpyridine ligand is 87.1° (Melanson & Rochon, 1977).

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## Structure of Ethylenediammonium *catena*-Poly[ $\mu$ -(2-pyridinecarboxylato- $\kappa$ N, $\kappa$ O: $\kappa$ O')-tris(2-pyridinecarboxylato- $\kappa$ N, $\kappa$ O)neodymate] Hexahydrate

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**Abstract.** C<sub>2</sub>H<sub>10</sub>N<sub>2</sub><sup>2+</sup>·[{Nd(C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>4</sub>}<sub>2</sub>]<sup>2-</sup>·6H<sub>2</sub>O, *M<sub>r</sub>* = 1435.5, monoclinic, *Cc*, *a* = 13.654 (9), *b* = 21.813 (11), *c* = 20.136 (12) Å,  $\beta$  = 99.36 (4)°, *V* = 5917 (7) Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.60, *D<sub>x</sub>* = 1.611 (2) Mg m<sup>-3</sup>,  $\lambda$ (Mo *K* $\alpha$ ) = 0.71069 Å,  $\mu$  = 1.83 mm<sup>-1</sup>, *F*(000) = 2880, *T* = 304 (1) K, final *R* = 0.0395 for 7450 reflections. The Nd ions are surrounded by four N and five carboxylic O atoms. The structure consists of a polymeric chain of complex anions, ethylenediammonium cations and water of hydration.

**Introduction.** In a previous paper (Starynowicz, 1991) the crystal structure of barium neodymium  $\alpha$ -picoli-

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nate has been reported. It seemed interesting to investigate neodymium coordination in another ( $\alpha$ -picolinato)neodymate system. This work is a part of our study on the structures and properties of complexes with lanthanide–nitrogen bonds.

**Experimental.** The title compound was prepared by adding ethylenediamine and 2-pyridinecarboxylic ( $\alpha$ -picolinic) acid to a warm aqueous suspension of freshly precipitated neodymium hydroxide. After two days, parallelepiped pink-violet crystals were formed. A specimen 0.7 × 0.35 × 0.2 mm was cut from a larger crystal. *D<sub>m</sub>* by flotation in C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>/CHCl<sub>3</sub>. Oscillation and Weissenberg photographs indicated