

## The Crystal Structure of *trans*-Dichloro(dimethyl sulphoxide)(2-picoline)platinum(II)

BY ROBERT MELANSON AND FERNANDE D. ROCHON

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

(Received 21 July 1977; accepted 5 October 1977)

*trans*-[Pt(dimethyl sulphoxide)(2-picoline)Cl<sub>2</sub>] forms monoclinic crystals,  $a = 11.522$ ,  $b = 10.686$ ,  $c = 10.382$  Å,  $\beta = 102.25^\circ$ ,  $Z = 4$ , space group  $P2_1/c$ . Positional and anisotropic thermal parameters were refined by full-matrix least-squares calculations to  $R = 0.045$  and  $R_w = 0.042$ . The coordination around the Pt atom is square planar. The Pt–Cl bond lengths are 2.282 and 2.295 Å. The Pt–S distance is 2.212 Å and the Pt–N distance is 2.046 Å. The 2-picoline ring lies at an angle of  $72.4^\circ$  to the coordination plane of the Pt atom.

### Introduction

Following a study by nuclear magnetic resonance of the reactions between some dimethyl sulphoxide (DMSO) platinum complexes and some pyridine (py) derivatives and the isomerization of [Pt(DMSO)(py)Cl<sub>2</sub>] (Kong, Iyamuremye & Rochon, 1976), we have studied the crystal structure of both *cis*- and *trans*-[Pt(DMSO)(2-picoline)Cl<sub>2</sub>] in order to confirm the *cis* and *trans* configurations assigned by NMR. DMSO has a relatively high *trans* influence (Kukushkin, Stetsenko, Strelin & Duibanova, 1972; Kukushkin & Vyaz'menskii, 1970). It was also hoped that information on the effect of the DMSO ligand on the *trans* bond would be obtained.

The crystal structure of the *cis* isomer was recently published (Melanson & Rochon, 1977). In this paper, we report our results on the study of *trans*-[Pt(DMSO)(2-picoline)Cl<sub>2</sub>].

### Experimental

#### Crystal data

PtCl<sub>2</sub>C<sub>8</sub>H<sub>13</sub>NOS,  $M_r = 437.26$ , monoclinic,  $P2_1/c$ ,  $a = 11.522$  (6),  $b = 10.686$  (7),  $c = 10.382$  (5) Å,  $\beta = 102.25$  (4) $^\circ$ ,  $Z = 4$ ,  $V = 1249$  (1) Å<sup>3</sup>,  $D_m = 2.31$  (2) (floatation),  $D_x = 2.325$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 123.7$  cm<sup>-1</sup> and  $t = 22^\circ\text{C}$ .

The compound was prepared by the reaction between [Pt(DMSO)<sub>2</sub>Cl<sub>2</sub>] and 2-picoline in DMSO solution, and recrystallized from acetone. A set of precession photographs showed that the  $h0l$ ,  $l = 2n + 1$  and  $0k0$ ,  $k = 2n + 1$  reflections are systematically absent, indicating the space group  $P2_1/c$ . The lattice parameters were calculated by least-squares refinement of the setting angles of 15 reflections, using a Syntex P1 diffractometer and graphite-monochromatized Mo  $K\alpha$  radiation.

#### Collection and reduction of intensity data

The intensity data were collected from a crystal measuring about  $0.26 \times 0.26 \times 0.31$  mm and having approximately 20 faces. A total of 4038 Mo  $K\alpha$  reflections ( $hkl$  and  $h\bar{k}l$ ) were measured up to a  $2\theta$  value of  $60^\circ$ . The intensities were collected by the  $2\theta/\theta$  scan technique at a variable rate (24 to  $1^\circ \text{ min}^{-1}$ ). Most of the reflections were measured at a rate of  $1^\circ \text{ min}^{-1}$ . The scan range extended from  $1^\circ$  below  $K\alpha_1$  to  $1^\circ$  above  $K\alpha_2$ . The background time to scan time ratio was 0.40. During the data collection, three standard reflections were measured after every 47 reflections as a test on crystal and instrument stability. No systematic changes were observed and the intensity fluctuations were within  $\pm 2\%$ .

The measurements reduced to a set of 3834 independent reflections after the systematically absent reflections were deleted. The standard deviations  $\sigma(I)$  were calculated as already described (Melanson & Rochon, 1975). A set of 2563 reflections for which  $I > 2.5\sigma(I)$  were considered as observed and later used in least-squares refinement. Because of the geometry of the crystal and the difficulty of identifying the faces, no absorption correction was applied. The usual corrections for polarization and Lorentz effects were applied.

The scattering factors used for the nonhydrogen atoms were taken from Cromer & Waber (1965), and the scattering curve of H was from Stewart, Davidson & Simpson (1965). The anomalous dispersion coefficients (Cromer, 1965) for the heavy atoms (Pt, Cl, S) were included in the calculations.

#### Structure determination

The structure was solved by the conventional heavy-atom method and refined by full-matrix least-squares calculations. The position of the Pt atom was easily determined from the three-dimensional Patterson map. The positions of all other nonhydrogen atoms were

obtained by structure factor and Fourier map calculations. Unit weight was assigned to all observed reflections during the early stages of refinement. Later, individual weights  $w$  according to the equation  $1/w = a + bF_o + cF_o^2$  were calculated. The constants of the equation were adjusted to make the distribution of  $w|AF|^2$  almost constant with respect to  $|F_o|$  and  $\sin \theta/\lambda$  ( $a = 15.0$ ,  $b = -0.20$  and  $c = 0.0008$ ). An isotropic secondary extinction coefficient was also included (Coppens & Hamilton, 1970). The H atoms on the four aromatic C atoms were placed at the calculated positions, while those on the terminal methyl groups could not be located on the final difference map. Each H atom was assigned the isotropic thermal parameter of the C atom to which it is bonded. The refinement of the scale factor, the coordinates and the anisotropic temperature factors of all nonhydrogen atoms converged to  $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$  of 0.045 and a weighted residual  $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$  of 0.042. The final difference Fourier map using only the observed reflections showed peaks lower than  $0.8 \text{ e } \text{Å}^{-3}$  less than  $1 \text{ Å}$  from the Pt atom. The refined atomic parameters are given in Table 1.\*

\* A list of structure factors and a table of the refined anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33104 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Final atomic parameters ( $\times 10^4$ )

Estimated standard deviations are given in parentheses.

	x	y	z
Pt	2355.0 (4)	352.6 (4)	2024.4 (4)
Cl(1)	539 (3)	415 (4)	2570 (3)
Cl(2)	4084 (3)	221 (4)	1268 (4)
S	2767 (3)	2330 (3)	2566 (3)
O	2836 (11)	3186 (8)	1514 (9)
N	2096 (7)	-1509 (9)	1600 (8)
C(1)	4130 (12)	2315 (14)	3785 (14)
C(2)	1813 (14)	3054 (14)	3503 (14)
C(3)	1260 (11)	-1793 (12)	459 (12)
C(4)	1045 (14)	-3014 (13)	68 (14)
C(5)	1677 (14)	-3950 (13)	750 (14)
C(6)	2489 (12)	-3646 (12)	1868 (14)
C(7)	2658 (9)	-2410 (11)	2260 (11)
C(8)	3611 (13)	-2113 (14)	3515 (13)

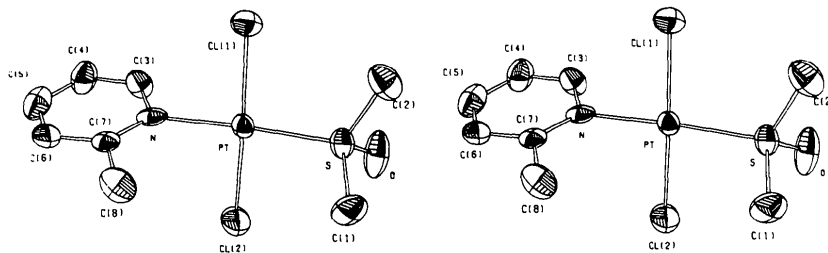


Fig. 1. Stereoscopic view of *trans*-[Pt(DMSO)(2-picoline)Cl<sub>2</sub>].

The calculations were made with a CDC 6400 computer using programs previously described (Melanson & Rochon, 1975).

## Results and discussion

A labelled stereoscopic view of the molecule is shown in Fig. 1. Two Cl, one S and one N atom form a square-planar coordination around the Pt atom. The weighted best plane was calculated through the five atoms. The deviations from this plane are Pt,  $-0.0024$ ; Cl(1),  $0.0851$ ; Cl(2),  $0.1014$ ; S,  $-0.0075$ ; and N,  $-0.1117$ . The bond lengths and angles are given in Table 2. The angles around the Pt atom are close to the expected values of  $90^\circ$  and  $180^\circ$ , but some deviation from the ideal square-planar coordination is apparent [angles Cl(1)-Pt-Cl(2) =  $174.2^\circ$  and S-Pt-N =  $175.8^\circ$ ].

As expected, the compound is the *trans* isomer. This analysis confirms the configuration assigned by our NMR studies (Kong, Iyamuremye & Rochon, 1976). The two Cl atoms are *trans* to each other. The Pt-Cl bonds ( $2.282$  and  $2.295 \text{ Å}$ ) are of normal length. They compare well with the values found for Pt-Cl in a position *cis* to DMSO in K[Pt(DMSO)Cl<sub>3</sub>] ( $2.302$  and

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

Pt-Cl(1)	2.282 (3)	Cl(1)-Pt-Cl(2)	174.2 (1)
Pt-Cl(2)	2.295 (4)	Cl(1)-Pt-S	93.9 (1)
Pt-S	2.212 (3)	Cl(1)-Pt-N	89.0 (3)
Pt-N	2.046 (10)	Cl(2)-Pt-S	89.5 (1)
S-O	1.440 (10)	Cl(2)-Pt-N	88.0 (3)
S-C(1)	1.796 (14)	S-Pt-N	175.8 (3)
S-C(2)	1.790 (16)	Pt-S-O	117.2 (5)
N-C(3)	1.393 (15)	Pt-S-C(1)	106.2 (5)
N-C(7)	1.275 (15)	Pt-S-C(2)	115.3 (5)
C(3)-C(4)	1.373 (19)	O-S-C(1)	111.1 (7)
C(4)-C(5)	1.347 (20)	O-S-C(2)	106.1 (7)
C(5)-C(6)	1.366 (20)	C(1)-S-C(2)	99.6 (7)
C(6)-C(7)	1.384 (18)	Pt-N-C(3)	116.0 (8)
C(7)-C(8)	1.549 (18)	Pt-N-C(7)	125.7 (8)
		N-C(3)-C(4)	120.4 (12)
		N-C(7)-C(6)	122.1 (11)
		N-C(7)-C(8)	119.1 (11)
		C(3)-C(4)-C(5)	120.5 (14)
		C(4)-C(5)-C(6)	117.8 (14)
		C(5)-C(6)-C(7)	120.3 (13)
		C(6)-C(7)-C(8)	118.2 (11)
		C(3)-N-C(7)	118.3 (10)

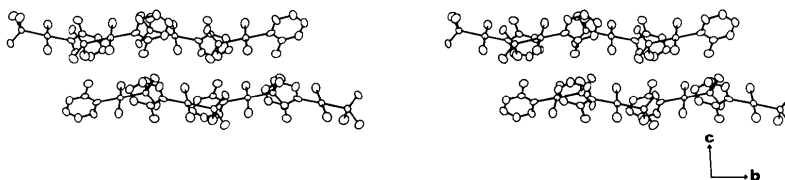


Fig. 2. Packing in the *trans*-[Pt(DMSO)(2-picoline)Cl<sub>2</sub>] crystal.

2.296 Å) (Melanson, Hubert & Rochon, 1976), in *cis*-[Pt(DMSO)(2-picoline)Cl<sub>2</sub>] (2.288 Å) (Melanson & Rochon, 1977) and in *trans*-[Pt(diisopropyl sulphoxide)(1-methylcytosine)Cl<sub>2</sub>] (2.304 and 2.287 Å) (Lock, Speranzini & Powell, 1976). Slightly higher values have been observed for bonds *trans* to DMSO (2.31–2.32 Å) compared to the *cis* bonds (2.29–2.30 Å), but the difference may not be significant. In the literature, there is no definite agreement as to how and by what amount a bond distance should be perturbed by a ligand with a high *trans* influence. The crystallographic results on acetylenic and olefinic Pt complexes have not shown any significant systematic lengthening or contraction of *trans* bonds (Jarvis, Kilbourn & Owston, 1971; Beauchamp, Rochon & Theophanides, 1973; Colapietro & Zambonelli, 1971; Spagna & Zambonelli, 1973). The Pt–N distance of 2.046 Å is of about the expected value, and agrees well with the value of 2.062 Å found for the corresponding *cis* isomer and the value of 2.058 Å found by Lock, Speranzini & Powell (1976).

The Pt–S bond (2.212 Å) is of normal length and compares well with the values of 2.19 to 2.24 Å already reported for the platinum dialkyl sulphoxide complexes mentioned above. The S atom in the DMSO molecule is in an approximate tetrahedral environment with angles ranging from 100 to 117°. The structure of the coordinated DMSO molecule is very similar to the structure of DMSO itself (Thomas, Shoemaker & Eriks, 1966; Viswamitra & Kannan, 1966). The S–O (1.440 Å) and S–C (1.796 and 1.790 Å) distances agree well with the published results.

The bond lengths within the aromatic ring vary from 1.28 to 1.39 Å and the angles are all close to 120°. The N–C(7) bond (1.28 Å) seems short, but the shortening is probably not significant. The refinement of the N atom parameters may have been influenced by the presence of the heavy Pt atom in its close environment. The ring is planar and lies at an angle of 72.4° with the coordination plane of the Pt atom. In the corresponding *cis* isomer the 2-picoline ring is perpendicular (87.1°) to the Pt plane (Melanson & Rochon, 1977), probably to minimize the interactions between the DMSO and the picoline ligands.

Fig. 2 illustrates the packing in the *trans*-[Pt(DMSO)(2-picoline)Cl<sub>2</sub>] crystal which consists of layers of molecules parallel to the *ab* plane. The environment (<3.6 Å) of the O atoms of the DMSO molecules was closely examined for possible hydrogen

bonding. There is no intramolecular hydrogen bonding. Two intermolecular contacts, S–C(2)···O [distance C(2)···O = 3.370 Å, angle = 102°] and S–C(1)···O [distance C(1)···O = 3.511 Å, angle = 97°] suggest that there might be some very weak intermolecular hydrogen bonding between the DMSO ligands. But the existence of C–H···O bonding is still not well established. If it exists in this crystal, the layers of molecules which are parallel to the *ab* plane would be weakly linked by hydrogen bonding in the *c* direction.

The authors are grateful to the National Research Council of Canada for financial support, to Dr Pi-Chang Kong for the synthesis of the compound analyzed and to Johnson Matthey & Co. Ltd for the loan of potassium chloroplatinite.

#### References

- BEAUCHAMP, A. L., ROCHON, F. D. & THEOPHANIDES, T. (1973). *Can. J. Chem.* **51**, 126–131.
- COLAPIETRO, M. & ZAMBONELLI, L. (1971). *Acta Cryst.* **B27**, 734–740.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- JARVIS, J. A. J., KILBOURN, B. T. & OWSTON, P. G. (1971). *Acta Cryst.* **B27**, 366–372.
- KONG, P.-C., IYAMUREMYE, D. & ROCHON, F. D. (1976). *Can. J. Chem.* **54**, 3224–3226.
- KUKUSHKIN, YU. N., STETSENKO, A. I., STRELIN, S. B. & DUBANOVA V. G. (1972). *Russ. J. Inorg. Chem.* **17**, 561–563.
- KUKUSHKIN, YU. N. & VYAZ' MENSII, YU. E. (1970). *Russ. J. Inorg. Chem.* **15**, 248–251.
- LOCK, C. J. L., SPERANZINI, R. A. & POWELL, J. (1976). *Can. J. Chem.* **54**, 53–58.
- MELANSON, R., HUBERT, J. & ROCHON, F. D. (1976). *Acta Cryst.* **B32**, 1914–1916.
- MELANSON, R. & ROCHON, F. D. (1975). *Can. J. Chem.* **53**, 2371–2374.
- MELANSON, R. & ROCHON, F. D. (1977). *Acta Cryst.* **B33**, 3571–3573.
- SPAGNA, R. & ZAMBONELLI, L. (1973). *Acta Cryst.* **B29**, 2302–2304.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- THOMAS, R., SHOEMAKER, C. B. & ERIKS, K. (1966). *Acta Cryst.* **21**, 12–20.
- VISWAMITRA, M. A. & KANNAN, K. K. (1966). *Nature (London)*, **209**, 1016–1017.