

have a lower energy than the twist-boat form (Hendrickson, 1961). A similar situation will occur for the piperazine ring. Therefore, all the reported piperazine structures have the chair form (Rérat, 1960; Koshino, Sasaki & Haisa, 1973; Mouillé, Cotrait, Hospital & Marsau, 1975; Okamoto, Sekido, Noguchi, Ono & Hirokawa, 1977). In the present compound, if the ring conformation takes a chair form, a large steric repulsion between the amide group and the vicinal equatorial methyl group is expected. This strain is relieved by the twist-boat conformation. Further details about the effects of other substituents will be discussed elsewhere (Tsuboyama *et al.*, 1977).

The calculations were performed on the FACOM 230-75 computer of this Institute, using the UNICS II program system (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974). The research was supported, in part, by a Scientific Grant (134041) from the Ministry of Education.

*Acta Cryst.* (1977). **B33**, 3571–3573

### *cis*-Dichloro(dimethyl sulphoxide)(2-picoline)platinum(II)

BY ROBERT MELANSON AND FERNANDE D. ROCHON

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

(Received 29 March 1977; accepted 27 June 1977)

**Abstract.**  $\text{PtCl}_2\text{C}_8\text{H}_{13}\text{NOS}$ ,  $M_r = 437.26$ ; monoclinic  $P2_1/c$ ,  $a = 8.004$  (7),  $b = 17.508$  (8),  $c = 9.176$  (5) Å,  $\beta = 105.29$  (6)°,  $Z = 4$ ,  $V = 1240$  (1) Å<sup>3</sup>,  $D_x = 2.341$ ,  $D_m = 2.33$  (1) g cm<sup>-3</sup> (flotation);  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 124.6$  cm<sup>-1</sup>,  $t = 22^\circ\text{C}$ . Positional and anisotropic thermal parameters were refined by full-matrix least-squares calculations to  $R = 0.049$  and  $R_w = 0.036$ . The coordination around Pt is planar. The *cis* Pt–Cl (relative to DMSO) bond length is 2.288 Å while *trans* Pt–Cl is 2.307 Å. The Pt–S distance is 2.200, and Pt–N 2.062 Å. The 2-picoline ring lies perpendicular to the coordination plane of the Pt atom (87.1°).

**Introduction.** Recently, we have studied by NMR the reactions of some dimethyl sulphoxide complexes of Pt with pyridine derivatives (py) and the isomerization of [Pt(DMSO)(py)Cl<sub>2</sub>] (Kong, Iyamuremye & Rochon, 1976). In order to confirm the *cis* configurations assigned by NMR, we have studied by X-ray diffraction, the crystal structure of *cis*-[Pt(DMSO)(2-picoline)Cl<sub>2</sub>].

The compound was synthesized from the isomerization of *trans*-[Pt(DMSO)(2-picoline)Cl<sub>2</sub>] in

### References

- HENDRICKSON, J. B. (1961). *J. Amer. Chem. Soc.* **83**, 4537–4547.
- KELLIE, G. M. & RIDDELL, F. G. (1974). *Topics in Stereochemistry*, Vol. 8, p. 225, edited by N. L. ALLINGER & E. L. ELIEL. New York: Interscience.
- KOSHINO, S., SASAKI, M. & HAISA, M. (1973). *Bull. Chem. Soc. Japan*, **46**, 1375–1379.
- MOUILLÉ, Y., COTRAIT, M., HOSPITAL, H. & MARSAU, P. (1975). *Acta Cryst.* **B31**, 1495–1496.
- OKAMOTO, T., SEKIDO, K., NOGUCHI, T., ONO, H. & HIROKAWA, S. (1977). Chem. Soc. Japan, 36th Annual Meeting, April, Osaka.
- RÉRAT, C. (1960). *Acta Cryst.* **13**, 459–468.
- SAKURAI, T., IWASAKI, H., WATANABE, Y., KOBAYASHI, K., BANDO, Y. & NAKAMICHI, H. (1974). *Rep. Inst. Phys. Chem. Res.* **50**, 78–91.
- TSUBOYAMA, S., TSUBOYAMA, K., UZAWA, J., KODA, R., NAKAMARU, M., KOBAYASHI, K. & SAKURAI, T. (1977). *Tetrahedron Lett.* pp. 2895–2898.

DMSO solution by the method recently described (Kong *et al.*, 1976). The crystals were recrystallized from acetone. A set of precession photographs showed that the  $h0l$ ,  $l = 2n + 1$  and  $0k0$ ,  $k = 2n + 1$  reflections are systematic absences indicating the  $P2_1/c$  space group. The cell parameters were obtained by least-squares refinement from the setting angles of 15 automatically centred reflections on a Syntex  $P\bar{1}$  diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation.

The intensity data were collected from a crystal measuring  $0.211 \times 0.135 \times 0.135$  mm elongated along *a* and bounded by the faces {100},  $\{\bar{1}00\}$ , {021},  $\{0\bar{2}1\}$ ,  $\{021\}$ , and  $\{0\bar{2}1\}$ . 3995 independent reflections were measured in the region of  $2\theta < 60^\circ$  by the  $2\theta/\theta$  scan technique with Mo  $K\alpha$  radiation. The data collection was done at a variable speed (24 to  $1^\circ \text{ min}^{-1}$ ). Most of the measurements were made at a speed of  $1^\circ \text{ min}^{-1}$ . A  $2\theta$  scan range of  $1.0^\circ$  below  $K\alpha_1$  and  $1.0^\circ$  above  $K\alpha_2$  was selected. The background to scan time ratio was 0.40. During the data collection three standard reflections were measured after every 47 reflections. Their variations were less than 2% of their respective means. The reflections for which  $I < 2.5\sigma(I)$  were

considered as unobserved. The standard deviation  $\sigma(I)$  was calculated as already described (Melanson & Rochon, 1975). An absorption correction based on the equations of the crystal faces was applied to the 2257 independent observed reflections. The transmission factors varied from 0.20 to 0.28. The data were then corrected for the Lorentz and polarization effects. The scattering factors for Pt, Cl, S, O, N and C were those of Cromer & Waber (1965) and those of Stewart, Davidson & Simpson (1965) were used for H. The anomalous dispersion terms (Cromer, 1965) of Pt, Cl and S were included in the calculations.

The position of Pt was easily located from the three-dimensional Patterson map. The positions of all other atoms except H were obtained by structure-factor and Fourier-map calculations. The quantity minimized in the full-matrix least-squares refinement was  $\sum w(F_o - F_c)^2$ . Individual weights,  $w$ , according to the equation  $1/w = a + bF_o + cF_o^2$  were calculated. The constants in the equation were adjusted to make the distribution of  $\langle w|\Delta F|^2 \rangle$  practically constant with respect to  $|F_o|$  and  $\sin \theta/\lambda$  ( $a = 48.0$ ,  $b = -0.52$  and  $c = 0.0015$ ). An isotropic secondary-extinction correction (Coppens & Hamilton, 1970) was also introduced. The H atoms on the four aromatic C were fixed at the calculated

positions, while those on the terminal methyl groups could not be located. The H atoms were assigned the isotropic temperature factor of the closest C atom. The refinement of the scale factor, the coordinates and anisotropic temperature factors of all nonhydrogen atoms converged to  $R = [\sum (|F_o| - |F_c|)/\sum |F_o|]$  of 0.049 and weighted residual  $R_w = \{[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}\}$  of 0.036. The standard deviation of an observation of unit weight is 1.091. The final difference Fourier map with all observed reflections only showed peaks lower than  $0.8 \text{ e } \text{Å}^{-3}$  (in the Pt environment). The refined parameters are given in Table 1.\*

The calculations were carried out with a CDC 6400 computer and the programs used are described elsewhere (Melanson & Rochon, 1975).

**Discussion.** A stereoscopic view of the molecule is shown in Fig. 1. The bond lengths and angles are given in Table 2. Two Cl, one S and one N atom form the square-planar coordination expected for  $\text{Pt}^{II}$  complexes. The weighted best plane was calculated through the five atoms. The deviations from this plane are: Pt 0.0007, Cl(1) -0.0029, Cl(2) -0.0129, S -0.0097 and N -0.0290 Å. The angles around Pt are close to the expected 90 and 180°.

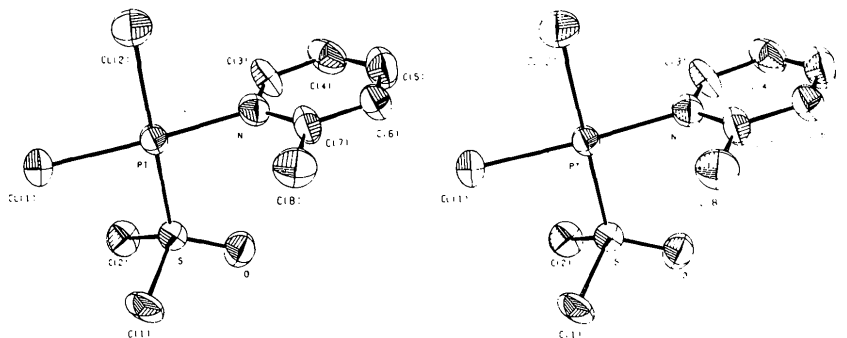
The compound has the *cis* configuration. This result confirmed the configurations assigned by our NMR studies (Kong *et al.*, 1976). The two Pt-Cl bond lengths (*cis* Pt-Cl = 2.288, *trans* Pt-Cl = 2.307 Å) are normal and agree well with the values found in  $\text{K}[\text{Pt}(\text{DMSO})\text{Cl}_3]$  (I) (*cis* Pt-Cl = 2.30, *trans* Pt-Cl = 2.32 Å) (Melanson, Hubert & Rochon, 1976), in *cis*- $[\text{Pt}(\text{DMSO})_2\text{Cl}_2]$  (II) (2.31 Å) (Melanson & Rochon, 1975), in  $\text{K}[\text{Pt}(2,6\text{-lutidine})\text{Cl}_3]$  (III) (2.30 Å) (Melanson & Rochon, 1976) and in *trans*- $[\text{Pt}(\text{diisopropyl sulphoxide})(N\text{-methylcytosine})\text{Cl}_2]$  (IV) (2.29 and 2.30 Å) (Lock, Speranzini & Powell, 1976).

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32829 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic positional parameters ( $\times 10^4$ )

Estimated standard deviations are given in parentheses.

	x	y	z
Pt	3488.2 (7)	1295.6 (3)	921.3 (5)
Cl(1)	4317 (5)	1444 (2)	-1265 (3)
Cl(2)	656 (4)	1161 (3)	-489 (4)
S	6190 (4)	1438 (2)	2251 (3)
O	6563 (12)	1381 (6)	3904 (10)
N	2623 (13)	1175 (7)	2836 (10)
C(1)	7508 (18)	762 (9)	1615 (15)
C(2)	6996 (18)	2355 (8)	1853 (16)
C(3)	2099 (19)	1787 (8)	3436 (17)
C(4)	1472 (19)	1753 (9)	4662 (16)
C(5)	1434 (20)	1065 (10)	5344 (15)
C(6)	1988 (17)	409 (8)	4757 (14)
C(7)	2601 (17)	468 (8)	3460 (13)
C(8)	3241 (19)	-225 (7)	2827 (16)



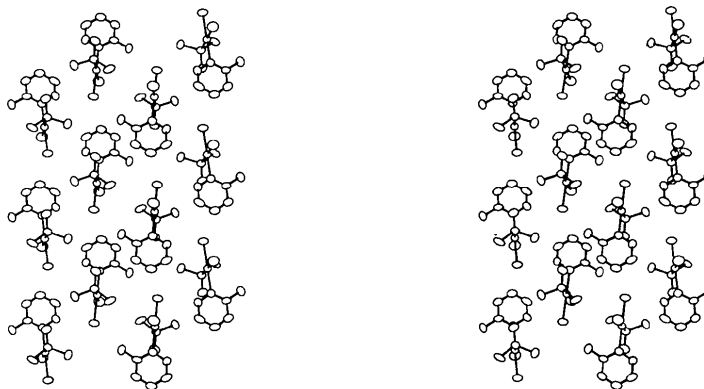
Fig. 2. Packing in the *cis*-[Pt(DMSO)(2-picoline)Cl<sub>2</sub>] crystal.

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

Pt—Cl(1)	2.288 (3)	Cl(2)—Pt—N	88.1 (3)
Pt—Cl(2)	2.307 (4)	S—Pt—N	92.4 (3)
Pt—S	2.200 (3)	Pt—S—O	117.8 (4)
Pt—N	2.062 (10)	Pt—S—C(1)	108.9 (5)
S—O	1.470 (9)	Pt—S—C(2)	109.9 (5)
S—C(1)	1.782 (16)	O—S—C(1)	108.4 (6)
S—C(2)	1.803 (14)	O—S—C(2)	106.5 (6)
N—C(3)	1.324 (18)	C(1)—S—C(2)	104.5 (7)
N—C(7)	1.366 (19)	Pt—N—C(3)	119.1 (9)
C(3)—C(4)	1.349 (21)	Pt—N—C(7)	119.6 (9)
C(4)—C(5)	1.361 (23)	N—C(3)—C(4)	122.6 (14)
C(5)—C(6)	1.390 (22)	N—C(7)—C(6)	117.8 (12)
C(6)—C(7)	1.406 (18)	N—C(7)—C(8)	122.0 (12)
C(7)—C(8)	1.493 (20)	C(3)—C(4)—C(5)	118.8 (15)
Cl(1)—Pt—Cl(2)	89.4 (1)	C(4)—C(5)—C(6)	120.3 (14)
Cl(1)—Pt—S	90.2 (1)	C(5)—C(6)—C(7)	119.1 (13)
Cl(1)—Pt—N	177.3 (3)	C(6)—C(7)—C(8)	120.2 (12)
Cl(2)—Pt—S	179.3 (1)	C(3)—N—C(7)	121.3 (12)

The Pt—S bond length (2.200 Å) is similar to the value (2.193 Å) found in (I) and slightly shorter than the values (2.244 and 2.229 Å) found for (II) and the value (2.232 Å) found in (IV). The S atom is in an approximately tetrahedral environment with angles ranging from 104 to 118°. The distances and angles found in the DMSO ligand agree well with the equivalent values found in DMSO itself (Thomas, Shoemaker & Eriks, 1966; Viswamitra & Kannan, 1966) and in the three sulphoxide Pt complexes mentioned above.

The Pt—N distance of 2.062 Å also seems normal and agrees well with the expected value (the radius sum is 2.02 Å). It is slightly longer than the value (2.011 Å) found in (III).

The bond lengths within the aromatic ring vary from 1.324 to 1.406 Å and the angles are all close to 120°. The 2-picoline ring is planar and lies almost perpendicular to the PtCl(1)Cl(2)SN plane (87.1°) as is shown in Figs. 1 and 2.

Fig. 2 illustrates the packing in the *cis*-[Pt(DMSO)-

(2-picoline)Cl<sub>2</sub>] crystal. It consists of layers of molecules parallel to the *ac* plane.

The environment of the C atoms (under 3.8 Å) has been closely examined for possible hydrogen bonding. The intramolecular contacts C(1)···O (2.64 Å) and C(2)···O (2.63 Å) are short but the S—C···O angles are unfavourable for hydrogen bonding (31.8 and 32.4°). There are a few intermolecular C···O contacts around 3.5 Å but the angles are also all unfavourable. It seems therefore that no hydrogen bonding exists in this crystal.

Grateful acknowledgement is made of financial support from the National Research Council of Canada. We thank Dr Pi-Chang Kong for the synthesis of the analysed compound and Johnson Matthey & Co. Ltd for the loan of potassium chloroplatinite.

## References

- 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.  
 KONG, P. C., IYAMUREMYE, D. & ROCHON, F. D. (1976). *Canad. J. Chem.* **54**, 3224–3226.  
 LOCK, C. J. L., SPERANZINI, R. A. & POWELL, J. (1976). *Canad. J. Chem.* **54**, 53–58.  
 MELANSON, R., HUBERT, J. & ROCHON, F. D. (1976). *Acta Cryst.* **B32**, 1914–1916.  
 MELANSON, R. & ROCHON, F. D. (1975). *Canad. J. Chem.* **53**, 2371–2374.  
 MELANSON, P. & ROCHON, F. D. (1976). *Canad. J. Chem.* **54**, 1002–1006.  
 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, Lond.* **209**, 1016–1017.