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Potassium Trichloro(dimethyl Sulphoxide)platinate(II)

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Abstract. $KPtCl_3C_2H_6SO$, M. W. 418·68; monoclinic, $C2/m$, $a=14{\cdot}969$ (7), $b=8{\cdot}116$ (4), $c=7{\cdot}746$ (4) Å, $\beta=105{\cdot}10$ (4)°, $Z=4$, $V=908{\cdot}6$ (8) Å^3, $D_x=3{\cdot}060$, $D_m=3{\cdot}07$ (1) g cm^{-3} (flotation); λ(Mo $K\alpha$)=0·71069 Å, μ(Mo $K\alpha$)=177·03 cm^{-1}; and $T=22$ °C. Positional and anisotropic thermal parameters were refined by full-matrix least-squares calculations to $R=0{\cdot}060$ and $R_w=0{\cdot}058$. The coordination around the platinum atom is planar. All the atoms, except the potassium ions and the two carbon atoms in the dimethyl sulphoxide ligand, are located on the mirror plane. The potassium ions are located on a twofold axis. Each potassium ion is surrounded by six chlorine and two oxygen atoms forming a distorted cube.

Introduction. The complex salt K[Pt(DMSO)Cl$_3$] (DMSO = dimethyl sulphoxide) was prepared by the method already described (Kukushkin, Vyazmenskii & Zorina, 1968) and recrystallized from water. A set of precession photographs indicated that the hkl, $h+k=2n+1$ reflexions are systematic absences. These extinctions are found for space groups $C2$, Cm and $C2/m$.

The intensity data were collected from a crystal measuring 0·293 × 0·207 × 0·046 mm (the short dimension being along the **c** direction) on a Syntex $P\bar{1}$ diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. A total of 1465 independent reflexions were measured in the region of $2\theta<60°$ by the $2\theta/\theta$ scan technique at a variable speed (24 to 1° min^{-1}). Most of the reflexions were measured at a speed of 1° min^{-1}. The background time to scan time ratio was 0·40. The reflexions for which the intensity was less than $2{\cdot}5\sigma(I)$ 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 observed reflexions. The data were then corrected for the Lorentz and polarization effects. The scattering factors were those of Cromer & Waber (1965) and the anomalous dispersions terms (Cromer, 1965) of platinum, potassium and chlorine were included in the calculations.

The platinum atom was easily located from the three-dimensional Patterson map which indicated either space group $C2$ or $C2/m$ (special positions). The positions of all other atoms, except the hydrogen atoms, were obtained by structure factor and Fourier map calculations. The refinement of the parameters was by full-matrix least-squares calculations for the two different space groups, since the $N(Z)$ test and the distribution of the normalized structure factors $|E|$ (Stout & Jensen, 1968) failed to distinguish between the two space groups. Identical agreement indices were obtained with the $C2/m$ space group using 52 parameters and with the $C2$ space group using 83 parameters. It

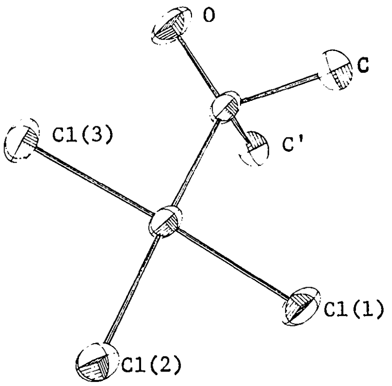

Fig. 1. Atom identification in the complex anion [Pt(DMSO)Cl$_3$]$^-$.

Table 1. *Final structure parameters and estimated standard deviations* (× 10^4)

The anisotropic thermal parameters are in the form
$\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$. Standard deviations are given in parentheses.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	2381·0 (6)	0·0	656 (1)	181·6 (3)	456·7 (5)	236·8 (4)	0·0	94·8 (3)	0·0
K	0·0	2660 (7)	0·0	360 (23)	517 (32)	438 (25)	0·0	197 (20)	0·0
Cl(1)	1467 (3)	0·0	2631 (7)	268 (23)	708 (44)	335 (26)	0·0	172 (21)	0·0
Cl(2)	1044 (3)	0·0	−1671 (7)	247 (23)	615 (40)	324 (26)	0·0	82 (20)	0·0
Cl(3)	3221 (4)	0·0	−1438 (7)	307 (25)	703 (44)	269 (24)	0·0	148 (20)	0·0
S	3620 (3)	0·0	2914 (6)	202 (21)	429 (31)	246 (22)	0·0	108 (18)	0·0
O	4535 (9)	0·0	2527 (21)	217 (67)	696 (104)	461 (88)	0·0	197 (64)	0·0
C	3589 (9)	1702 (20)	4336 (19)	370 (75)	351 (85)	367 (74)	−45 (69)	121 (61)	−106 (67)

was therefore assumed that $C2/m$ was the correct space group (Hamilton, 1965). In the early stages of refinement unit weight was assigned to all observed reflexions. Individual weights w, according to the equation $1/w=a+bF_o+cF_o^2$, were later calculated. a, b and c were adjusted to make the distribution of $w|\Delta F_o|^2$ constant with respect to $|F_o|$ and $\sin\theta/\lambda$ ($a=55{\cdot}0$, $b=-0{\cdot}31$ and $c=0{\cdot}0005$). An isotropic secondary extinction correction (Coppens & Hamilton, 1970) was also introduced. The refinement of the scale factor, the coordinates and anisotropic temperature factors of all non-hydrogen atoms converged to an $R=\sum(|F_o|-|F_c|)/\sum|F_o|$ of 0·060 and a weighted residual $R_w=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0·058.* The refined parameters are given in Table 1.

Discussion. The atoms in the molecule were labelled according to Fig. 1.

All the atoms in the crystal except the potassium ions and the two carbon atoms of the DMSO ligand are located on the mirror plane. The potassium ions are also located on special positions, namely on the twofold axis (equipoint *g*) (Table 1).

As expected, the dimethyl sulphoxide molecule is bonded to the platinum atom through sulphur. One sulphur and three chlorine atoms form a square-planar coordination around the platinum atom. The bond distances and angles are listed in Table 2. The angles around the platinum atom are close to the expected 90 and 180°.

The Pt–S bond (2·193 Å) is slightly shorter than the values (2·244 and 2·229 Å) found for *cis*-$[Pt(DMSO)_2Cl_2]$ (Melanson & Rochon, 1975) and the value (2·232 Å) found in *trans*-{$PtCl_2$[S-bis(isopropyl) sulphoxide](*N*-1-methylcytosine)} (Lock, Speranzini & Powell, 1976). The sulphur atom is in an approximate tetrahedral environment with angles ranging from 102 to 118°. The distances and angles found in the DMSO ligand agree well with the equivalent values found in DMSO itself (Viswamitra & Kannan, 1966; Thomas, Shoemaker & Eriks, 1966) and in the two sulphoxide platinum complexes mentioned above.

The two *cis* Pt–Cl bonds, 2·303 (5) and 2·297 (5) Å, are normal. The *trans* Pt–Cl, 2·318 (5) Å, also seems to be of normal length. We do not believe that the slightly higher value observed for the *trans* bond is significant. At the moment, there is no definite agreement as to how and by what amount a bond distance should be perturbed when the position is occupied by a ligand with a high *trans* influence. The crystallographic data on olefinic and acetylenic platinum complexes failed to show any significant systematic lengthening or contraction of the *trans* bond.

Fig. 2 illustrates the packing in the $K[Pt(DMSO)Cl_3]$ crystal. It consists of alternate layers of $[Pt(DMSO)Cl_3]^-$ anions and potassium cations parallel to the *ac* plane. Each potassium ion is surrounded by six chlorine and two oxygen atoms, at distances smaller than 3·36 Å (Table 3), forming a distorted cube.

Table 2. *Bond distances and bond angles in the* $[Pt(DMSO)Cl_3]^-$ *ion*

Distance (Å)		Angle (°)	
Pt–Cl(1)	2·302 (6)	Cl(1)–Pt–Cl(2)	88·6 (2)
Pt–Cl(2)	2·318 (5)	Cl(1)–Pt–Cl(3)	176·9 (2)
Pt–Cl(3)	2·296 (6)	Cl(1)–Pt–S	89·8 (2)
Pt–S	2·193 (5)	Cl(2)–Pt–Cl(3)	88·3 (2)
S—O	1·476 (15)	Cl(2)–Pt–S	178·3 (2)
S—C	1·776 (16)	Cl(3)–Pt–S	93·3 (2)
		Pt——S—O	118·3 (5)
		Pt——S—C	110·0 (5)
		O——S—C	107·6 (7)
		C——S—C′	102·2 (7)

Table 3. *The* K–Cl *and* K–O *distances and related angles*

Symmetry code

Superscript							
None	x	y	z	(ii)	$-x$	$-y$	$-z$
(i)	$x-\frac{1}{2}$	$\frac{1}{2}+y$	z	(iii)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$-z$

K–Cl(1)	3·363 (6)	K–Cl(3)^{i}	3·224 (6)
K–Cl(2)	3·136 (6)	K–O^{i}	2·938 (12)

Cl(1)–K–Cl(2)	59·4 (1)	Cl(3)^{i}–K–O^{i}	62·1 (3)
Cl(1)–K–Cl(3)^{i}	159·7 (2)	Cl(3)^{i}–K–Cl(1)^{ii}	79·5 (1)
Cl(1)–K–O^{i}	104·0 (3)	Cl(3)^{i}–K–Cl(2)^{ii}	95·3 (1)
Cl(1)–K–Cl(1)^{ii}	100·1 (1)	Cl(3)^{i}–K–Cl(3)^{iii}	107·8 (2)
Cl(1)–K–Cl(2)^{ii}	68·0 (1)	O^{i}——K–Cl(1)^{ii}	126·0 (3)
Cl(2)–K–Cl(3)^{i}	135·9 (2)	O^{i}——K–Cl(2)^{ii}	86·6 (3)
Cl(2)–K–O^{i}	161·8 (3)	O^{i}——K–Cl(3)^{iii}	72·9 (3)
Cl(2)–K–Cl(2)^{ii}	93·0 (1)	O^{i}——K–O^{iii}	99·5 (4)

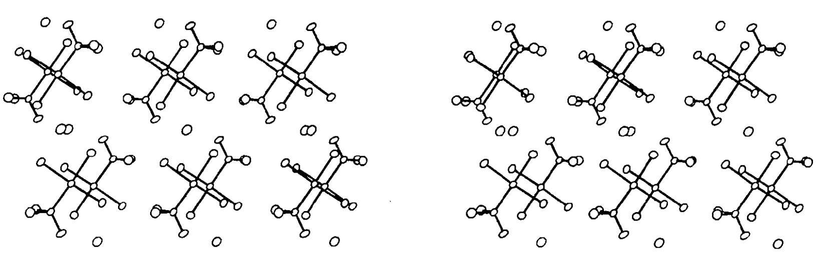

Fig. 2. Stereoscopic view of the packing in the $K[Pt(DMSO)Cl_3]$ crystal.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31655 (11 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The environment of the carbon atoms (below 4 Å) has been closely examined for possible hydrogen bonding. The hydrogen atoms could not be localized. The intramolecular contacts C···O (2·63 Å) and C···Cl(1) (3·40 Å) are short but the angles are unfavourable [S–C···O=32·4° and S–C···Cl(1)=67·4°]. The shortest C···O intermolecular contacts are 3·48 Å with an angle S–C···O of 118·7°. The long intermolecular C···Cl(1) [3·58 Å, angle S–C···Cl(1)=177·3°] and C···Cl(2) [3·51 Å, angle S–C···Cl(2)=101·2°] contacts do not suggest that hydrogen bonding would be very important in this crystal.

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A Refinement of the Crystal Structure of *N,N'*-Diglycyl-L-cystine Dihydrate

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Abstract. The structure of the title compound has been re-refined by full-matrix least squares, including anisotropic thermal parameters for the heavy atoms. Bond distances and angles are near to the previously published values, except for the angle C–C–S which is now no longer anomalously small. A revised scheme for the hydrogen bonding at the water molecule is suggested.

Introduction. During a survey of the geometries of the disulfide linkages in cystines, various derivatives of it, and related compounds (Donohue, 1976), it was noted that while there was generally good agreement among the values of various molecular features in these compounds, the value of 105·0 (2·1)° reported for the C–C–S bond angle in the diglycylcystine molecule (Yakel & Hughes, 1954, hereinafter YH) differed markedly from the average of 114·6 (1·9)° for fifteen other observed values of this feature. In their full-matrix least-squares refinement YH used one fixed isotropic temperature factor of 3·5 Å^2 which had been determined by the Wilson method. We decided that further refinement of this structure was necessary in order to learn whether the C–C–S bond angle was really abnormally small in this peptide.

YH reported that the crystals are monoclinic, space group $A2$, with two molecules in a unit cell having $a=12{\cdot}26$ (1), $b=4{\cdot}84$ (1), $c=17{\cdot}17$ (1) Å, and $\beta=124{\cdot}4$ (3)°. The molecules lie across crystallographic twofold axes.

The list of observed structure factors was obtained from the Library of Congress. It was found to contain 657 observed F_{hkl} instead of 630 as stated by YH. The ratio of number of observations to number of variables in least-squares refinements of the heavy atoms with anisotropic thermal motion is thus 6·1. Our full-matrix least squares began with three cycles with individual isotropic temperature factors, on the 12 heavy atoms. The weighting scheme used was that of Hughes (1941), with $4F_{\min}$ equal to 6·8. YH did not state which weighting scheme they used, presumably it was the same one. The structure factors were those in *International Tables for X-ray Crystallography* (1974). The initial three cycles reduced R to 15·6%. Three cycles with anisotropic temperature parameters were then calculated, reducing R to 11·3%. The 11 H atoms were then introduced at fixed assumed positions, with isotropic temperature factors of 5·0 Å^2, and an additional six cycles calculated. The parameter shifts in the last