$[Co(ox)(en)_2]^+$ (ox = oxalate) which has the $\Delta(\delta\lambda)$ conformation: the oblique-parallel type conformation (Aoki, Matsumoto, Ooi & Kuroya, 1973, and references therein). The bond distances and angles are similar to those of $[Co(ox)(en)_2]^+$, although the Co—N distances [1·937 (8)–1·960 (7) Å, average 1·949 Å] of the present complex are somewhat shorter than those [1·97 (2)–1·99 (2) Å, average 1·983 Å] of the ox complex.

There are some hydrogen bonds between the dicobalt complex cations and/or the water molecules, N(*B*2)···O(*A*2) [3·031 (11) Å], N(*B*2)···O(*A*4) [2·862 (11) Å], N(*B*3)···O(*A*4) [2·966 (11) Å], O1···O(*W*1) [2·950 (11) Å], O(*A*2)···O(*W*2) [2·811 (11) Å], N(*A*1)···O(*W*2) [2·954 (11) Å], O(*W*1)···O(*W*2) [2·873 (13) Å], and O(*W*2)···O(*W*3) [2·761 (13) Å].

References

AMA, T., KAWAGUCHI, H. & YASUI, T. (1988). *Bull. Chem. Soc. Jpn*, **61**, 1141–1146.

AOKI, T., MATSUMOTO, K., OOI, S. & KUROYA, H. (1973). *Bull. Chem. Soc. Jpn*, **46**, 159–162.

DAS, K., SINHA, U. C., PHULAMBRIKAR, A., CHATTERJEE, C. & BOHRA, R. (1989). *Acta Cryst.* C**45**, 398–400.

HAMADA, K., OHTA, E., FUJIWARA, T. & AMA, T. (1989). *Bull. Chem. Soc. Jpn*, **62**, 1328–1329.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1991). C**47**, 2101–2104

cis/trans Influences on Square-Planar Platinum(II) Complexes. Structure of *cis*-Bis(dimethyl sulfoxide)dinitratoplatinum(II)

BY D. BOSTRÖM AND R. STRANDBERG

Department of Inorganic Chemistry, University of Umeå, S-90187 Umeå, Sweden

AND B. NORÉN AND Å. OSKARSSON

Inorganic Chemistry, Chemical Center, University of Lund, PO Box 124, *S-221 00 Lund, Sweden*

(*Received* 11 *April* 1991; *accepted* 3 *May* 1991)

Abstract. *cis*-$[Pt\{(CH_3)_2SO\}_2(NO_3)_2]$, $M_r = 475{\cdot}36$, monoclinic, $P2_1/c$, $a = 9{\cdot}006$ (1), $b = 14{\cdot}209$ (2), $c = 10{\cdot}908$ (2) Å, $\beta = 117{\cdot}88$ (1)°, $V = 1233{\cdot}9$ (2) Å^3, $Z = 4$, $D_x = 2{\cdot}559$ Mg m^{-3}, $\bar{\lambda}$(Mo $K\alpha$) = 0·7107 Å, $\mu = 11{\cdot}84$ mm^{-1}, $F(000) = 896$, $T = 293$ K, $R = 0{\cdot}033$ for 1763 unique reflections [$I > 3\sigma(I)$]. The Pt atom coordinates two S atoms from two dimethyl sulfoxide ligands and two O atoms from different nitrate ions in a slightly distorted square-planar geometry (maximal deviation 0·10 Å) in a *cis* arrangement. The compound consists of van der Waals packed molecules appearing in pairs with a Pt—Pt distance of 4·008 (1) Å. The acceptor–donor distances observed are: Pt—S = 2·214 (3), 2·220 (3) and Pt—O = 2·040 (9), 2·059 (9) Å. These are almost the same as the corresponding ones previously found in tetrakis(dimethyl sulfoxide)platinum(II) bis(trifluoromethanesulfonate) where two dimethyl sulfoxide ligands bond to Pt *via* their O atoms, also in a *cis* position. A literature survey of platinum dimethyl sulfoxide compounds shows that the Pt—S distance is significantly affected by both *cis* and *trans* influences.

Introduction. Dimethyl sulfoxide, $(CH_3)_2SO$ = DMSO, possesses two potential donor sites, *i.e.* the S and the O atoms. Hence it can act as an ambidentate ligand in coordinating metal ions (Cotton & Francis, 1960; Davies, 1981). In Pd^{II} and Pt^{II} complexes sulfur bonding is predominant. Recently, the crystal structure of tetrakis(dimethyl sulfoxide)platinum(II) bis(trifluoromethanesulfonate) was determined (Elding & Oskarsson, 1987). The coordination around Pt was found to be distorted square planar with two S- and two O-bonded DMSO ligands in a *cis* arrangement. The cyclic thioether 1,4-thioxane, C_4H_8OS, is also expected to be capable of ambidentate coordination in a similar arrangement. However, the crystal structure determination of tetrakis(1,4-thioxane)platinum(II) bis(trifluoromethanesulfonate) shows this not to be the case. All four thioxane molecules bond to platinum *via* their S atoms (Bugarcic, Norén, Oskarsson, Stålhandske & Elding, 1991). The Pt—S bond length is significantly longer than in the corresponding dimethyl sulfoxide compound. The different coordination ability of these two ambidentate ligands towards Pt^{II} may be

0108-2701/91/102101-04$03.00 © 1991 International Union of Crystallography

explained by internal steric conditions or different donor properties of the O atoms. Besides DMSO complexes, the crystal structures of only a few Pt^{II} compounds with O-bonded ligands have been determined. Hence the present investigation of *cis*-$[Pt(DMSO)_2(NO_3)_2]$ was performed.

The *cis/trans* influence of *X*, *Y*, *Z* on the bond length *M*—*L* in a square-planar complex [*MLXYZ*] has been defined as the shortening or lengthening of the *M*—*L* distance as compared to the distance *M*—*L* in [ML_4] (Bugarcic *et al.*, 1991). In order to check the relative importance of packing effects and cis and *trans* influences on Pt—S distances, we have compiled Pt—S distances from Pt^{II} dimethyl sulfoxide compounds reported in the literature and divided them into different classes (constant *cis/trans* influence, constant *cis* influence, constant *trans* influence). By comparing the distribution of the Pt—S distances in these classes it should be possible to discriminate between the relative importance of packing forces, and *cis* and *trans* influences.

Experimental. *cis*-$[Pt(DMSO)_2(NO_3)_2]$ was synthesized from solid *cis*-$[Pt(DMSO)_2Cl_2]$ and aqueous $AgNO_3$ according to

$$cis\text{-}[Pt(DMSO)_2Cl_2](s) + 2AgNO_3(aq) \rightarrow Pt(DMSO)_2(NO_3)_2(aq) + 2AgCl(s).$$

The silver chloride was filtered off. Spontaneous evaporation of the filtrate at room temperature gave a solid, which on recrystallization from nitrobenzene gave pale yellow plates of *cis*-bis(dimethyl sulfoxide)-dinitratoplatinum(II).

A single crystal with the dimensions 0·16 × 0·05 × 0·10 mm was used for data collection at room temperature on a CAD-4 diffractometer employing monochromated Mo $K\alpha$ radiation. Laue class and systematic extinctions were consistent with the space group $P2_1/c$. This setting was chosen, since it is the one reported for the isostructural compound *cis*-$[Pd(DMSO)_2(NO_3)_2]$ (Langs, Hare & Little, 1967; the 'best' choice would be $P2_1/n$ with $c = 10{\cdot}403$ Å and $\beta = 112{\cdot}05°$). Unit-cell dimensions were obtained from 50 θ values in the range $7 < \theta < 23°$ determined as $\theta_{hkl} = (\omega_{hkl} - \omega_{\overline{hkl}})/2$. The intensities of 2295 reflections in one quarter of the reflection sphere (h,k,l range; $-10 \rightarrow 10$, $0 \rightarrow 16$, $-12 \rightarrow 0$) obeying $3 < \theta < 25°$ were measured with the ω–2θ scan technique ($\Delta\omega = 0{\cdot}75° + 0{\cdot}50°\tan\theta$). The ratio $\sigma(I)/I$ requested in a scan was 0·028 and the maximum recording time 120 s. Two standard reflections were recorded at regular intervals. The intensity decreased linearly by exposure time (a total of 6%). All the collected reflections were corrected, by a least-square fit, for this intensity decrease, giving a random variation of the standard reflections within ±1·5%. I and $\sigma(I)$ were corrected for Lorentz, polarization and absorption effects. The latter was performed according to the method of Walker & Stuart (1983). The corrections were in the range 0·88–1·09 for $A_{p,s}$ and 0·99–1·07 for A_θ (Ugozzoli, 1987), resulting in corrections on F_o in the interval 2·74–3·33. Reflections with $I < 3\sigma(I)$ were considered insignificantly different from the background and excluded from all subsequent calculations which resulted in 1763 reflections being used ($R_{int} = 0{\cdot}050$). $\sigma(I)$ was based on counting statistics.

The structure was solved from Patterson and $\Delta\rho$ maps. The atomic parameters for the non-H atoms were refined by full-matrix least-squares calculations. The positions of the H atoms could not be found in the last difference map and were not included in the structure-factor calculations. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with empirical weights $w^{-1} = \sigma^2/4|F_o|^2 + (0{\cdot}012|F_o|)^2 + 4{\cdot}0$. Scattering factors with corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The C and O atoms of the two DMSO ligands were refined with isotropic displacement parameters. All the other atoms were refined anisotropically. The total number of parameters varied was 124. The refinement converged at $R = 0{\cdot}033$, $wR = 0{\cdot}052$, $S = 1{\cdot}51$ and $(\Delta/\sigma)_{max} = 0{\cdot}007$. The heights in the final difference map were $(\Delta\rho)_{max} = 1{\cdot}1$ and $(\Delta\rho)_{min} = -1{\cdot}4$ e Å^{-3}. A δR plot (Abrahams & Keve, 1971) resulted in an approximately straight line with slope 0·98 and intercept −0·13. Computer programs used were those compiled and amended by Lundgren (1982). The final positional and thermal parameters are given in Table 1.* Interatomic distances and angles around the Pt atom are given in Table 2.

Discussion. A perspective view of a single molecule of *cis*-$[Pt(DMSO)_2(NO_3)_2]$ showing the atom-numbering scheme is presented in Fig. 1. A diagram of a unit-cell content is shown in Fig. 2 and illustrates that the present compound consists of van der Waals packed molecules appearing in pairs. The shortest Pt—Pt intermolecular distance is 4·008 (1) Å. In one of the nitrate groups the coordinated O atom (O21) is rather close to the Pt atom in the nearest neighbouring complex.

The coordination around Pt is distorted square planar. The deviations from the least-squares plane through Pt and the donor atoms are 0·053 (Pt), −0·079 (S1), 0·072 (S2), 0·054 (O11) and −0·100 Å

* Lists of structure factors, anisotropic displacement parameters and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54251 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic temperature factor coefficients with e.s.d.'s*

$U_{eq} = 1/3\Sigma\Sigma U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq} (Å^2)
Pt	0·68507 (6)	0·01137 (3)	0·19513 (5)	0·0217 (2)
S1	0·80898 (43)	0·14691 (21)	0·28858 (36)	0·0292 (12)
O1	0·7110 (13)	0·2118 (7)	0·3269 (11)	0·041 (2)*
C11	0·8665 (21)	0·2040 (12)	0·1689 (18)	0·050 (4)*
C12	1·0057 (20)	0·1300 (11)	0·4408 (18)	0·047 (4)*
S2	0·55168 (37)	0·01103 (21)	0·32176 (30)	0·0243 (11)
O2	0·6649 (12)	0·0220 (7)	0·4707 (10)	0·040 (2)*
C21	0·3889 (19)	0·0963 (10)	0·2595 (16)	0·039 (3)*
C22	0·4365 (17)	−0·0959 (9)	0·2908 (15)	0·033 (3)*
N1	0·9449 (15)	−0·0477 (9)	0·1259 (14)	0·038 (5)
O11	0·7940 (11)	−0·0036 (7)	0·0690 (10)	0·037 (4)
O12	1·0416 (14)	−0·0391 (10)	0·2474 (13)	0·062 (6)
O13	0·9761 (16)	−0·0954 (9)	0·0462 (14)	0·059 (6)
N2	0·6365 (16)	−0·1813 (8)	0·1037 (14)	0·039 (6)
O21	0·5507 (11)	−0·1036 (6)	0·0834 (10)	0·032 (4)
O22	0·7667 (15)	−0·1908 (8)	0·2092 (14)	0·064 (6)
O23	0·5751 (18)	−0·2407 (8)	0·0156 (14)	0·070 (6)

* Refined isotropically

Table 2. *Interatomic distances* (Å) *and angles* (°) *around the* Pt *atom with e.s.d.'s*

Pt—S1	2·220 (3)	S1—Pt—S2	91·1 (1)
Pt—S2	2·214 (3)	S1—Pt—O11	95·9 (3)
Pt—O11	2·040 (9)	S2—Pt—O21	91·6 (3)
Pt—O21	2·059 (9)	O11—Pt—O21	81·5 (4)
		S1—Pt—O21	171·9 (3)
		S2—Pt—O11	173·0 (3)

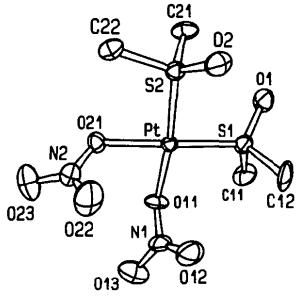

Fig. 1. View and numbering scheme of *cis*-[Pt(DMSO)$_2$(NO$_3$)$_2$].

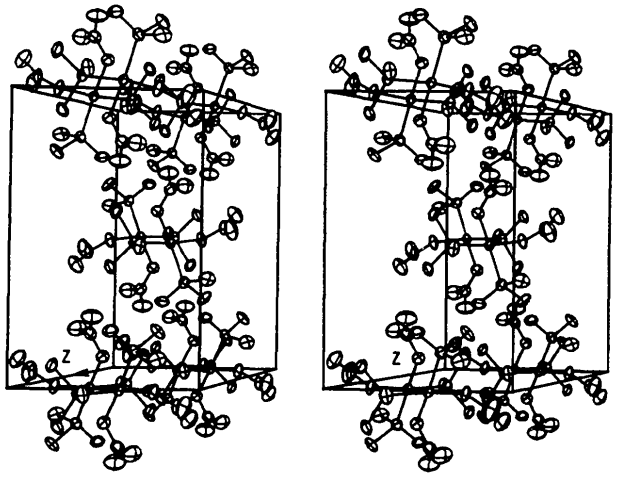

Fig. 2. Packing diagram of *cis*-[Pt(DMSO)$_2$(NO$_3$)$_2$].

Table 3. Pt—S *distances in square-planar* Pt^{II} *complexes containing dimethyl sulfoxide as an* S*-bonded ligand*

For the ligands in a *cis* or *trans* position to dimethyl sulfoxide only the kind of donor atom is given. The references are given in Codens-type notation according to *Checklist for Authors* (1985).

D_{Pt-S} (Å)		*trans* Partner	*cis* Partners	Reference		
2·174 (2)		O	N, Cl	JCDTBI	1986	1101
2·185 (2)	2·198 (2)	O	N, Cl	INOCAJ	29	1352
2·185 (5)		Cl	Cl, Cl	ZOKHA4	58	2297
2·186 (4)		Cl	N, Cl	ASBSDK	34	941
2·189 (4)		Cl	Cl, Cl	ACSCEE	44	92
2·191 (4)		Cl	O, Cl	INOCAJ	29	2708
2·193 (5)		Cl	Cl, Cl	ASBSDK	32	1914
2·197 (2)		Cl	N, N	ACSCEE	41	702
2·200 (3)		Cl	N, Cl	ASBSDK	33	3571
2·200 (3)		Cl	Cl, Cl	ACSCEE	43	1690
2·205 (4)	2·208 (3)	O	O, S	ICHAA3	130	209
2·214 (3)	2·220 (3)	O	O, S	This work		
2·216 (2)	2·224 (3)	Cl	N, Cl	ICHAA3	169	101
2·21 (1)		N	N, Cl	ICHAA3	26	L13
2·217 (2)		O	O, Cl	INOCAJ	29	2708
2·212 (3)		N	Cl, Cl	ASBSDK	34	1125
2·220 (2)		N	Cl, Cl	ACSCEE	40	793
2·220 (4)		N	Cl, Cl	INOCAJ	17	679
2·224 (2)		N	Cl, Cl	ASBSDK	36	713
2·225 (2)		Cl	N, Cl	INOCAJ	29	1352
2·228 (4)	2·233 (5)	Br	N, Br	ICHAA3	169	101
2·229 (2)	2·244 (2)	Cl	S, Cl	CJCHAG	53	2371
2·238 (3)	2·251 (3)	Cl	S, Cl	KOKHDC	11	129
2·248 (6)	2·248 (6)	N	N, S	CSCMCS	11	1369
2·315 (2)	2·324 (2)	C	C, S	CSCMCS	10	301

(O21). As seen in Fig. 1, the dimethyl sulfoxide ligands are S bonded and the nitrate groups are monodentate. Both of the nitrate ligands are almost planar. The largest deviation from planarity being as low as 0·013 Å. The nitrate groups are *trans* to the DMSO ligands. The same coordination geometry is found in *cis*-[Pd(DMSO)$_2$(NO$_3$)$_2$], which is isostructural with the present compound (Langs *et al.*, 1967). The Pt—S bond lengths [2·214 (3) and 2·220 (3) Å] are the same within experimental errors as is also true for the two Pt—O bond lengths [2·040 (9) and 2·059 (9) Å]. They also agree well with the Pt—S (2·205–2·208 Å) and Pt—O (2·040–2·051 Å) distances in [Pt(DMSO)$_4$](CF$_3$SO$_3$)$_2$ (Elding & Oskarsson, 1987) with two S and two O atoms bonded in a *cis* position. The *cis*/*trans* influences of O in a nitrate ion compared to O in DMSO are thus very similar. The bond lengths and angles of the coordinated DMSO molecules and nitrate ions do not differ significantly from those usually found.* Table 3 reports Pt—S distances from a number of crystallographically determined Pt^{II} dimethyl sulfoxide compounds. The large span of the observed Pt—S distance, 2·17–2·32 Å, reflects not only experimental errors but also packing forces, *cis*/*trans* influences and the steric requirements of the ligands. However, there are no bulky ligands in the compounds in Table 3 and the

* See deposition footnote.

steric factors must be of minor importance. In Table 3 there are four complexes $[Pt(DMSO)Cl_3]^-$, for which both the *cis* and the *trans* influence is constant. The distribution of 0·006 Å for the Pt—S distance in these complexes, calculated as $\sigma = [\Sigma(d_n - \bar{d})/(n-1)]^{1/2}$, indicates that experimental errors and packing forces are of minor importance as compared to other factors. If complexes [Pt(DMSO)-Cl*XY*], with Cl *trans* to S (15 distances, constant *trans* influence), are included in the calculation the distribution is increased to 0·022 Å, which thus emphasizes the importance of the *cis* influence of *X*/*Y* on S. If, on the other hand, the distribution is calculated for complexes $[Pt(DMSO)Cl_2X]$, with the two Cl atoms in the *cis* position (eight distances, constant *cis* influence), it is only slightly smaller, 0·017 Å. Hence it may be concluded that both *cis* and *trans* influences are important for the distribution of the Pt—S distance and that they are significantly larger than the effect of packing forces.

Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

References

ABRAHAMS, S. C. & KEVE, E. T. (1971). *Acta Cryst.* A**27**, 157–165.

BUGARCIC, Z., NORÉN, B., OSKARSSON, Å., STÅLHANDSKE, C. & ELDING, L. I. (1991). *Acta Chem. Scand.* **45**, 361–366.

Checklist for Authors (1985). *Acta Cryst.* B**41**, 1–4.

COTTON, F. A. & FRANCIS, R. (1960). *J. Am. Chem. Soc.* **82**, 2986–2991.

DAVIES, J. A. (1981). *Adv. Inorg. Chem. Radiochem.* **24**, 115–187.

ELDING, L. I. & OSKARSSON, Å. (1987). *Inorg. Chim Acta*, **130**, 209–213.

LANGS, D. A., HARE, C. R. & LITTLE, R. G. (1967). *Chem. Commun.* pp. 1080–1081.

LUNDGREN, J. O. (1982). Crystallographic computer programs. Report No. UUIC-B13-4-05. Univ. of Uppsala, Sweden.

UGOZZOLI, F. (1987). *Comput. Chem.* **11**, 109–120.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1991). C**47**, 2104–2107

Structure of 1-(*S*)-(3-Hydroxy-2-phosphonylmethoxypropyl)cytosine; an Antiviral Agent

BY JINDŘICH SYMERSKÝ*

The University of Oklahoma, Department of Chemistry and Biochemistry, Norman, OK 73019, *USA*

AND ANTONÍN HOLÝ

Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 *Praha* 6, *Czechoslovakia*

(*Received* 3 *July* 1990; *accepted* 22 *November* 1990)

Abstract. 4-Amino-1-(*S*)-{2-[(dihydroxyphosphoryl)-methoxy]-3-hydroxypropyl}-2(1*H*)-pyrimidinone, $C_8H_{14}N_3O_6P$, $M_r = 279{\cdot}19$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}926$ (1), $b = 9{\cdot}084$ (2), $c = 18{\cdot}602$ (3) Å, $V = 1170{\cdot}4$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}58$ (1) Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 2{\cdot}4$ mm^{-1}, $F(000) = 584$, $T = 168$ K, final $R = 0{\cdot}024$ for 1393 unique observed reflections. The molecule has been found to exist in a folded zwitterionic form where the negatively charged phosphonyl group and the positively charged cytosine ring are in proximity. The crystal packing involves significant intermolecular hydrogen-bond contacts.

Introduction. The recent discovery of the potent antiviral activity of several (*S*)-*N*-(3-hydroxy-2-phosphonylmethoxypropyl) derivatives of heterocyclic bases (DeClercq, Holý, Rosenberg, Sakuma, Balzarini & Maudgal, 1986) has attracted considerable attention to this novel group of nucleotide analogues. The chemical structure of these compounds is characterized by a replacement of the nucleotide carbohydrate moiety with a 2,3-dihydroxypropyl chain linked to the heterocyclic base by the stable C—N linkage and by regiospecific substitution of the phosphonylmethyl ether group for the phosphoric acid ester residue. It is assumed (Holý, 1986) that these compounds might adopt conformations resembling those of their natural nucleotide counterparts and, consequently, might replace nucleotides in enzyme–substrate/product complexes. The biological

* Permanent address: Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Praha 6, Czechoslovakia.

0108-2701/91/102104-04$03.00 © 1991 International Union of Crystallography