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Crystal and Molecular Structure of *trans*-Dichloro(dimethyl sulfoxide)(cytidine)platinum(II)

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The crystal and molecular structure of *trans*-dichloro(dimethyl sulfoxide)(cytidine)platinum(II) has been determined by single-crystal x-ray diffraction. The crystals are orthorhombic, space group $P2_12_12_1$ with $a = 6.607$ (3) Å, $b = 24.238$ (12) Å, $c = 10.851$ (11) Å, and $Z = 4$. The structure was refined by full-matrix least-squares analysis to a conventional R factor of 0.043. The coordination around the platinum atom is planar. The bond lengths are Pt–Cl(1) = 2.291 (5) Å, Pt–Cl(2) = 2.310 (4) Å, Pt–S = 2.220 (4) Å, and Pt–N(1) = 2.034 (13) Å. Distances within the ligands are normal. The plane of the pyrimidine ring is at 77.4° to the plane formed by the ligands around the platinum atom.

Introduction

Recently, we have studied the reactions between some nucleosides and *cis*-[$Pt(Me_2SO)_2Cl_2$].[1] The latter was chosen partly because dimethyl sulfoxide (Me_2SO) has been used as solvent for testing the antitumor activity of some platinum complexes and partly because it has some common features with *cis*-[$Pt(NH_3)_2Cl_2$], a potent antitumor compound, both having two neutral ligands and two chlorine atoms in cis positions. Since *cis*-[$Pt(Me_2SO)_2Cl_2$] is not an antitumor compound,[2] it was worth comparing the reaction mechanism of the two platinum complexes with nucleosides, in order to understand variations in the antitumor activities of the platinum compounds. The binding sites of the nucleosides in the reaction products were also investigated.

The reactions were studied by nuclear magnetic resonance.[1] In order to confirm the NMR configuration assignments of the platinum complexes formed in these reactions, some typical products were examined by x-ray diffraction. Here we report the molecular and crystal structure of the first of a series of platinum nucleoside complexes, *trans*-[$Pt(Me_2SO)(Cyd)Cl_2$].

Experimental Section

The crystals were obtained directly from the reaction of K[$Pt(Me_2SO)Cl_3$] and cytidine in water. A set of precession photographs indicated the $P2_12_12_1$ space group in the orthorhombic system. The cell parameters were calculated by refinement of the setting angles of 15 independent peaks centered on a Syntex $P\bar{1}$ diffractometer using graphite monochromatized Mo Kα radiation.

Crystal Data. $PtCl_2C_{11}H_{19}N_3SO_6$: formula weight, 587.35; orthorhombic; $P2_12_12_1$; $a = 6.607$ (3), $b = 24.238$ (12), $c = 10.851$ (11) Å; $V = 1737$ (2) Å^3; $d_x = 2.241$, $d_m = 2.23$ (1) g cm^{-3} (flotation); $Z = 4$; μ(Mo Kα) = 89.27 cm^{-1}; λ(Mo Kα) = 0.710 69 Å; $T = 22$ °C.

Collection and Reduction of Intensity Data. The intensity data were collected from a crystal measuring 0.624 × 0.104 × 0.052 mm, elongated along the a axis. A total of 2901 independant reflections were measured in the region of $2\theta < 60°$ by the $2\theta/\theta$ scan technique using Mo Kα radiation. During the data collection, three standard reflections were measured after every 47 reflections. Their variations were less than 2% from their respective means. The reflections for which the intensity was less than $2.5\sigma(I)$ were considered as unobserved. The standard deviation $\sigma(I)$ was calculated as already described.[3] A total of 1908 observed reflections remained. An absorption correction based on the equations of the crystal faces was then applied. The transmission factors varied from 0.3784 to 0.5255. The data were finally corrected for the Lorentz and polarization effects. The scattering factors of Cromer and Waber[4] were used for platinum, chlorine, sulfur, oxygen, nitrogen, and carbon; those of Stewart et al.[5] were used for hydrogen. The anomalous dispersion terms[6] of platinum, chlorine, and sulfur were included in the calculations.

Structure Determination. The structure was solved by the conventional heavy-atom method and refined by full-matrix least squares. The position of the platinum atom was easily located from the three-dimensional Patterson map. The positions of all the other atoms, except the hydrogen atoms, were obtained by structure factor and Fourier map calculations. In the early stages of refinement unit weight was assigned to all reflections. 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 $w|\Delta F|^2$ almost constant with respect to $|F_o|$ and $(\sin\theta)/\lambda$ ($a = 52.4$, $b = -0.392$, and $c = 0.000\,92$). An isotropic secondary extinction correction was also made.[7] The hydrogen atoms on the carbon atoms in the cytidine moiety were fixed at the calculated positions (C–H distance = 0.95 Å) and assigned isotropic temperature factors of 7. The refinement of the scale factor, the coordinates, and anisotropic temperature factors of all the nonhydrogen atoms converged to $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.043$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.041$. The final difference Fourier map did not show peaks higher than 0.8 e/Å^3. The surroundings of the two methyl carbon atoms in the Me_2SO molecule and of the oxygen and nitrogen atoms in the cytidine were carefully searched but no hydrogen atoms were found. The torsion angles within the ribose segment confirmed the *d* configuration of the molecule.

The calculations were carried out with a CDC 6400 computer, and the programs used have already been described.[3] A table of observed and calculated structure factors is available.[8]

Results and Discussion

The refined atomic parameters and the anisotropic temperature factors are listed in Table I. A labeled stereoscopic view of the molecule is show in Figure 1. The bond lengths and angles are given in Table II. As expected, the compound is the trans isomer. The dimethyl sulfoxide molecule is bonded to the platinum atom through the sulfur atom and the cytidine molecule is attached to the platinum atom through the other ring nitrogen atom. The coordination around the platinum atom is square planar. The weighted best plane was calculated through the five atoms. The deviations from this plane are the following: Pt, 0.0014; Cl(1), −0.0315; Cl(2), −0.0215; S, −0.0052; N, −0.0375 Å. The angles around the platinum are close to the expected 90 and 180°. The pyrimidine ring is planar and makes an angle of 77.4° with the platinum coordination plane as shown in Figures 1 and 2.

The Pt–Cl bond lengths (2.291 and 2.310 Å) are normal and agree well with the published results which are in the range 2.28–2.32 Å.[3,9-12] The Pt–S bond length (2.222 Å) is in the

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Table I. Final Structure Parameters and Anisotropic Thermal Parameters[a]

Structure Parameters (×10^4)

Atom	x	y	z	Atom	x	y	z
Pt	−28 (1)	875.6 (2)	4005 (5)	N(3)	−4305 (23)	1439 (7)	4302 (12)
Cl(1)	−1149 (9)	82 (2)	3081 (5)	C(1)	−1120 (25)	1369 (8)	1619 (12)
Cl(2)	917 (7)	1707 (2)	4878 (4)	C(2)	−4245 (23)	1782 (7)	1073 (16)
S	1855 (7)	389 (2)	5301 (4)	C(3)	−4960 (34)	1725 (6)	2219 (13)
O(1)	2881 (26)	690 (6)	6305 (13)	C(4)	−3721 (24)	1485 (6)	3117 (15)
O(2)	569 (17)	1203 (5)	1310 (10)	C(5)	−1351 (23)	1768 (6)	−434 (12)
O(3)	−2508 (18)	2176 (4)	−1051 (11)	C(6)	−1392 (22)	1257 (7)	−1287 (12)
O(4)	475 (22)	1300 (6)	−1978 (13)	C(7)	−3226 (25)	1354 (7)	−2062 (14)
O(5)	−3133 (23)	1072 (5)	−3214 (10)	C(8)	−3227 (26)	1967 (6)	−2200 (15)
O(6)	−6655 (22)	2098 (7)	−1509 (14)	C(9)	−5295 (42)	2217 (7)	−2481 (16)
N(1)	−1826 (21)	1301 (5)	2818 (11)	C(10)	3716 (32)	0 (9)	4451 (23)
N(2)	−2377 (19)	1632 (6)	785 (11)	C(11)	411 (34)	−170 (9)	5953 (24)

Anisotropic Thermal Parameters (×10^3)[b]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	20.6 (2)	25.8 (3)	18.9 (3)	5.3 (3)	−1.8 (4)	−1.3 (3)
Cl(1)	55.4 (30)	33.9 (24)	47.6 (27)	−1.4 (23)	−12.3 (27)	−13.6 (21)
Cl(2)	38.0 (23)	35.3 (21)	35.7 (21)	1.1 (20)	−3.8 (20)	−4.4 (19)
S	31.2 (21)	40.4 (24)	19.5 (17)	13.1 (20)	−2.1 (17)	−2.2 (17)
O(1)	70 (11)	61 (10)	46 (9)	18 (9)	−26 (8)	−4 (7)
O(2)	26 (6)	53 (7)	26 (6)	18 (5)	8 (5)	3 (5)
O(3)	39 (6)	19 (5)	22 (5)	1 (5)	8 (6)	−6 (5)
O(4)	47 (10)	79 (10)	45 (8)	9 (8)	16 (7)	−5 (8)
O(5)	60 (9)	39 (7)	19 (5)	−6 (7)	−6 (6)	−3 (5)
O(6)	38 (8)	72 (10)	51 (8)	32 (8)	7 (7)	−13 (8)
N(1)	26 (6)	36 (6)	19 (6)	0 (5)	−6 (5)	1 (5)
N(2)	22 (6)	43 (7)	15 (6)	3 (6)	16 (5)	−0 (5)
N(3)	36 (8)	66 (10)	18 (6)	0 (8)	−2 (6)	13 (7)
C(1)	26 (8)	50 (10)	8 (5)	−4 (8)	−0 (6)	−3 (6)
C(2)	22 (7)	41 (9)	24 (7)	9 (7)	0 (7)	−11 (7)
C(3)	18 (6)	42 (8)	31 (7)	7 (9)	18 (10)	3 (6)
C(4)	22 (7)	26 (7)	27 (8)	12 (6)	−1 (7)	−1 (6)
C(5)	28 (7)	29 (7)	4 (5)	−7 (6)	−0 (5)	4 (5)
C(6)	12 (6)	42 (8)	11 (6)	6 (6)	3 (5)	2 (5)
C(7)	29 (8)	31 (8)	23 (7)	−21 (7)	−11 (7)	9 (6)
C(8)	27 (8)	24 (7)	28 (8)	4 (6)	12 (7)	3 (6)
C(9)	60 (16)	29 (8)	35 (8)	21 (10)	−7 (11)	1 (7)
C(10)	40 (11)	53 (12)	75 (17)	27 (10)	8 (11)	−5 (12)
C(11)	51 (15)	67 (14)	68 (14)	−13 (11)	−15 (13)	42 (13)

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

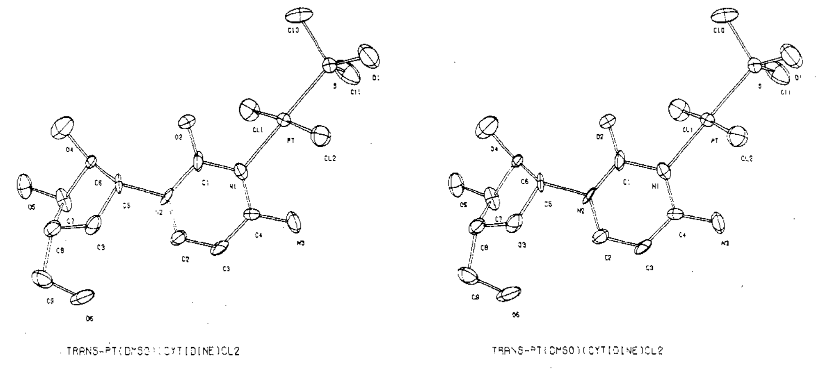

Figure 1. Labeled stereoscopic view of the molecule *trans*-[Pt(Me_2SO)(Cyd)Cl_2].

range (2.19–2.24 Å) reported for other (dialkyl sulfoxide)-platinum complexes.[3,9-12] The sulfur atom in the Me_2SO molecule is in an approximate tetrahedral environment. The distance and angles found in the Me_2SO group, agree well with equivalent values found in Me_2SO itself[13,14] and in the platinum complexes mentioned above.[3,9-12]

The Pt–N distance of 2.034 (13) Å is about the expected value. Me_2SO has a relatively high trans influence[15,16] but does not seem to have a marked influence on the trans Pt–N bond length. Values of 2.058 (7) and 2.046 (10) Å were found in *trans*-[Pt(diisopropyl sulfoxide)(1-methylcytosine)Cl_2][10] and in *trans*-[Pt(Me_2SO)(2-picoline)Cl_2],[12] respectively. A value of 2.062 (10) Å was found in *cis*-[Pt(Me_2SO)(2-picoline)Cl_2].[11]

The bond lengths in the pyrimidine ring vary from 1.33 to 1.40 Å and the angles are all close to 120°. They are similar to those found in *trans*-[Pt(diisopropyl sulfoxide)(1-methylcytosine)Cl_2][10] and in cytosine rings mentioned in a review by Voet and Rich.[17] They are identical with those found in cytidine.[18] The C(1)–O(2) bond of 1.24 Å is probably significantly longer than the normal double bond distance. The corresponding bond in cytidine was 1.246 Å, but O(2) in cytidine is involved in a hydrogen bonding system. In this structure O(2) does not seem to be involved in any hydrogen bonding. The angles in the ribose ring are close to the tet-

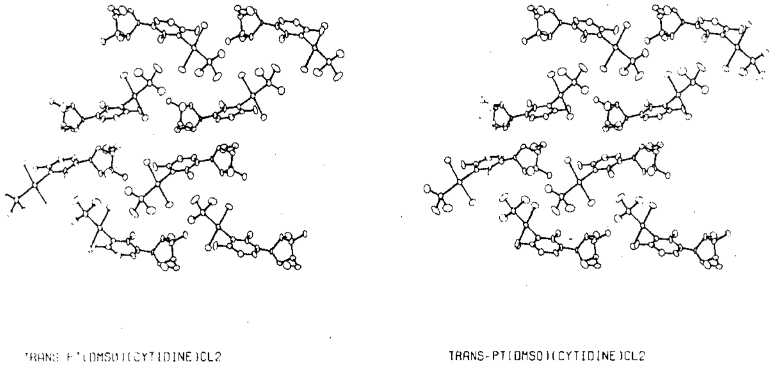

Figure 2. Stereoscopic diagram of the packing in the *trans*-[Pt(Me_2SO)(Cyd)Cl_2] crystal.

Table II. Bond distances (A) and Bond Angles (deg)

	Distance		
Pt-Cl(1)	2.291 (5)	C(4)-N(3)	1.35 (2)
Pt-Cl(2)	2.310 (4)	C(4)-N(1)	1.37 (2)
Pt-S	2.220 (4)	N(2)-C(5)	1.52 (2)
Pt-N(1)	2.034 (13)	C(5)-O(3)	1.42 (2)
S-O(1)	1.48 (2)	C(5)-C(6)	1.55 (2)
S-C(10)	1.80 (2)	C(6)-O(4)	1.45 (2)
S-C(11)	1.80 (2)	C(6)-C(7)	1.50 (2)
N(1)-C(1)	1.39 (1)	C(7)-O(5)	1.42 (2)
C(1)-O(2)	1.24 (2)	C(7)-C(8)	1.49 (2)
C(1)-N(2)	1.38 (2)	C(8)-O(3)	1.43 (2)
N(2)-C(2)	1.33 (2)	C(8)-C(9)	1.53 (3)
C(2)-C(3)	1.34 (2)	C(9)-O(6)	1.49 (3)
C(3)-C(4)	1.40 (2)		
	Angle		
Cl(1)-Pt-N(1)	87.5 (4)	N(2)-C(1)-O(2)	121 (1)
Cl(2)-Pt-N(1)	88.7 (4)	N(2)-C(2)-C(3)	121 (1)
Cl(1)-Pt-Cl(2)	176.1 (1)	C(2)-C(3)-C(4)	119 (1)
Cl(2)-Pt-S	92.9 (2)	N(1)-C(4)-N(3)	117 (1)
Cl(1)-Pt-S	90.8 (1)	N(1)-C(4)-C(3)	121 (1)
S-Pt-N(1)	178.0 (4)	N(3)-C(4)-C(3)	122 (1)
Pt-S-O(1)	117.6 (6)	N(2)-C(5)-C(6)	110 (1)
Pt-S-C(10)	109.8 (7)	N(2)-C(5)-O(3)	109 (1)
Pt-S-C(11)	110.3 (8)	C(6)-C(5)-O(3)	105 (1)
Pt-N(1)-C(1)	117 (1)	C(5)-C(6)-C(7)	103 (1)
Pt-N(1)-C(4)	124 (1)	C(5)-C(6)-O(4)	104 (1)
O(1)-S-C(11)	109 (1)	C(7)-C(6)-O(4)	113 (1)
O(1)-S-C(10)	109 (1)	C(6)-C(7)-C(8)	102 (1)
C(10)-S-C(11)	100 (1)	C(6)-C(7)-O(5)	112 (1)
C(1)-N(1)-C(4)	119 (1)	C(8)-C(7)-O(5)	113 (1)
C(1)-N(2)-C(2)	122 (1)	C(7)-C(8)-C(9)	114 (1)
C(1)-N(2)-C(5)	113 (1)	C(7)-C(8)-O(3)	105 (1)
C(2)-N(2)-C(5)	124 (1)	C(9)-C(8)-O(3)	109 (1)
N(1)-C(1)-N(2)	117 (1)	C(8)-C(9)-O(6)	110 (2)
N(1)-C(1)-O(2)	121 (1)	C(5)-O(3)-C(8)	110 (1)

Table III. Intermolecular Contacts

Atoms	Transformation	Distance, A
O(5)···O(1)	$-x, y, -z$	2.85 (2)
O(4)···O(6)	$x + 1, y, z$	2.76 (2)
N(3)···Cl(2)	$x - 1, y, z$	3.30 (1)
O(5)···Cl(1)	$-x - {}^1/_2, -y, z - {}^1/_2$	3.16 (1)

Atoms	Angle, deg	Atoms	Angle, deg
C(7)-O(5)···O(1)	106 (1)	C(4)-N(3)···Cl(2)	116 (1)
C(6)-O(4)···O(6)	123 (1)	C(7)-O(5)···Cl(1)	92 (1)
C(9)-O(6)···O(4)	116 (1)		

rahedral values. The relative orientation of the pyrimidine ring and the ribose ring corresponds to an anti conformation of the nucleoside. The same conformation was observed in cytidine.[18] The Pt(Me_2SO)Cl_2 group seems therefore to have almost no effect on the structure of cytidine in the complex.

The environments of the oxygen atoms O(4), O(5), and O(6) in the hydroxyl groups and of the nitrogen atom N(3) in the amino group have been closely examined for possible hydrogen bonding. No hydrogen atoms were found on the last Fourier difference map. Some short intermolecular O···O contacts with favorable angles (Table III) suggest that hydrogen bonding is important in the crystal. The oxygen atom of the Me_2SO molecule, O(1), is involved in hydrogen bonding with one hydroxyl group O(5) of the ribose ring (distance O(5)···O(1) = 2.85 Å and the angle C(7)–O(5)···O(1) is 106°). The two other hydroxyl groups O(4) and O(6) on the sugar moiety seem also to be hydrogen bonded. The distance O(4)···O(6) (2.76 Å) is short and the angles are not too unfavorable (C(9)–O(6)···O(4) = 116° and C(6)–O(4)···O(6) = 123°). One chlorine atom might also participate in hyrogen bonding. The distance of Cl(2)···N(3) is 3.30 Å and the angle is 116°. The distance Cl(1)···O(5) is also short 3.16 Å (angle C(7)–O(5)···Cl(1) = 92°), but since O(5) seems already involved in hydrogen bonding with O(1), we do not believe that Cl(1) has an important role in the hydrogen bonding system. No intramolecular hydrogen bonding was found.

The packing in the crystal is shown on Figure 2. It consists of molecules parallel to the *ac* plane and the molecules are hydrogen bonded mostly along the *a* direction.

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Registry No. *trans*-[Pt(Me_2SO)(Cyd)Cl_2], 65150-38-1.

Supplementary Material Available: A listing of structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

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