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cis-Dichloro(dimethyl sulfoxide-*S*)-(2-methoxypyridine-*N*)platinum(II)

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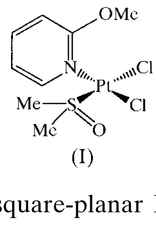
The title complex, $[PtCl_2(C_6H_7NO)(C_2H_6OS)]$, exhibits square-planar geometry. The plane of the pyridine ring makes a dihedral angle of 67.2 (3)° with the square plane of the metal center. The S—O bond is nearly aligned with the adjacent Pt—N bond, leaving the methyl groups of the dimethyl sulfoxide ligand to stagger the Pt—Cl bond.

Comment

Cisplatin, *cis*-$[Pt(NH_3)_2Cl_2]$, is extensively used in the treatment of a variety of cancers (Kelland *et al.*, 1992). Most of its second generation analogs are simple amines with a *cis* geometry about the metal, which is in either the +2 or +4 oxidation state. These compounds share a common rationale in their design (Cleare & Hoeschle, 1973). Reports of the biological effects of unusual Pt derivatives (Hambley, 1997), such as triamine complexes (Hollis *et al.*, 1989; Baird *et al.*, 1997) or those with a *trans* geometry (Van Beusichem & Farrell, 1992), have appeared in the literature. The antitumor activity of sulfoxide derivatives has also been noted (Farrell *et al.*, 1990). This has prompted us to investigate the antitumor activity of both *cis* and *trans* isomers of the general formula (N-Het)Pt(dmso)Cl_2, where N-Het is a nitrogen heterocycle. The title compound, (I), is a member of a series of complexes prepared as part of our study.



(I)

Compound (I) is a square-planar Pt derivative with bond distances and angles at the Pt atom in the normal range (Sundquist *et al.*, 1987; Melanson & Rochon, 1977*b*). The Pt atom deviates by 0.012 (1) Å from the mean plane of the ligand atoms (N—S—Cl1—Cl2). The structure validates ^{195}Pt NMR chemical shift data, which suggested a *cis* geometry for the product. The Pt—Cl bond *cis* to the dimethyl sulfoxide (dmso) ligand is slightly shorter than the *trans*-Pt—Cl bond, in line with the trend generally observed for ligands with a *trans* influence. While the Pt—S distance is within the range reported for other Pt^{II}–sulfoxide derivatives (Pasini *et al.*, 1994; Sundquist *et al.*, 1987), it is noteworthy that this bond length of 2.220 (3) Å is greater than the value expected when considering the *cis* influence of related ligands (Belsky *et al.*, 1991). This is likely to be due to the electron-donating ability of the methoxy group in the 2-position of the ring.

The S atom of the coordinated dmso ligand is tetrahedral. The S—O distance in Pt–dmso complexes is typically shorter than in the free ligand, and (I) also possesses a shortened bond. A near eclipsing of the Pt—N bond by the S—O group has been observed in other *cis*-Pt–dmso complexes (Melanson & Rochon, 1977*b*; Dyksterhouse *et al.*, 2000) and compound (I) is no exception. The resulting coplanarity of the S—O bond with the square plane of the metal atom in (I) [torsion angle O2—S—Pt—N 7.3 (4)°] and other *cis* complexes contrasts with *trans* derivatives, in which the S—O bond is perpendicular to the Pt square plane.

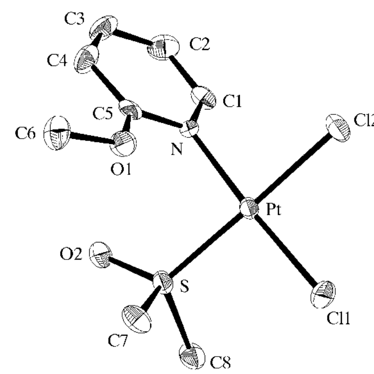


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-labeling scheme. H atoms have been omitted for clarity.

Another feature of (I) is a weak association of O1 to Pt, with a contact of 2.972 (8) Å. Furthermore, the dihedral angle between the pyridine plane and the metal coordination plane is 67.2 (3)°. This value is between that of the more hindered 2-methylpyridine ligand (Melanson & Rochon, 1977*b*) and of pyridine itself (Belsky *et al.*, 1991). The angle of the pyridine ring with the Pt plane in *cis* complexes is closer to perpendicular than in *trans* complexes (Melanson & Rochon, 1977*a*) in order to minimize contact between the dmso and pyridine ligands. This may imply that the proximity of O1 to Pt in the case of (I) is favored on steric grounds.

Intermolecular contacts which result in the packing of the crystal are dominated by van der Waals interactions between adjacent asymmetric units within the crystal. Intermolecular distances (except those involving hydrogen) are greater than 3.3 Å and the closest of such contacts involve the O atoms.

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Experimental

Compound (I) was synthesized from K_2PtCl_4 in three steps. K[(dmso)$PtCl_3$] was prepared from commercially available K_2PtCl_4 according to the literature method of Annibale *et al.* (1983). 2-Methoxypyridine (0.5 mmol) in ethanol (5 ml) was added to K[(dmso)$PtCl_3$]Cl (0.5 mmol, 209 mg) in H_2O (5 ml) and the mixture was stirred for 12 h. The solid yellow product, *trans*-dichloro(dimethyl sulfoxide)(2-methoxypyridine)platinum(II), (II), was collected and dried (70% yield). Isomerization was carrried out by dissolving (II) (15 mg) in dry dimethyl sulfoxide (800 µl). The mixture was periodically monitored by ^{195}Pt NMR and after 1 h, H_2O (2 ml) was added. X-ray quality crystals of (I) resulted from the standing solution.

Crystal data

[$PtCl_2(C_6H_7NO)(C_2H_6OS)$]	D_x = 2.356 Mg m^{-3}
M_r = 453.25	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
a = 8.749 (2) Å	θ = 12.5–17.5°
b = 8.486 (2) Å	μ = 11.499 mm^{-1}
c = 17.325 (3) Å	T = 193 K
β = 96.62 (2)°	Block, colorless
V = 1277.7 (4) Å^3	0.46 × 0.26 × 0.22 mm
Z = 4	

Data collection

Rigaku AFC-6*S* diffractometer	R_{int} = 0.033
$\omega/2\theta$ scans	θ_{max} = 25°
Absorption correction: empirical *via* ψ scan (North *et al.*, 1968)	h = 0 → 9
	k = 0 → 9
T_{min} = 0.032, T_{max} = 0.080	l = −19 → 19
2078 measured reflections	3 standard reflections
1936 independent reflections	every 100 reflections
1388 reflections with $I > 3\sigma(I)$	intensity decay: none

Refinement

Refinement on F	H-atom parameters constrained
R = 0.029	$w = 1/[\sigma^2(F) + 0.01F^2]$
wR = 0.036	$(\Delta/\sigma)_{max} < 0.001$
S = 1.42	$\Delta\rho_{max}$ = 1.82 e Å^{-3}
1388 reflections	$\Delta\rho_{min}$ = −1.72 e Å^{-3}
137 parameters	

Table 1
Selected geometric parameters (Å, °).

Pt—Cl1	2.293 (3)	S—C8	1.78 (1)
Pt—Cl2	2.311 (3)	O1—C5	1.35 (1)
Pt—S	2.220 (3)	O1—C6	1.46 (1)
Pt—N	2.033 (8)	N—C1	1.34 (1)
S—O2	1.461 (7)	N—C5	1.37 (1)
S—C7	1.773 (10)		
Cl1—Pt—Cl2	90.35 (10)	C5—O1—C6	115.4 (8)
Cl1—Pt—S	91.49 (9)	Pt—N—C1	120.3 (6)
Cl1—Pt—N	177.0 (2)	Pt—N—C5	121.0 (6)
Cl2—Pt—S	177.94 (9)	C1—N—C5	118.5 (9)
Cl2—Pt—N	87.1 (2)	N—C1—C2	122.9 (9)
S—Pt—N	91.1 (2)	O1—C5—N	112.2 (9)
Pt—S—O2	115.9 (3)	O1—C5—C4	125.9 (10)
Pt—S—C7	109.8 (4)	N—C5—C4	121.8 (9)
Pt—S—C8	110.8 (4)		

H atoms were treated as riding with C—H distances of 0.93 and 0.96 Å. The maximum and minimum residual electron densities are located in the vicinity of the Pt atom.

Data collection, cell refinement and data reduction: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1995); molecular graphics: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1145). Services for accessing these data are described at the back of the journal.

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