Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

cis- and *trans*-Dichloro(3,6-dihydro-1,2-oxazine-*N*)(dimethyl sulfoxide-*S*)-platinum(II)

R. Max Dyksterhouse, Bob A. Howell and Philip J. Squattrito*

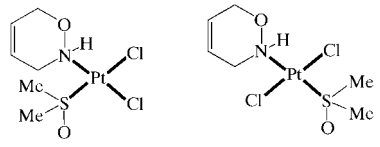
Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan 48859, USA
Correspondence e-mail: p.squattrito@cmich.edu

Received 25 August 1999
Accepted 26 October 1999

Both the *cis*, (I), and *trans*, (II), isomers of the title complex, $[PtCl_2(C_4H_7NO)(C_2H_6OS)]$, possess relatively undistorted square-planar geometries about the Pt atoms. For (I), *cis* *L*—Pt—*L* angles are in the range 88.8 (2)–91.08 (8)°, while *trans* angles are 178.61 (8) and 179.4 (2)°. For (II), *cis* *L*—Pt—*L* 86.1 (3)–93.7 (1)°, and *trans* *L*—Pt—*L* 175.5 (1) and 179.1 (3)°. The dimethyl sulfoxide (dmso) ligand adopts a normal pyramidal geometry in both complexes. In (I), the S═O bond essentially eclipses the adjacent Pt—N bond, while the oxazine ligand in (I) is twisted so as to avoid steric interactions with the adjacent chloride ligand. By contrast, the dmso ligand in (II) is rotated such that the S═O bond is approximately perpendicular to the square plane, while the oxazine ligand is once again twisted out of the plane by a similar amount as in (I). These are the first structural examples of square-planar platinum(II) complexes containing a 1,2-oxazine ligand.

Comment

Since the discovery of the antitumor activity of *cis*-diamminedichloroplatinum(II) (cisplatin), a large number of square-planar platinum complexes have been studied as potential chemotherapeutic drugs which might maintain the efficacy of cisplatin without the undesirable side effects (Lippard, 1982; Rosenberg, 1985). Typically, these complexes consist of two inert *cis*-ammine ligands and two labile *cis* ligands which act as leaving groups in the body, thus allowing the platinum to coordinate to the DNA of cancer cells. One complex which has achieved widespread use as an alternative to cisplatin is *cis*-diammine(1,1-cyclobutanedicarboxylato)-platinum(II) (carboplatin). The use of 1,2-oxazines as nitrogen ligands could lead to novel compounds with increased anti-tumor activity or decreased toxicity due to the demonstrated biological activity of the oxazine and the easily cleaved N—O bond in the oxazine ring. Compounds (I) and (II) were obtained from an unsuccessful effort to synthesize *cis*-bis-(3,6-dihydro-1,2-oxazine)1,1-cyclobutanedicarboxylato-platinum(II) through an intermediate dmso complex. They represent new members of a modest family of square planar $[PtCl_2(DMSO)(amine)]$ complexes whose structural features they share.



The *cis* isomer (I) of dichloro(3,6-dihydro-1,2-oxazine-*N*)-(dimethyl sulfoxide-*S*)platinum(II) is shown in Fig. 1. The Pt coordination geometry (Table 1) is quite regular, with all angles within 1.4° of their ideal values. The mean deviation from the $PtCl_2SN$ least-squares plane is 0.011 (3) Å. The Pt—Cl distance opposite the dmso ligand is 0.015 (3) Å longer than that opposite the oxazine ligand. This is consistent with what is observed in most of the reported *cis*-$[PtCl_2(dmso)(amine)]$ complexes (Melanson & Rochon, 1977; Belsky *et al.*, 1990, 1991; Rochon *et al.*, 1990, 1994; Neuse *et al.*, 1995; Caldwell *et al.*, 1995; Cornia *et al.*, 1997). The Pt—S and Pt—N distances are also within the reported ranges [2.184 (3)–2.225 (2) and 1.950 (6)–2.06 (1) Å, respectively], including those of two platinum 1,3-oxazine complexes (Albinati *et al.*, 1989; Michelin *et al.*, 1994). The pyramidal dmso ligand is positioned so that the S═O bond is nearly coplanar with the square plane [torsion angle O2—S—Pt—N −4.6 (3)°], while the S—C bonds are staggered between the Pt—Cl1 bond [torsion angle Cl1—Pt—S—C5 −62.6 (4)°]. This arrangement is also observed when the amine ligand is 2-picoline (Melanson & Rochon, 1977), pyridine (Belsky *et al.*, 1991), cyclopentylamine (Caldwell *et al.*, 1995), *tert*-butylamine

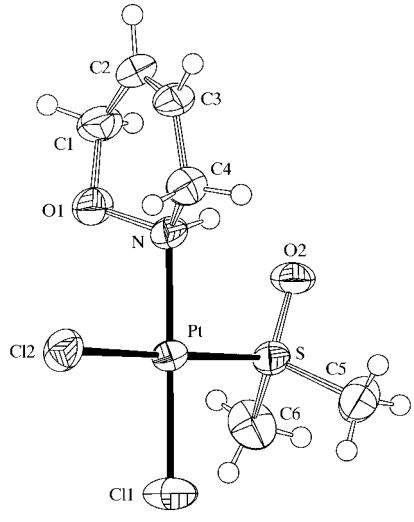


Figure 1
An *ORTEP*II diagram (Johnson, 1976) showing the molecular structure and atom-labeling scheme of (I). The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

(Neuse *et al.*, 1995), and thiazole (Cornia *et al.*, 1997). For acetonitrile, two structures have been reported, one with S═O eclipsing Pt—N (Rochon *et al.*, 1990) and one with an S—C bond approximately aligned with Pt—N (Belsky *et al.*, 1990). The latter conformation is also found in the propionitrile complex (Rochon *et al.*, 1994). The S═O bond at 1.489 (5) Å is significantly shorter than that in the free molecule at 278 K [1.531 (5) Å; Davies, 1981], but is at the high end of the range found in similar Pt complexes [1.44 (3)–1.48 (1) Å]. As in the free DMSO, the O—S—C angles are larger than the C—S—C angle, though the difference is smaller in the complex. The oxazine molecule shows bond distances and angles consistent with those found in non-coordinated 1,2-oxazine derivatives (Riddell *et al.*, 1974; Holzapfel *et al.*, 1987). It is positioned so that the N—O1 and N—C4 bonds are staggered about Cl2 [torsion angles Cl2—Pt—N—C4 62.2 (5) and Cl2—Pt—N—O1 −63.3 (4)°].

The *trans* isomer (II) is shown in Fig. 2. The Pt coordination geometry (Table 2) is slightly less regular than that of the *cis* isomer in that the Cl—Pt—Cl angle is closed 4.5° from ideal, causing a similar *ca* 3–4° distortion in the Cl2—Pt—S and Cl2—Pt—N angles. The mean deviation from the $PtCl_2SN$ plane is 0.021 (4) Å, with the two chloride ligands displaced 0.041 (4) and 0.035 (4) Å to the same side of the plane. As is the case in *trans*-[$PtCl_2$(dmso)(amine)] complexes (Melanson & Rochon, 1978; Caruso *et al.*, 1980; Viossat *et al.*, 1991; Lövqvist & Oskarsson, 1992; Cornia *et al.*, 1997), the Pt—Cl bond distances are closer to one another than in (I) and within experimental error. The Pt—S distance [2.230 (3) Å] is nearly 0.01 Å longer than the longest reported distance for this type of complex, while the Pt—N distance [2.067 (9) Å] is to the high end of the reported range [2.03 (1)–2.08 (2) Å] as is the S—O bond length. The dmso ligand is positioned quite differently from that in (I). The S═O bond is almost perpendicular to the square plane [torsion angle Cl2—Pt—S—O2 100.5 (4)°], while the S—C5 bond is the closest to being in the plane [torsion angle Cl2—Pt—S—C5 −24.6 (6)°]. A similar arrangement is found in *trans*-[$PtCl_2$(dmso)(NH_3)] (Viossat *et al.*, 1991), while other skewed orientations with the S═O group directed away from the square plane are found in the pyridine (Caruso *et al.*, 1980), piperidine (Lövqvist & Oskarsson, 1992) and thiazole (Cornia *et al.*, 1997) complexes. Only the cytidine complex (Melanson & Rochon, 1978) differs in having the S═O bond eclipsing an adjacent ligand as in (I). The bond distances and angles within the oxazine ligand do not differ significantly from those in (I). The conformation of the ring is also essentially the same [torsion angles for (I) and (II), respectively: N—C4—C3—C2 12 (1), 14 (2)°; N—O1—C1—C2 −49.6 (8), −48 (1)°]. The ring is positioned similarly to that in the *cis* isomer with the N—O1 and N—C4 bonds rotated away from the adjacent Cl ligands [torsion angles Cl1—Pt—N—O1 −55.6 (6) and Cl1—Pt—N—C4 67.9 (9)°].

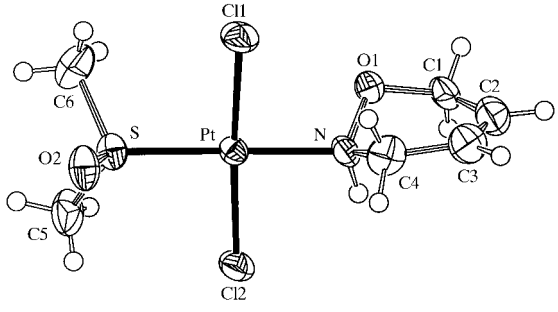


Figure 2
An *ORTEP*II diagram (Johnson, 1976) showing the molecular structure and atom-labeling scheme of (II). The displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

Experimental

For (I), a solution of *cis*-bis(dimethyl sulfoxide)(1,1-cyclobutanedicarboxylato)platinum(II) (0.502 g, 0.95 mmol) and 3,6-dihydro-1,2-oxazinium chloride (0.239 g, 1.95 mmol) in water (30 ml) was stirred at room temperature for 0.5 h. The yellow crystals which formed were collected by filtration, washed with several portions of distilled water, and dried at 323 K and 2700 Pa to provide *cis*-dichloro(3,6-dihydro-1,2-oxazine-*N*)(dimethyl sulfoxide-*S*)platinum(II) (0.269 g). For (II), to a stirred solution of *cis*-bis(dimethyl sulfoxide)(1,1-cyclobutanedicarboxylato)platinum(II) (0.314 g, 0.60 mmol) in water (20 ml) was added, dropwise, a solution of 3,6-dihydro-1,2-oxazine (0.149 g, 1.23 mmol) in water (5.0 ml) (pH adjusted to 4.0 with aqueous hydrochloric acid solution). The resulting solution was stirred at 328 K for 2 h and then allowed to stand at room temperature for 2 d. The volume of solution was reduced by rotary evaporation of the solvent at reduced pressure. The solid product was collected, washed repeatedly with distilled water, and dried at 323 K and 2700 Pa to provide *trans*-dichloro(3,6-dihydro-1,2-oxazine-*N*)(dimethyl sulfoxide-*S*)platinum(II) (0.167 g).

Compound (I)

Crystal data

$[PtCl_2(C_4H_7NO)(C_2H_6OS)]$	$Z = 2$
$M_r = 429.23$	$D_x = 2.403$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 8.177$ (4) Å	Cell parameters from 22 reflections
$b = 8.517$ (4) Å	$\theta = 20.6$–$22.4°$
$c = 10.297$ (4) Å	$\mu = 12.6$ mm^{-1}
$\alpha = 105.84$ (3)°	$T = 296$ K
$\beta = 104.42$ (3)°	Slab, pale yellow
$\gamma = 111.16$ (3)°	0.25 × 0.12 × 0.10 mm
$V = 593.2$ (5) Å^3	

Data collection

Rigaku AFC-6*S* diffractometer	$R_{int} = 0.013$
ω–2θ scans	$\theta_{max} = 25°$
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 9$
$T_{min} = 0.190$, $T_{max} = 0.284$	$k = -10 \rightarrow 9$
2249 measured reflections	$l = -12 \rightarrow 11$
2089 independent reflections	3 standard reflections every 150 reflections
1820 reflections with $I > 3\sigma(I)$	intensity decay: 2.3%

Refinement

Refinement on F^2	H-atom parameters not refined
$R(F) = 0.026$	$w = 4F_o^2/\sigma^2(F_o^2)$
$wR(F^2) = 0.059$	$(\Delta/\sigma)_{max} = 0.001$
$S = 2.23$	$\Delta\rho_{max} = 0.73$ e Å^{-3}
2087 reflections	$\Delta\rho_{min} = -1.75$ e Å^{-3}
118 parameters	

Table 1
Selected geometric parameters (Å, °) for (I).

Pt—Cl1	2.310 (2)	O1—N	1.452 (7)
Pt—Cl2	2.325 (2)	O1—C1	1.458 (9)
Pt—S	2.207 (2)	N—C4	1.480 (9)
Pt—N	2.062 (6)	C1—C2	1.49 (1)
S—O2	1.489 (5)	C2—C3	1.32 (1)
S—C5	1.776 (9)	C3—C4	1.47 (1)
S—C6	1.783 (8)		
Cl1—Pt—Cl2	90.07 (8)	Pt—S—C6	111.2 (3)
Cl1—Pt—S	91.08 (8)	O2—S—C5	107.9 (4)
Cl1—Pt—N	179.4 (2)	O2—S—C6	108.9 (4)
Cl2—Pt—S	178.61 (8)	C5—S—C6	102.7 (4)
Cl2—Pt—N	90.1 (2)	N—O1—C1	110.2 (5)
S—Pt—N	88.8 (2)	Pt—N—O1	109.8 (4)
Pt—S—O2	113.8 (2)	Pt—N—C4	117.1 (5)
Pt—S—C5	111.7 (3)	O1—N—C4	109.4 (5)

Table 2
Selected geometric parameters (Å, °) for (II).

Pt—Cl1	2.300 (3)	O1—N	1.44 (1)
Pt—Cl2	2.294 (3)	O1—C1	1.44 (1)
Pt—S	2.230 (3)	N—C4	1.48 (1)
Pt—N	2.067 (9)	C1—C2	1.47 (2)
S—O2	1.480 (8)	C2—C3	1.33 (2)
S—C5	1.79 (1)	C3—C4	1.51 (2)
S—C6	1.78 (1)		
Cl1—Pt—Cl2	175.5 (1)	Pt—S—C6	110.2 (5)
Cl1—Pt—S	90.4 (1)	O2—S—C5	108.2 (6)
Cl1—Pt—N	89.8 (3)	O2—S—C6	108.3 (6)
Cl2—Pt—S	93.7 (1)	C5—S—C6	100.8 (7)
Cl2—Pt—N	86.1 (3)	N—O1—C1	111.5 (9)
S—Pt—N	179.1 (3)	Pt—N—O1	109.9 (6)
Pt—S—O2	115.7 (4)	Pt—N—C4	115.2 (8)
Pt—S—C5	112.5 (4)	O1—N—C4	109 (1)

Compound (II)

Crystal data

$[PtCl_2(C_4H_7NO)(C_2H_6OS)]$
M_r = 429.23
Orthorhombic, *Pbca*
a = 16.532 (3) Å
b = 13.868 (2) Å
c = 10.182 (4) Å
V = 2334 (1) Å^3
Z = 8
D_x = 2.442 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
θ = 15.5–20.3°
μ = 12.8 mm^{-1}
T = 296 K
Hexagonal plate, pale yellow
0.30 × 0.10 × 0.03 mm

Data collection

Rigaku AFC-6*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.242, T_{max} = 0.681
2053 measured reflections
2053 independent reflections
1277 reflections with $I > 3\sigma(I)$
θ_{max} = 25°
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 16$
$l = -12 \rightarrow 0$
3 standard reflections
every 150 reflections
intensity decay: 0.1%

Refinement

Refinement on F^2
$R(F)$ = 0.032
$wR(F^2)$ = 0.074
S = 1.71
2049 reflections
119 parameters
H-atom parameters not refined
$w = 4F_o^2/\sigma^2(F_o^2)$
$\Delta\rho_{max}$ = 1.95 e Å^{-3}
$\Delta\rho_{min}$ = −2.09 e Å^{-3}
Extinction correction: Zachariasen (1968) type 2 Gaussian isotropic
Extinction coefficient: 1.0 (5) × 10^{-7}

For structure (I), the minimum and maximum points on the final difference electron-density map were 1.03 and 1.27 Å, respectively, from the Pt atom. For structure (II), the minimum and maximum peaks in the final difference electron-density map were 1.02 Å from Pt and 1.63 Å from H9, respectively.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1991); program(s) used to solve structure: *MITHRIL* (Gilmore, 1983); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Partial support of this work by the Elsa U. Pardee Foundation and the Michigan Research Excellence Fund is gratefully acknowledged. The Herbert H. and Grace A. Dow Foundation and The Dow Chemical Company Foundation provided funding for the establishment of the CMU X-ray Crystallography Facility.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1238). Services for accessing these data are described at the back of the journal.

References

Albinati, A., Arz, C. & Pregosin, P. S. (1989). *J. Organomet. Chem.* **371**, C18–20.
Belsky, V. K., Konovalov, V. E. & Kukushkin, V. Y. (1991). *Acta Cryst.* C**47**, 292–294.
Belsky, V. K., Konovalov, V. E., Kukushkin, V. Y. & Moiseev, A. I. (1990). *Inorg. Chim. Acta*, **169**, 101–107.
Caldwell, G., Neuse, E. W., Perlwitz, A. G., Field, J. S. & Ramesar, N. (1995). *Transition Met. Chem.* **20**, 200–202.
Caruso, F., Spagna, R. & Zambonelli, L. (1980). *Acta Cryst.* B**36**, 713–715.
Cornia, A., Fabretti, A. C., Bonivento, M. & Cattalini, L. (1997). *Inorg. Chim. Acta*, **255**, 405–409.
Davies, J. A. (1981). *Adv. Inorg. Chem. Radiochem.* **24**, 115–187.
Gilmore, C. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*. Department of Chemistry, University of Glasgow, Scotland.
Holzapfel, C. W., Kruger, G. J. & Van Dyk, M. S. (1987). *Acta Cryst.* C**43**, 598–601.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Lippard, S. J. (1982). *Science*, **218**, 1075–1082.
Lövqvist, K. & Oskarsson, Å. (1992). *Acta Cryst.* C**48**, 2073–2075.
Melanson, R. & Rochon, F. D. (1977). *Acta Cryst.* B**33**, 3571–3573.
Melanson, R. & Rochon, F. D. (1978). *Inorg. Chem.* **17**, 679–681.
Michelin, R. A., Belluco, U., Mozzon, M., Berin, P., Bertani, R., Benetollo, F., Bombieri, G. & Angelici, R. J. (1994). *Inorg. Chim. Acta*, **220**, 21–33.
Molecular Structure Corporation (1988). *MSC*/AFC Diffractometer Control Software. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1991). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Neuse, E. W., Perlwitz, A. G., Field, J. S. & Ramesar, N. (1995). *Transition Met. Chem.* **20**, 62–66.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Riddell, F. G., Murray-Rust, P. & Murray-Rust, J. (1974). *Tetrahedron*, **30**, 1087–1096.
Rochon, F. D., Kong, P.-C. & Melanson, R. (1990). *Inorg. Chem.* **29**, 1352–1356.
Rochon, F. D., Kong, P.-C. & Melanson, R. (1994). *Inorg. Chim. Acta*, **216**, 163–167.
Rosenberg, B. (1985). *Cancer*, **55**, 2303–2314.
Viossat, B., Khodadad, P. & Rodier, N. (1991). *Acta Cryst.* C**47**, 1316–1317.
Zachariasen, W. H. (1968). *Acta Cryst.* A**24**, 212–216.