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trans-Dichloro(dimethyl sulfide-*κS*)(pyridine-*κN*)platinum(II)

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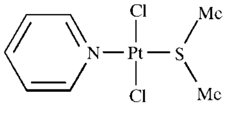
The structure of the title compound, [$PtCl_2(C_5H_5N)(C_2H_6S)$], consists of discrete molecules in which the Pt-atom coordination is slightly distorted square planar. The Cl atoms are *trans* to each other, with a Cl—Pt—Cl angle of 176.60 (7)°. The pyridine ligand is rotated 64.5 (2)° from the Pt square plane and one of the Pt—Cl bonds essentially bisects the C—S—C angle of the dimethyl sulfide ligand. In the crystal structure, there are extensive weak C—H···Cl interactions, the shortest of which connects molecules into centrosymmetric dimers. A comparison of the structural *trans* influence on Pt—S and Pt—N distances for $PtS(CH_3)_2$ and Pt(pyridine) fragments, respectively, in square-planar Pt^{II} complexes is presented.

Comment

The *trans* influence, *i.e.* the change in ground-state thermodynamic properties due to *trans* ligand effects, has been widely studied, particularly for square-planar Pt^{II} complexes (Pidcock *et al.*, 1966; Crabtree, 1988, Anderson & Orpen, 2001). Zumdahl & Drago (1968) have shown that the *trans* influence is due to the σ-donation ability of the *trans* ligand; stronger σ donors show a stronger *trans* influence, as noted by a weaker overlap of the ligand *trans* to the Pt atom. Some *cis* influence is also predicted. X-ray crystallographic studies have clearly shown the *trans* influence in Pt—Cl bond distances (Appleton *et al.*, 1973; Kapoor *et al.*, 1996, 1998; Norén *et al.*, 1997; Otto & Johansson, 2002). In the title compound, *trans*-[$PtCl_2(NC_5H_5)S(CH_3)_2$], (I), the dimethyl sulfide ligand is *trans* to the pyridine ligand. Compound (I) is the first structurally characterized *trans*-[Pt*L*SMe_2Cl_2] complex to be published.

In (I), the Pt atom is in a slightly distorted square-planar environment, with the coordination sphere consisting of *trans* Cl atoms, a dimethyl sulfide ligand and a pyridine ligand (Fig. 1). Selected geometric parameters for (I) are given in Table 1. The geometry about the Pt atom deviates little from an ideal square plane; the S—Pt—Cl1 angle [92.65 (8)°] is slightly larger than 90° in order to accommodate the methyl groups of the dimethyl sulfide ligand. The Pt atom is almost exactly coplanar with the plane defined by the four atoms bonded to it, with a deviation from the plane of 0.0029 (19) Å. The pyridine ring is tilted at an angle of 64.5 (2)° to the square plane. The angle between the $PtCl_2NS$ and SC_2 planes is 87.0 (2)°.



(I)

In the crystal structure of (I), there are extensive weak C—H···Cl interactions (Table 2), the shortest of which connects molecules into centrosymmetric dimers (Fig. 2).

The dimethyl sulfide ligand is bonded *via* the S atom, which shows trigonal–pyramidal geometry. The S—C distances and C—S—C angles are close to the averages found for square-planar Pt^{II} complexes in the Cambridge Structural Database (CSD, Version 5.24; Allen, 2002); the minimum and maximum C—S distances are 1.78 (2) and 1.796 (14) Å, respectively, and the mean C—S—C angle is 99.3 (8)° for 21 observations. The Pt—Cl distance in (I) is comparable with those in *trans*-$PtCl_2$ moieties, which have an average of 2.300 (11) Å for 397 examples in the CSD, and the Pt—N distance is about the same as the average [2.05 (4) Å, 44 observations].

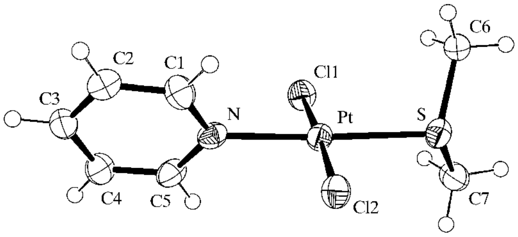


Figure 1
A view of the molecule of (I) with the atomic labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

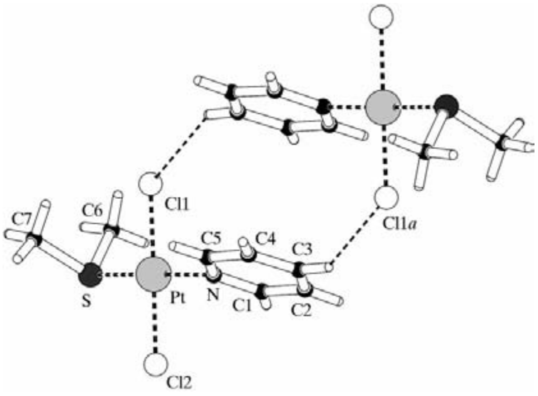


Figure 2
A diagram showing the molecules of (I) connected into centrosymmetric dimers by weak C—H···Cl interactions (shown as dashed lines). Atom Cl1*a* is related by the symmetry code (−*x*, 1 − *y*, −*z*).

A total of seven complexes with the general formula [PtSMe$_2L_3$], and 15 complexes of the general formula [Pt(pyridine)L_3], where L is a simple monodentate ligand, have been structurally characterized and reported in the CSD. Table 3 lists the average Pt—S distances *versus* the *trans* ligand for the first type. The structural *trans* influence series from these observations is phenyl ≫ pyridine > SMe$_2$ > Cl$^-$.

Table 4 lists the average Pt—N distances *versus* the *trans* ligand for the second type of complex, [Pt(pyridine)L_3]. The Pt—N distances in *trans*-[Pt(pyridine)$_2$Cl$_2$] (CLPYPT; Colamarino & Orioli, 1975) are unusually short [1.98 (1) Å] compared with the average calculated for *trans*-pyridine ligands. As the authors state that the refinement showed problems, this value has been omitted. The structural *trans* influence series follows the order: phenyl > AsPh$_3$ > –CH$_2$NC$_5$H$_5$ > –SCN$^-$ > pyridine > Cl$^-$ > –ONO$_2{}^-$.

Experimental

Compound (I) was crystallized from a solution of dichlorobis(dimethyl sulfide)platinum(II) in dichloromethane containing a small quantity of pyridine.

Crystal data

[PtCl$_2$(C$_5$H$_5$N)(C$_2$H$_6$S)]
M_r = 407.22
Monoclinic, $P2_1/c$
a = 8.5159 (17) Å
b = 5.9128 (12) Å
c = 21.586 (4) Å
β = 96.32 (3)°
V = 1080.3 (4) Å^3
Z = 4
D_x = 2.504 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 36 336 reflections
θ = 4.1–27.5°
μ = 13.62 mm^{-1}
T = 100 (2) K
Block, orange
0.22 × 0.22 × 0.19 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*DENZO–SMN*; Otwinowski & Minor, 1997)
$T_{\min}$ = 0.060, $T_{\max}$ = 0.075
11 912 measured reflections
2459 independent reflections
1756 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.096
$\theta_{\max}$ = 27.5°
$h = -11 \rightarrow 11$
$k = -7 \rightarrow 7$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R(F)$ = 0.038
$wR(F^2)$ = 0.082
S = 0.97
2459 reflections
111 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0353P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 2.14 e Å^{-3}
$\Delta\rho_{\min}$ = −1.94 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt—N	2.042 (6)	Pt—Cl2	2.307 (2)
Pt—S	2.275 (2)	S—C6	1.794 (8)
Pt—Cl1	2.309 (2)	S—C7	1.813 (8)
N—Pt—S	176.36 (18)	C6—S—C7	98.9 (4)
Cl2—Pt—Cl1	176.60 (7)		
Cl1—Pt—S—C6	52.9 (3)	Cl2—Pt—N—C1	67.0 (6)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7B···Cl1	0.98	2.85	3.484 (9)	123
C4—H4···Cl1$^{\rm i}$	0.95	2.95	3.752 (9)	142
C3—H3···Cl1$^{\rm ii}$	0.95	2.82	3.632 (8)	144
C6—H6B···Cl2$^{\rm iii}$	0.98	2.90	3.773 (8)	148
C6—H6A···Cl2$^{\rm iv}$	0.98	2.90	3.711 (8)	140
C7—H7A···Cl2$^{\rm iv}$	0.98	2.99	3.772 (9)	138
C3—H3···Cl2$^{\rm v}$	0.95	2.99	3.640 (9)	127

Symmetry codes: (i) $-x, 2-y, -z$; (ii) $-x, 1-y, -z$; (iii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iv) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (v) $1-x, 1-y, -z$.

Table 3
The *trans* ligand effect on the Pt—S distance (Å) for [Pt(SMe$_2$)L_3] complexes.

L_{trans}	Mean Pt—S	CSD refcode(s)	Reference
Cl$^-$	2.268 (4)	JASMUL	Huffman & Lloyd (1989)
		MINNEC	Otto & Johansson (2002)
		VAYWOH	Horn *et al.* (1990)
		WENJII	Kapoor *et al.* (1998)
SMe$_2$	2.292 (3)	RIXSAX	Wendt *et al.*, 1997
		TIVLOZ	Kapoor *et al.* (1996)
Phenyl	2.380 (10)	FAZVOR	Alibrandi *et al.* (1987)

Table 4
The *trans* ligand effect on the Pt—N distance (Å) for [Pt(pyridine)L_3] complexes.

L_{trans}	Mean Pt—N	CSD refcode(s)	Reference
–ONO$_2{}^-$	2.01 (2)	ICUVEH	Tessier & Rochon (2001)
Cl$^-$	2.026 (12)	CCPYPT	Colamarino & Orioli (1975)
		KIHYOP	Belsky *et al.* (1991)
		IGOROL	Skvortsov *et al.* (2002)
Pyridine	2.027 (6)	CIWKEY01	Wei *et al.* (1989)
		ICUVAD	Tessier & Rochon (2001)
		MIJWEH	Fontes *et al.* (2001)
		SESDOJ	Pombrik *et al.* (1988)
		TCPYPT	Caira &Nassimbeni (1975)
I$^-$	2.044 (6)	KARTIG	Tessier & Rochon (1999)
S(═O)(p-tol)(Me)	2.048 (9)†	IGORUR	Skvortsov *et al.* (2002)
–CH$_2$NC$_5$H$_5$	2.101 (10)†	FEZWEM	Hanks *et al.* (1987)
AsPh$_3$	2.109 (5)†	XOTRIH	Kuznik & Wendt (2002)
Phenyl	2.140 (4)†	HEWNUS	Romeo *et al.* (1994)

† Estimated s.u. for the bond length.

The H atoms of the dimethyl sulfide ligand were refined as riding atoms, with an ideal tetrahedral geometry allowed to rotate to fit the electron density; C—H = 0.98 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C). The H atoms on the pyridine ring were constrained to positions bisecting the C—C—C angles; C—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The largest residual peak in the difference Fourier map is 2.04 Å from atom H4 and the largest hole is 0.94 Å from the Pt atom.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1718). Services for accessing these data are described at the back of the journal.

References

Alibrandi, G., Bruno, G., Lanza, S., Minniti, D., Romeo, M. L. & Tobe, M. L. (1987). *Inorg. Chem.* **26**, 185–190.

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Anderson, K. M. & Orpen, A. G. (2001). *Chem. Commun.* pp. 2682–2683.

Appleton, T. G., Clark, H. C. & Manzler, L. E. (1973). *Coord. Chem. Rev.* **10**, 335–422.

Belsky, V. K., Konovalov, V. E. & Kukushkin, V. Yu. (1991). *Acta Cryst.* C**47**, 292–294.

Caira, M. R. & Nassimbeni, L. R. (1975). *Acta Cryst.* B**31**, 581–582.

Colamarino, P. & Orioli, P. L. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1656–1659.

Crabtree, R. (1988). *The Organometallic Chemistry of the Transition Metals*, p. 6. New York: John Wiley & Sons.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Fontes, A. P. S., Oskarsson, Å., Lovquist, K. & Farrell, N. (2001). *Inorg. Chem.* **40**, 1745–1750.

Hanks, T. W., Ekeland, R. Å., Emerrson, K., Larson, R. D. & Jennings, P. W. (1987). *Organometallics*, **6**, 28–32.

Horn, G. W., Kumar, R., Maverick, A. W., Fronczek, F. R. & Watkins, S. F. (1990). *Acta Cryst.* C**46**, 135–137.

Huffman, J. C. & Lloyd, B. R. (1989). *Inorg. Chem.* **28**, 3087–3091.

Kapoor, P., Kukushin, V. Y., Lövqvist, K. & Oskarsson, Å (1996). *J. Organomet. Chem.* **517**, 71–79.

Kapoor, P., Lövqvist, K. & Oskarsson, Å. (1998). *J. Mol. Struct.* **470**, 39–47.

Kuznik, N. & Wendt, O. F. (2002). *J. Chem. Soc. Dalton Trans.* pp. 3074–3078.

Nonius (1997). *KappaCCD Server Software*. Nonius BV, Delft, The Netherlands.

Norén, B., Oskarsson, Å. & Svensson, C. (1997). *Acta Chem. Scand.* **51**, 289–293.

Otto, S. & Johansson, M. H. (2002). *Inorg. Chim. Acta*, **329**, 135–140.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Pidcock, A., Richards, R. E. & Venanzi, L. M. (1966). *J. Chem. Soc. A*, pp. 1707–1710.

Pombrik, S. I., Pachevskaya, V. M., Golovchenko, L. S., Peregudov, A. S., Kravtsov, D. N., Batsonov, A. S. & Struchkov, Yu. T. (1988). *Metalloorg. Khim.* **1**, 379–383.

Romeo, R., Arena, G., Scolaro, L. M., Plutino, M. P., Bruno, G. & Nicolo, F. (1994). *Inorg. Chem.* **33**, 4029–4037.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Skvortsov, A. N., Vekki, D. A., Stash, A. J., Belsky, V. K., Spevak, V. N. & Skvortsov, N. K. (2002). *Tetrahedron: Asymmetry*, **13**, 1663–1671.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Tessier, C. & Rochon, F. D. (1999). *Inorg. Chim. Acta*, **295**, 25–38.

Tessier, C. & Rochon, F. D. (2001). *Inorg. Chim. Acta*, **322**, 37–46.

Wei, C. H., Hingerty, B. E. & Busing, W. R. (1989). *Acta Cryst.* C**45**, 26–30.

Wendt, O. F., Oskarsson, Å., Leipoldt, J. G. & Elding, L. I. (1997). *Inorg. Chem.* **36**, 4514–4519.

Zumdahl, S. S. & Drago, R. S. (1968). *J. Am. Chem. Soc.* **90**, 6669–6675.

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