

In the solid state, the cyclic amine in *cis*-[PtCl₂-(C₄H₇NH₂)(NH₃)] blocks only one axial site, but in solution, free rotation around the Pt-N bond is assumed and both sites should be partly protected, but less than in the di(cyclic amine) complex. This explanation for the large difference in the toxicity of *cis*-[PtCl₂(C₄H₇NH₂)₂] (~100 mg kg⁻¹) and *cis*-[PtCl₂-(C₄H₇NH₂)(NH₃)] (~10 mg kg⁻¹) does not seem sufficient. Other factors like hydrogen bonding might be important. The structure of *cis*-[PtCl₂(C₄H₇NH₂)(NH₃)] has shown extensive hydrogen bonding of the NH₃ ligand. In this crystal, the NH₃ ligand forms three strong hydrogen bonds with the chlorine atoms [N(1)···Cl = 3.34–3.37 Å] while the cyclic amine seems to play a minor role in the hydrogen-bonding system (Table 2). Therefore we suggest that this factor should be considered as a partial explanation of the toxicities of the *cis*-[PtCl₂(cyclic amine)(NH₃)] complexes.

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada and to the Ministère de l'Éducation (FCAR) for financial support.

References

- BRADDOCK, P. D., CONNORS, T. A., JONES, M., KHOKHAR, A. R., MELZACK, D. H. & TOBE, M. L. (1975). *Chem. Biol. Interactions*, **11**, 145–161.
- BRADFORD, J. P., FAGGIANI, R. & LOCK, C. J. L. (1981). *Acta Cryst.* **B37**, 243–246.
- COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* **A26**, 71–83.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- HOWARD-LOCK, H. E., LOCK, C. J. L., TURNER, G. & ZVAGULIS, M. (1981). *Can. J. Chem.* **59**, 2737–2745.
- LIPPERT, B., LOCK, C. J. L. & SPERANZINI, R. A. (1981). *Inorg. Chem.* **20**, 808–813.
- LOCK, C. J. L., SPERANZINI, R. A. & ZVAGULIS, M. (1980). *Acta Cryst.* **B36**, 1789–1793.
- LOCK, C. J. L. & ZVAGULIS, M. (1981). *Inorg. Chem.* **20**, 1817–1823.
- MELANSON, R. & ROCHON, F. D. (1975). *Can. J. Chem.* **53**, 2371–2374.
- MELANSON, R. & ROCHON, F. D. (1985). *Acta Cryst.* **C41**, 350–352.
- ROCHON, F. D. & KONG, P. C. (1986a). *J. Clin. Hematol. Oncol.* Submitted.
- ROCHON, F. D. & KONG, P. C. (1986b). *Can. J. Chem.* In the press.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- ZANOTTI, G., DEL PRA, A., BOMBIERI, G. & TAMBURRO, M. (1978). *Acta Cryst.* **B34**, 2138–2141.

Acta Cryst. (1986). **C42**, 1294–1296

Structure of the Palladium(II) Sulfimide Complex *trans*-Dichloro(*S,S*-dimethyl-*N*-2-pyridylsulfimide)(triethylphosphine)palladium(II)

BY KENNETH W. MUIR AND LJUBICA MANOJLOVIĆ-MUIR

Chemistry Department, Glasgow University, Glasgow G12 8QQ, Scotland

(Received 6 April 1986; accepted 29 April 1986)

Abstract. [PdCl₂(C₇H₁₀N₂S)(C₆H₁₅P)], *M_r* = 449.7, orthorhombic, *P*2₁2₁2₁, *a* = 8.247 (1), *b* = 10.936 (2), *c* = 21.707 (4) Å, *U* = 1957.7 (6) Å³, *Z* = 4, *D_x* = 1.526 g cm⁻³, Mo *Kα*, λ = 0.71069 Å, μ = 13.9 cm⁻¹, *F*(000) = 912, *T* = 293 K, *R* = 0.027 for 2824 unique reflections with *I* ≥ 3σ(*I*). The Pd^{II} ion has a *trans*-square-planar coordination, with Pd–P = 2.241 (2) Å and Pd–Cl = 2.292 (2) and 2.309 (2) Å. The sulfimide is attached to the metal through the imide N atom with Pd–N = 2.127 (4) Å.

Introduction. The title compound is one of a series of palladium and platinum sulfimide complexes synthesized by Davidson, Preston & Spankie (1986). Its structure has been determined by X-ray analysis in order to establish the mode of attachment of the sulfimide ligand to the metal and also to assess whether structural changes occur in the sulfimide molecule on its coordination to palladium.

Experimental. Pale yellow needle, 0.50 × 0.14 × 0.10 mm, elongated along *b*; Enraf–Nonius CAD-4F diffractometer, Mo X-rays, graphite monochromator; cell dimensions by least-squares fit to the setting angles of 23 automatically centred reflections with 11 < θ < 17°; intensities of 6310 reflections, with 2 ≤ θ ≤ 30° and *h* 0→11, *k* 0→15, *l* –30→30, measured from continuous θ/2θ scans of (0.60 + 0.35tanθ)° in θ, increased by 25% at each end to assess background effects; corrections for Lp and absorption [empirical method of Walker & Stuart (1983), transmission factors on *F* 0.81–1.09], no correction required for decomposition (111 and 222 standard intensities showed <3% fluctuation about their means) or for extinction; *R*_{int} 0.021 for 621 independent reflections measured at least twice; 5688 independent structure amplitudes (point group 222 assumed); of these 2824 with *I* ≥ 3σ(*I*), including 1030 Friedel pairs, used in the structure analysis. Patterson and difference syntheses;

Table 1. Fractional coordinates and isotropic displacement parameters (\AA^2) for non-H atoms U_{iso} is the mean latent root of the anisotropic displacement tensor.

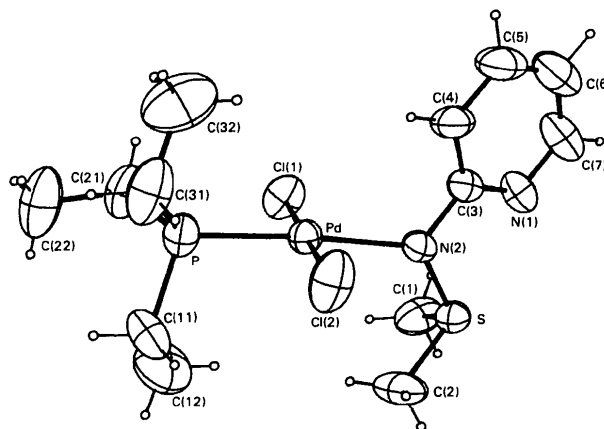
	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
Pd	0.12871 (4)	0.11190 (3)	0.13961 (1)	0.039
Cl(1)	0.26133 (17)	-0.07215 (11)	0.14286 (6)	0.063
Cl(2)	-0.00863 (18)	0.29576 (12)	0.13673 (6)	0.074
P	0.22127 (17)	0.16513 (12)	0.23287 (6)	0.051
S	0.15390 (14)	0.10409 (11)	-0.01343 (5)	0.044
N(1)	-0.0789 (4)	-0.0647 (4)	-0.0177 (2)	0.053
N(2)	0.0485 (4)	0.0730 (3)	0.0485 (2)	0.041
C(1)	0.3203 (6)	0.0010 (5)	-0.0176 (3)	0.066
C(2)	0.2570 (8)	0.2372 (5)	0.0098 (3)	0.073
C(3)	-0.0761 (5)	-0.0101 (4)	0.0369 (2)	0.039
C(4)	-0.1953 (6)	-0.0290 (5)	0.0811 (2)	0.057
C(5)	-0.3185 (6)	-0.1091 (6)	0.0669 (3)	0.074
C(6)	-0.3220 (7)	-0.1628 (6)	0.0110 (4)	0.080
C(7)	-0.2010 (7)	-0.1417 (5)	-0.0290 (3)	0.072
C(11)	0.3728 (10)	0.2862 (6)	0.2218 (3)	0.097
C(12)	0.5218 (9)	0.2382 (9)	0.1848 (4)	0.115
C(21)	0.3226 (7)	0.0473 (6)	0.2766 (2)	0.076
C(22)	0.4072 (10)	0.0906 (7)	0.3356 (3)	0.114
C(31)	0.0728 (9)	0.2284 (6)	0.2842 (3)	0.087
C(32)	-0.0684 (10)	0.1348 (8)	0.2951 (3)	0.119

full-matrix least-squares refinement on F ; $w^{-1} = \sigma^2(F) + 2.25 \times 10^{-4}F^2$; H atoms riding on bonded C atoms with $C-H = 0.96 \text{ \AA}$; final adjustment of 186 parameters [isotropic U refined for H(4)–H(7), otherwise $U(H) = U(C)$, anisotropic U_{ij} for all non-H atoms] gave $R = 0.027$, $wR = 0.029$, $S = 1.2$; maximum $\Delta/\sigma = 0.037$; final $|\Delta\rho|$ values $< 0.47 \text{ e \AA}^{-3}$; chirality parameter (Rogers, 1981) $\eta = +1.03$ (8); this structural model is clearly superior to the alternative with N(1) interchanged with C(4)–H(4) which gave $R = 0.029$, $wR = 0.032$ and $U = 0.25$ (6) \AA^2 compared with 0.05 (1) \AA^2 for H(4); neutral-atom scattering factors and complex anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); *GX* crystallographic program package (Mallinson & Muir, 1985). Final atomic coordinates are presented in Table 1.*

Discussion. The crystals contain *trans*-[PdCl₂{N(SMe₂)C₅H₄N}(PEt₃)] molecules (Fig. 1) separated by van der Waals distances. The Pd^{II} atom displays the expected square-planar coordination. A Cl₂PN donor set around the metal is completed by the attachment of the sulfimide ligand through N(2). Bond lengths and angles involving Pd (Table 2) agree well with those in other Pd^{II} complexes with *trans*-Cl₂PN donor sets (Olmstead, Guimerans, Farr & Balch, 1983; Keijsper, van der Poel, Polm, van Koten, Vrieze, Seignette, Varenhorst & Stam, 1983). In particular, the Pd–N(2)

bond length [2.127 (4) \AA] is virtually identical to those in *trans*-[PdCl₂{N(Bu')=CHCH=NBU'}(PPh₃)] [2.126 (5) and 2.130 (7) \AA] which, according to Keijsper *et al.* (1983), are the longest Pd^{II}–N_{sp}² distances so far reported. These Pd–N bonds are, of course, subject to the high *trans* influence of PR₃ ligands (Manojlović-Muir & Muir, 1974a).

The phosphine ligand adopts one of the low-energy conformations of the free PEt₃ molecule (Solomon, 1979), with staggering about the P–C bonds and a dihedral angle of 86.6° between the mean planes defined by the atoms P, C(21), C(22) and P, C(11), C(12), C(31), C(32), the latter group being coplanar to

Fig. 1. A perspective view of the *trans*-[PdCl₂{N(SMe₂)C₅H₄N}(PEt₃)] molecule showing 50% vibrational ellipsoids for non-H atoms. H atoms are represented by spheres of arbitrary size.Table 2. Selected interatomic distances (\AA) and angles ($^\circ$)

Pd–Cl(1)	2.292 (2)	Pd–Cl(2)	2.309 (2)
Pd–P	2.241 (2)	Pd–N(2)	2.127 (4)
P–C(11)	1.837 (7)	P–C(21)	1.805 (6)
P–C(31)	1.794 (7)	S–N(2)	1.638 (4)
S–C(1)	1.778 (6)	S–C(2)	1.760 (6)
N(1)–C(3)	1.328 (6)	N(1)–C(7)	1.335 (7)
N(2)–C(3)	1.395 (6)	C(3)–C(4)	1.389 (6)
C(4)–C(5)	1.377 (7)	C(5)–C(6)	1.348 (9)
C(6)–C(7)	1.342 (9)	C(11)–C(12)	1.559 (11)
C(21)–C(22)	1.533 (8)	C(31)–C(32)	1.569 (10)
Cl(1)–Pd–Cl(2)	179.1 (3)	Cl(1)–Pd–P	92.2 (1)
Cl(1)–Pd–N(2)	90.1 (1)	Cl(2)–Pd–P	88.0 (1)
Cl(2)–Pd–N(2)	89.8 (2)	P–Pd–N(2)	175.9 (1)
Pd–P–C(11)	107.5 (2)	Pd–P–C(21)	116.6 (3)
Pd–P–C(31)	115.4 (3)	C(11)–P–C(21)	105.6 (3)
C(11)–P–C(31)	105.5 (4)	C(21)–P–C(31)	105.3 (3)
N(2)–S–C(1)	108.7 (3)	N(2)–S–C(2)	101.1 (3)
C(1)–S–C(2)	99.6 (3)	C(3)–N(1)–C(7)	117.4 (5)
Pd–N(2)–S	123.8 (2)	Pd–N(2)–C(3)	121.9 (3)
S–N(2)–C(3)	112.2 (3)	N(1)–C(3)–N(2)	117.9 (4)
N(1)–C(3)–C(4)	122.5 (5)	N(2)–C(3)–C(4)	119.5 (5)
C(3)–C(4)–C(5)	117.5 (5)	C(4)–C(5)–C(6)	119.6 (5)
C(5)–C(6)–C(7)	119.5 (6)	N(1)–C(7)–C(6)	123.4 (6)
P–C(11)–C(12)	111.1 (6)	P–C(21)–C(22)	115.4 (5)
P–C(31)–C(32)	110.4 (5)		

* Lists of structure amplitudes, anisotropic displacement parameters, H-atom parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43032 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

within 0.10 Å. The orientation of the PEt₃ ligand with respect to the Pd coordination plane, with Cl(1)–Pd–P–C(21) = –9.8 (3) and Pd–P–C(21)–C(22) = 171.0 (6)°, resembles closely those found in *trans*-Pt^{II}Cl₂(PEt₃) species (*e.g.* Manojlović-Muir & Muir, 1974*b*) but does not seem to have been described previously for Pd^{II}.

The bonds radiating from the sulfimide N(2) atom deviate slightly from planarity, N(2) lying 0.143 (4) Å from the PdSC(3) plane. The N(2)–S and N(2)–C(3) bonds are roughly normal to the Pd coordination plane [Cl(1)–Pd–N(2)–S = –86.8 (3), Cl(1)–Pd–N(2)–C(3) = 75.3 (3)°]. The N(2)–S distance [1.638 (4) Å] is consistent with some multiple-bond character. This bond nearly eclipses C(3)–N(1) [S–N(2)–C(3)–N(1) = 9.3 (4)°]. The C(3)–N(2)–S–X torsion angles are –91.7 (4) and 164.2 (4)° for X = C(1) and C(2), respectively. The N(2)–S and N(2)–C(3) bond lengths, the torsion angles across these bonds and the S–N(2)–C(3) bond angle are in excellent agreement with corresponding values in the uncomplexed sulfimides Me₂S=N–C₆H₄X, X = *m*- or *p*-NO₂ (Cameron, Freer & Maltz, 1981). Evidently the Pd atom has little effect on the bonding or conformation of the sulfimide ligand. This conformation is such that the lone pairs on S and N(1) both point away from the Pd atom, the S...N(1) intramolecular distance [2.665 (4) Å] being notably short. Finally, Cameron *et al.* (1981) have shown that

the protonated sulfimide cation, (Me₂S=NH–C₆H₄–Cl-*p*)⁺, adopts a different conformation from those of the unprotonated sulfimide molecules or from that of the Pd complex, even though the site of protonation, like that of metallation, is the imide-N atom.

We thank the SERC for help with the purchase of equipment.

References

- CAMERON, A. F., FREER, A. A. & MALTZ, A. (1981). *Acta Cryst.* B37, 1608–1613.
 DAVIDSON, J. L., PRESTON, P. N. & SPANKIE, S. A. (1986). Personal communication.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
 KEUSPER, J., VAN DER POEL, H., POLM, L. H., VAN KOTEN, G., VRIEZE, K., SEIGNETTE, P. F. A. B., VARENHORST, R. & STAM, C. (1983). *Polyhedron*, 2, 1111–1116.
 MALLINSON, P. R. & MUIR, K. W. (1985). *J. Appl. Cryst.* 18, 51–53.
 MANOJLOVIĆ-MUIR, L. J. & MUIR, K. W. (1974*a*). *Inorg. Chim. Acta*, 10, 47–49.
 MANOJLOVIĆ-MUIR, L. J. & MUIR, K. W. (1974*b*). *J. Chem. Soc. Dalton Trans.* pp. 2427–2433.
 OLMSTEAD, M. M., GUIMERANS, R. R., FARR, J. P. & BALCH, A. L. (1983). *Inorg. Chim. Acta*, 75, 199–208.
 ROGERS, D. (1981). *Acta Cryst.* A37, 734–741.
 SOLOMUN, T. (1979). PhD Thesis, Univ. of Glasgow.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* A39, 158–166.

Acta Cryst. (1986). C42, 1296–1298

The Structure of *cis,trans,cis*-Diaquabis(5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine-*N*³)-bis(thiocyanato-*N*)iron(II)

BY MARINA BIAGINI CINGI, ANNA MARIA MANOTTI LANFREDI AND ANTONIO TIRIPICCHIO

Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffraattometrica del CNR, 43100 Parma, Italy

AND JOOST P. CORNELISSEN, JAAP G. HAASNOOT AND JEAN REEDIJK

Department of Chemistry, Gorlaeus Laboratories, State University Leiden, PO Box 9502, 2300 RA Leiden, The Netherlands

(Received 21 January 1986; accepted 17 April 1986)

Abstract. C₁₄H₁₆FeN₁₀O₂S₂, *M_r* = 476.31, monoclinic, *C*2/*c*, *a* = 15.765 (5), *b* = 7.909 (2), *c* = 16.211 (7) Å, β = 94.68 (3)°, *V* = 2015 (1) Å³, *Z* = 4, *D_m* = 1.55, *D_x* = 1.57 Mg m⁻³, Mo *K*α, λ̄ = 0.71069 Å, μ = 0.979 mm⁻¹, *F*(000) = 976, room temperature, *R* = 0.036, *wR* = 0.042, 1088 independent observed reflections. The structure consists of Fe²⁺ ions pseudo-octahedrally coordinated by two water

molecules (*cis*), two N-bonding thiocyanate groups (*cis*) and two N₃-coordinating 5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidine (C₆H₆N₄) ligands (*trans*). The Fe–O(water) bonds are 2.156 (5) Å, the Fe–N(thiocyanate group) bonds are 2.109 (5) Å and the Fe–N(organic ligand) bonds are 2.225 (5) Å. The organic ligands are associated, by stacking interactions, in pairs arranged in chains running along the [011] direction.