[2·594 (1), 2·540 (1) Å] are longer than those in $[TlBr_3(tppo)_2]$ [2·515 (2), 2·503 (2), 2·497 (3) Å] but similar to that observed in $[TlBrI_2(tppo)_2]$ [2·580 (1) Å]. This variation in bond distances is also observed for the Tl—I bond, with the bond length of 2·647 (1) Å shorter than those in $[TlI_3(3\text{-}CH_3C_5H_4NO)_2]$ [2·700 (1) Å] (Bermejo, Castineiras, Gayoso, Hiller, Englert & Strähle, 1984) or in $[TlBrI_2(tppo)_2]$ [2·685 (1), 2·667 (1) Å]. The Tl—O distances in the title compound [2·426 (4), 2·457 (5) Å] are longer than those in $[TlBr_3(tppo)_2]$ [2·38 (2), 2·39 (2) Å]. These effects are attributed to distinct halide atoms in equatorial positions.

The geometry of the tppo ligand is very similar to that of the free ligand (Bandoli, Bortolazzo, Clemente, Croato & Panattoni, 1970).

We thank the Ministerio de Educación y Ciencia (Spain) for financial support (AC) and Dr Kanellopoulos for helpful discussion.

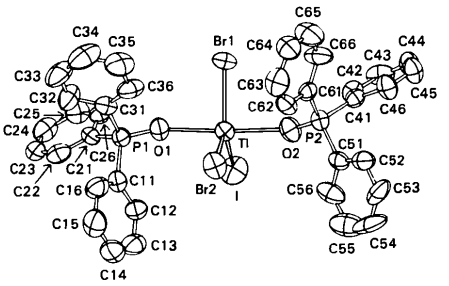

Fig. 1. View of the molecule with the labelling scheme used. Thermal ellipsoids at 80% probability level.

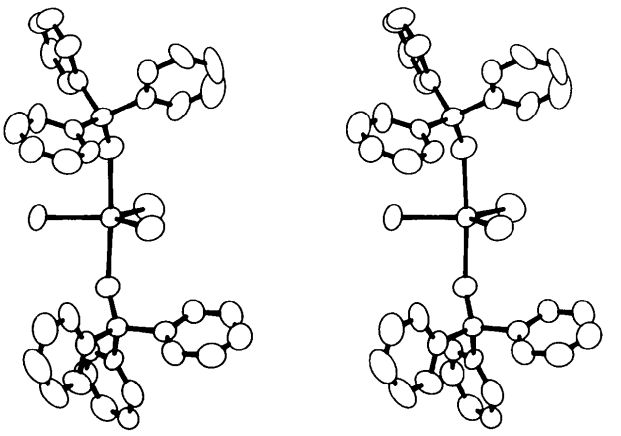

Fig. 2. Stereoscopic view of the molecule.

References

B. A. FRENZ & ASSOCIATES INC. (1985). VAX*SDP Structure Determination Package*, version 2.2. College Station, Texas, and Enraf–Nonius, Delft.

BANDOLI, G., BORTOLAZZO, G., CLEMENTE, D. A., CROATO, U. & PANATTONI, G. (1970). *J. Chem. Soc. A*, pp. 2778–2780.

BERMEJO, M. R., CASTINEIRAS, A., GAYOSO, M., HILLER, W., ENGLERT, U. & STRÄHLE, J. (1984). *Z. Naturforsch. Teil B*, **39**, 1159–1161.

CASTINEIRAS, A., HILLER, W., STRÄHLE, J., BERMEJO, M. R. & GAYOSO, M. (1985). *An. Quím.* In the press.

CASTINEIRAS, A., HILLER, W., STRÄHLE, J., BERMEJO, M. R. & GAYOSO, M. (1986). *Inorg. Chem.* In the press.

International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

JEFFS, S. E., SMALL, R. W. H. & WORRALL, I. J. (1984). *Acta Cryst.* C**40**, 381–383.

WALKER, N. & STUART, D. (1983). *Acta Cryst.* A**39**, 158–166.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1986). C**42**, 1291–1294

Structure of an Antitumor Platinum(II) Compound *cis*-$[PtCl_2(Cyclobutylamine)(NH_3)]$

BY F. D. ROCHON AND ROBERT MELANSON

Département de Chimie, Université du Québec à Montréal, CP 8888, *succ. A, Montréal, Canada H3C 3P8*

(*Received* 16 *September* 1985; *accepted* 29 *April* 1986)

Abstract. *cis*-Amminedichloro(cyclobutylamine)-platinum(II), $C_4H_{12}Cl_2N_2Pt$, $M_r = 354{\cdot}15$, monoclinic, $P2_1/c$, $a = 8{\cdot}730$ (3), $b = 9{\cdot}944$ (3), $c = 10{\cdot}082$ (4) Å, $\beta = 105{\cdot}01$ (2)°, $V = 845{\cdot}4$ (5) Å^3, $Z = 4$, $D_x = 2{\cdot}782$, $D_m = 2{\cdot}77$ (2) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 17·976 mm^{-1}, $F(000) = 648$, $T = 295$ K, $R = 0{\cdot}057$ for 1806 unique observed reflections. The coordination around the Pt atom is *cis* square planar, Pt—Cl 2·308 (4) and 2·312 (4) Å, Pt—N 2·053 (14) and 2·067 (13) Å. Hydrogen bonding involving the NH_3 ligand plays an important role in stabilizing the crystal.

Introduction. Platinum amine complexes of the types *cis*-$[PtCl_2(L)_2]$ and *cis*-$[PtCl_2(NH_3)(L)]$, with L = cyclic amine, have shown a better therapeutic index and a greater antitumor activity against several animal tumors than cisplatin, *cis*-$Pt[Cl_2(NH_3)_2]$ or non-cyclic

0108-2701/86/101291-04$01.50

amine complexes (Braddock, Connors, Jones, Khokhar, Melzack & Tobe, 1975; Rochon & Kong, 1986*a*). The greater therapeutic index of the *cis*-$[PtCl_2(L)]$ compounds is caused by a considerable decrease in toxicity as ring size of the amine increases. The LD_{50} range for cyclopropylamine to cyclohexylamine is 57 to 3200 mg kg^{-1} and 13 mg kg^{-1} for cisplatin (ADJ/PC6A system). Attempts to correlate therapeutic index with aqueous or chloroform solubility were not conclusive. The changes in toxicity were therefore postulated to be related to the structure of the platinum compounds (Braddock *et al.*, 1975). As a result, a few structures of *cis* and *trans*-$[PtX_2(L)_2]$ where L = cyclopropylamine (Howard-Lock, Lock, Turner & Zvagulis, 1981), cyclobutylamine (Lock & Zvagulis, 1981), cyclohexylamine (Lock, Speranzini & Zvagulis, 1980; Zanotti, Del Pra, Bombieri & Tamburro, 1978) and cycloheptylamine (Bradford, Faggiani & Lock, 1981) have been determined.

The compounds *cis*-$[PtCl_2(L)(NH_3)]$ are much more toxic than the corresponding *cis*-$[PtCl_2(L)_2]$ but there is also a slight decrease in toxicity of *cis*-$[PtCl_2(L)(NH_3)]$ as the ring size of the amine increases (Rochon & Kong, 1986*a*). The approximate toxicity values for *cis*-$[PtCl_2(L)(NH_3)]$ are 6 mg kg^{-1} (L = cyclopropylamine), 10 mg kg^{-1} (L = cyclobutylamine) and 15–20 mg kg^{-1} (L = cyclopentylamine) for the L1210/CD_2F_1 tumor system. The toxicity of these compounds is therefore similar to that of cisplatin.

We have recently devised a good method to synthesize mixed amine platinum(II) compounds (Rochon & Kong, 1986*b*). Several of these compounds were tested for antitumor activity. The most active was found to be *cis*-$[PtCl_2$(cyclobutylamine)$(NH_3)]$ (Rochon & Kong, 1986*a*). The structure of this compound was determined by X-ray diffraction and is reported here.

Experimental. The title compound was prepared from the aqueous reaction of *cis*-$[PtI_2(C_4H_9N)(NH_3)]$ with $AgNO_3$ and KCl, according to the recently published method (Rochon & Kong, 1986*b*). The crystals were obtained directly from the reaction.

Rod-like crystal, dimensions (mm): 0·189 (011–0$\bar{1}\bar{1}$) × 0·189 (0$\bar{1}$1–01$\bar{1}$) × 0·604 (100–$\bar{1}$00); density by flotation in thallous malonate aqueous solution; space group $P2_1/c$; Syntex $P\bar{1}$ diffractometer; graphite-monochromatized Mo $K\alpha$ radiation, cell parameters from refined angles of 15 centered reflections (2θ range: 11–26°); 2496 independent reflections measured up to $2\theta < 60°$ by θ–2θ scan technique, range of hkl: $h = 0 \rightarrow 12$, $k = 0 \rightarrow 14$, $l = -13 \rightarrow 13$; standard reflections 310, 020 and 002 every 47 reflections; variations < 2%; reflections with $I_{net} < 2{\cdot}5\sigma(I)$ unobserved, $\sigma(I)$ calculated as in Melanson & Rochon (1975); absorption correction based on equations of crystal faces, transmission factors from 0·042 to 0·107; data corrected for Lorentz and polarization effects; 1806 unique observed reflections; atomic scattering factors of Cromer & Waber (1965) for Pt, Cl, N, C and of Stewart, Davidson & Simpson (1965) for H; anomalous-dispersion terms of Pt and Cl from Cromer (1965).

Patterson map indicated position of Pt; other atoms (except H) located by structure factors and Fourier-map calculations; isotropic secondary-extinction correction (Coppens & Hamilton, 1970); $w = 1/\sigma^2(F)$; H atoms (except in NH_3) fixed at calculated positions (C–H = 0·95 and N–H = 0·85 Å) with isotropic $B = 6{\cdot}0$ Å^2. Ratio of maximum least-squares shift to e.s.d. in final refinement cycle (on F): < 0·03, $\rho_{max} = 2{\cdot}00$, $\rho_{min} = -1{\cdot}5$ e Å^{-3} (close to Pt), in final Fourier synthesis. $R = 0{\cdot}057$ and $wR = 0{\cdot}062$, calculations on Cyber 171 with programs of Melanson & Rochon (1975).*

Discussion. The refined atomic parameters and temperature factors are listed in Table 1. A labeled diagram of the molecule is shown in Fig. 1. The coordination around the Pt atom is square planar. The deviations from the weighted best plane are Pt −0·0002 (5), Cl(1) 0·000 (4), Cl(2) 0·006 (4), N(1) 0·071 (12) and N(2) −0·004 (12) Å. N(1) (from NH_3) seems to be very slightly out of plane, probably because of extensive hydrogen bonding. The angles around the Pt atom are close to the expected values of 90 and 180° (Table 2).

As expected from the synthetic procedure, the compound is the *cis* isomer. The infrared spectrum of the compound showed one large stretching ν(Pt–Cl) vibration at 320 cm^{-1}. *cis*-$[PtCl_2$(cyclobutylamine)$_2]$ showed a ν(Pt–Cl) vibration at 311 cm^{-1} while the *trans* isomer also showed one band but at slightly higher wavenumber, 333 cm^{-1} (Lock & Zvagulis, 1981). Therefore the configuration of $[PtCl_2$-(cyclobutylamine)$(NH_3)]$ could not be determined by IR spectroscopy alone.

The Pt–Cl bond distances [2·308 (4) and 2·312 (4) Å] are of normal length. The Pt–N bond lengths [2·053 (14) and 2·067 (13) Å] are normal and agree well with the published values on Pt–amine compounds (Lock & Zvagulis, 1981; Melanson & Rochon, 1985; Lock, Speranzini & Zvagulis, 1980; Lippert, Lock & Speranzini, 1981).

The N–C and C–C bond distances (Table 2) of the organic ligand are normal. The angles around the C atoms (86–89°) show considerable strain inside the four-membered ring as observed in *cis* and *trans*-

* Lists of structure factors, anisotropic thermal parameters, H coordinates, deviations from best planes and equations of weighted least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43018 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters, with their e.s.d.'s and temperature factors (all* $\times 10^4$*)*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$.

	x	y	z	U_{eq}(Å^2)
Pt	4213·3 (5)	1115·8 (5)	971·3 (5)	264
Cl(1)	5578 (4)	580 (4)	3190 (3)	400
Cl(2)	2437 (4)	−630 (4)	870 (4)	415
N(1)	5844 (14)	2619 (11)	1032 (13)	394
N(2)	3027 (14)	1637 (12)	−1013 (11)	366
C(1)	1468 (16)	2246 (13)	−1162 (13)	319
C(2)	498 (18)	2578 (16)	−2636 (14)	441
C(3)	−85 (21)	3842 (17)	−2074 (19)	579
C(4)	1427 (17)	3739 (15)	−785 (16)	476

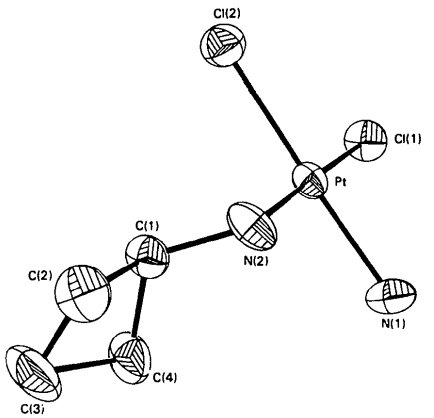

Fig. 1. Labeled diagram of the molecule *cis*-$[PtCl_2(C_4H_9N)(NH_3)]$.

Table 2. *Bond distances* (Å), *bond angles, torsion angles* (°), *and hydrogen-bond distances and angles*

Pt–Cl(1)	2·308 (4)	Cl(1)–Pt–Cl(2)	92·4 (2)
Pt–Cl(2)	2·312 (4)	Cl(1)–Pt–N(1)	87·7 (4)
Pt–N(1)	2·053 (14)	Cl(1)–Pt–N(2)	178·6 (4)
Pt–N(2)	2·067 (13)	Cl(2)–Pt–N(1)	177·9 (4)
N(2)–C(1)	1·46 (2)	Cl(2)–Pt–N(2)	89·0 (4)
C(1)–C(2)	1·54 (2)	N(1)–Pt–N(2)	90·9 (5)
C(1)–C(4)	1·54 (2)	Pt–N(2)–C(1)	115 (1)
C(2)–C(3)	1·52 (3)	N(2)–C(1)–C(2)	117 (1)
C(3)–C(4)	1·59 (3)	N(2)–C(1)–C(4)	117 (1)
		C(1)–C(2)–C(3)	88 (1)
		C(2)–C(3)–C(4)	88 (1)
		C(1)–C(4)–C(3)	86 (1)
		C(2)–C(1)–C(4)	89 (1)
N(1)···Cl(1^{i})	3·34 (1)	Pt–N(1)···Cl(1)	118·2 (6)
N(1)···Cl(1^{ii})	3·36 (1)	Pt–N(1)···Cl(1)	110·5 (5)
N(1)···Cl(2^{iii})	3·37 (1)	Pt–N(1)···Cl(2)	87·9 (5)
N(1)···Cl(2^{ii})	3·55 (1)	Pt–N(1)···Cl(2)	121·0 (5)
N(2)···Cl(1^{i})	3·54 (1)	C(1)–N(2)···Cl(1)	130·9 (9)
		Pt–N(2)···Cl(1)	106·1 (5)

Pt	N(2)	C(1)	C(2)*	−176·7	C(1)	C(2)	C(3)	C(4)	21·5
Pt	N(2)	C(1)	C(4)	79·1	C(2)	C(3)	C(4)	C(1)	−21·7
N(2)	C(1)	C(2)	C(3)	−142·8	C(3)	C(4)	C(1)	C(2)	21·3
N(2)	C(1)	C(4)	C(3)	141·4	C(4)	C(1)	C(2)	C(3)	−22·4

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

* The conventions suggested by Sundaralingam [*Biopolymers* (1969), **7**, 821] and Trueblood and co-workers [*J. Mol. Biol.* (1960), **2**, 363; *Acta Cryst.* (1965), **18**, 1067] have been used.

$[PtCl_2(C_4H_9N)_2]$ (Lock & Zvagulis, 1981). As a result, the N–C–C angles are larger than the tetrahedral value [117 (1)°]. The Pt–N(2)–C(1) angle is also larger than expected [115 (1)°]. Similar values were obtained by Lock & Zvagulis (1981) for *cis* and *trans*-[$PtCl_2$-(cyclobutylamine)$_2$]. The best plane through the four carbon atoms of the cyclobutyl ring was calculated. The deviations from the plane are C(1) −0·10 (1), C(2) 0·15 (2), C(3) −0·20 (2) and C(4) 0·14 (2) Å. The angle between the platinum plane and this plane is 57°.

The torsion angles in the cyclobutylamine moiety were calculated (Table 2). These values agree well with those found in *cis*-[$PtCl_2$(cyclobutylamine)$_2$] (Lock & Zvagulis, 1981). The dihedral angle between C(1)-C(2)C(4) and C(2)C(3)C(4) in the cyclobutylamine ring is 31·1°.

The structure (Fig. 2) consists of layers of molecules parallel to the *bc* plane. The cyclobutylamine ligands are located around $x = 0$ while the $PtCl_2N(1)$ moieties are centered around $x = \frac{1}{2}$. Hydrogen bonding plays an important role in stabilizing the crystal, especially around the NH_3 ligand (Table 2).

It was suggested that the low toxicity of the cyclic amine complexes, *cis*-[$PtCl_2(L)_2$], was caused by the flexibility of the larger rings, allowing orientation of the rings so that they protect the axial positions above and below the square plane, thus preventing coordination to the S atoms in the kidney tubules (Lock, Speranzini & Zvagulis, 1980). The crystal structure analyses of *cis*-[$PtCl_2$(cyclohexylamine)$_2$] (Lock, Speranzini & Zvagulis, 1980) and *cis*-[$PtCl_2$(cyclobutylamine)$_2$] (Lock & Zvagulis, 1981) have confirmed that a few C atoms of the rings are in a position to block partially the two axial sites. But the structure determination of *cis*-[$PtCl_2$(cyclopropylamine)$_2$] (Howard-Lock, Lock, Turner & Zvagulis, 1981) has shown that the two cyclopropylamine ligands are on the same side of the platinum plane, leaving the second axial site completely open in the solid state, although in solution there is rotation around the Pt bonds and again the two axial positions would be partly blocked.

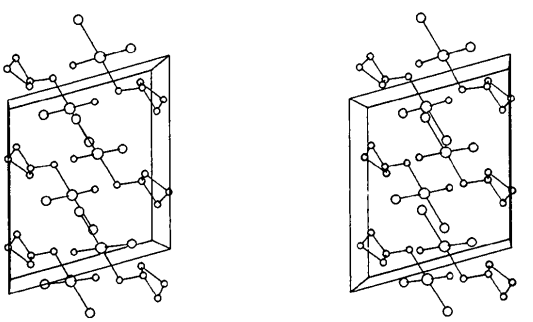

Fig. 2. Stereoscopic diagram of the packing in the *cis*-[$PtCl_2$-$(C_4H_9N)(NH_3)$] crystal (*c* axis vertical, down *b* axis).

In the solid state, the cyclic amine in *cis*-[$PtCl_2(C_4H_7NH_2)(NH_3)$] 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*-[$PtCl_2(C_4H_7NH_2)_2$] ($\sim$100 mg kg^{-1}) and *cis*-[$PtCl_2(C_4H_7NH_2)(NH_3)$] ($\sim$10 mg kg^{-1}) does not seem sufficient. Other factors like hydrogen bonding might be important. The structure of *cis*-[$PtCl_2(C_4H_7NH_2)(NH_3)$] has shown extensive hydrogen bonding of the NH_3 ligand. In this crystal, the NH_3 ligand forms three strong hydrogen bonds with the chlorine atoms [N(1)$\cdots$Cl = 3·34–3·37 Å] while the cyclic amine seems to play a minor role in the hydrogen-bonding system (Table 2). Therefore we suggest that this factor should be considered as a partial explanation of the toxicities of the *cis*-[$PtCl_2$(cyclic amine)(NH_3)] complexes.

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada and to the Ministère de l'Education (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.* B**37**, 243–246.

COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A**26**, 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.* B**36**, 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.* C**41**, 350–352.

ROCHON, F. D. & KONG, P. C. (1986*a*). *J. Clin. Hematol. Oncol.* Submitted.

ROCHON, F. D. & KONG, P. C. (1986*b*). *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.* B**34**, 2138–2141.

Acta Cryst. (1986). C**42**, 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. [$PdCl_2(C_7H_{10}N_2S)(C_6H_{15}P)$], $M_r = 449·7$, orthorhombic, $P2_12_12_1$, $a = 8·247$ (1), $b = 10·936$ (2), $c = 21·707$ (4) Å, $U = 1957·7$ (6) Å^3, $Z = 4$, $D_x = 1·526$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 13·9$ cm^{-1}, $F(000) = 912$, $T = 293$ K, $R = 0·027$ for 2824 unique reflections with $I \geq 3\sigma(I)$. 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 $11 < \theta < 17°$; intensities of 6310 reflections, with $2 \leq \theta \leq 30°$ and h 0→11, k 0→15, l −30→30, measured from continuous $\theta/2\theta$ scans of $(0·60 + 0·35\tan\theta)°$ 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 $2\bar{2}2$ 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 $I \geq 3\sigma(I)$, including 1030 Friedel pairs, used in the structure analysis. Patterson and difference syntheses;

0108-2701/86/101294-03$01.50