Substitution of Pyridine Ligands from Platinum(II) Iodo Complexes by Dimethyl Sulphoxide: Crystal Structure of *trans*-(3,5-Dimethylpyridine)(dimethyl sulphoxide-*S*)di-iodoplatinum†

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Dimethyl sulphoxide substitutes one pyridine or substituted pyridine (Xpy = pyridine, 4-methylpyridine, 3,5-dimethylpyridine, 4-chloropyridine, or 4-cyanopyridine) from *cis*-$[Pt(Xpy)_2I_2]$ to form *trans*-$[Pt(Xpy)(dmso)I_2]$ complexes. The dmso ligand is bound through the sulphur (from i.r. and ^1H n.m.r. spectra). The *trans* structure was confirmed by Pt–H coupling constants and an *X*-ray crystal structure determination of *trans*-$[Pt(3,5Me_2\text{-}py)(dmso)I_2]$. Crystals are orthorhombic, space group *Pbca*, with cell parameters $a = 10.617(9)$, $b = 17.052(6)$, $c = 16.951(6)$ Å, and $Z = 8$. The crystal structure was determined by standard methods and refined to $R = 0.065$ and R' 0.087 based on 2 848 observed reflections. Co-ordination of the ligands is square planar with the bond distances Pt–N 2.08(2), Pt–S 2.233(5), and Pt–I 2.598(2), 2.613(2) Å.

Dimethyl sulphoxide (dmso) is an ambidentate ligand towards many metal ions, binding either through the sulphur or the oxygen atoms.[1] In general, sulphoxides should bind *via* oxygen to the hard first-row transition metals and *via* sulphur to soft metals, such as those of Group 8.[2,3]

In this paper, we describe mixed-ligand complexes containing a N-donor ligand, dmso, and iodide. While several chloro complexes of this type have been synthesized,[4–8] to our knowledge no iodo complexes have been prepared. In the case of *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$, dmso substitutes a chloride ligand giving *cis*- and *trans*-$[Pt(NH_3)_2(dmso)Cl]^+$ respectively.[9] Secondary reactions have been reported,[10a] so that six products are ultimately formed. It has been suggested from studies of ^{195}Pt n.m.r. spectra of *cis*-$[Pt(NH_3)_2I_2]$ in deuteriated dmso that *cis*-$[Pt(NH_3)(dmso)I_2]$ is formed in the mixture of products, but the complex was not isolated.[10b] We now report the preparation of $[Pt(Xpy)(dmso)I_2]$ complexes (Xpy = substituted pyridine) and their characterization by i.r. and n.m.r. spectroscopy and single-crystal *X*-ray crystallography.

Results and Discussion

Synthesis and Characterization of the Products.—The *cis*-$[Pt(Xpy)_2I_2]$ complexes (Xpy = pyridine, 4-methylpyridine, 4-chloropyridine, 4-cyanopyridine, or 3,5-dimethylpyridine) were prepared by a slight modification of the method of Dhara,[11] as shown in equations (1) and (2).

$$4\,I^- + [PtCl_4]^{2-} \longrightarrow [PtI_4]^{2-} + 4Cl^- \quad (1)$$

$$[PtI_4]^{2-} + 2\,Xpy \longrightarrow cis\text{-}[Pt(Xpy)_2I_2] + 2\,I^- \quad (2)$$

The solution formed *via* equation (1) was slowly added to an aqueous solution of Xpy and gave the product as a bright yellow powder. In the presence of an excess of Xpy the reaction was rapid.

Dissolution of *cis*-$[Pt(Xpy)_2I_2]$ in deuteriated dmso (4 mg complex per cm^3 of dmso) immediately gave two sets of ^1H n.m.r. signals, one with platinum coupling to the α ring protons attributable to $[Pt(Xpy)(dmso)I_2]$ and the second at lower chemical shift corresponding to free Xpy. The reaction was essentially complete under those conditions for all the complexes studied. Small peaks corresponding to two minor components (about 3—8% *vs.* the dmso complex) were observed: the first component was the starting material and the second, *trans*-$[Pt(Xpy)_2I_2]$, which was identified by comparison with a spectrum of the pure compound.

The complexes $[Pt(Xpy)(dmso)I_2]$ (Xpy = pyridine, 4-chloropyridine, or 4-cyanopyridine) were obtained by dissolving *cis*-$[Pt(Xpy)_2I_2]$ in a minimum of dmso (which corresponds nevertheless to 40—400 fold molar excess). Multiple extractions by diethyl ether removed the excess of dmso, Xpy, and $[Pt(Xpy)_2I_2]$. The desired complex precipitated as an orange solid. Yields were much lower than expected from the n.m.r. spectra in deuteriated dmso.

The same method used for 4-methylpyridine and 3,5-dimethylpyridine gave very poor results. A variant method was preferred; *cis*-$[Pt(Xpy)_2I_2]$ was dissolved in a very large amount of dmso (*ca.* 4000-fold molar excess), the dmso and substituted pyridines released were then removed by distillation under vacuum. Orange crystals precipitated from dmso and these could be recrystallized from chloroform.

Elemental analyses were good for all the products (Table 1). The i.r. spectra recorded in Nujol (Table 2) showed a strong band at 1 120—1 138 cm^{-1}, which was assigned to the S–O stretching vibrations[4,5,12] and is fully consistent with linkage to platinum through sulphur.[13] The two bands at 440—445 and 377—387 cm^{-1} probably arise from the dimethyl sulphoxide ligand.[5]

The ^1H n.m.r. spectra of $[Pt(Xpy)(dmso)I_2]$ in $CDCl_3$ showed a sharp singlet at δ 3.84—3.88 with ^{195}Pt satellites [*J*(Pt–H) = 21.5—22.8 Hz] (Table 3) consistent with S-bonded dmso.[14] A higher-field singlet assigned to O-bonded dmso[14] was absent.

The Pt–H coupling constants for the H(2) pyridine proton of $[Pt(Xpy)(dmso)I_2]$ were of the order of 33 Hz (Table 3).

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

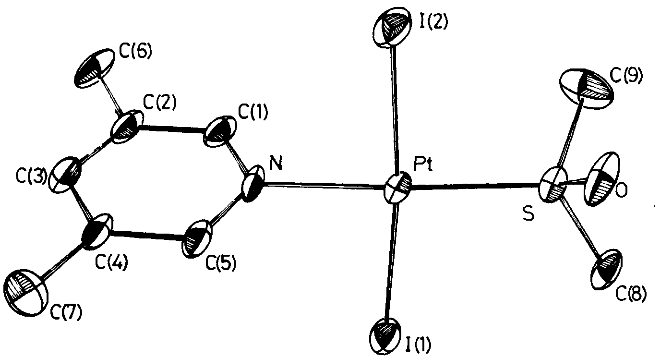


Figure. Perspective view of *trans*-[Pt(3,5Me$_2$-py)(dmso)I$_2$]

Table 1. Analytical data (%)* for the *trans*-[Pt(Xpy)(dmso)I$_2$] complexes

Xpy	C	H	N
py	13.9(13.9)	1.7(1.8)	2.1(2.3)
4Cl-py	13.3(13.1)	1.6(1.6)	2.2(2.2)
4CN-py	15.2(15.2)	1.5(1.6)	4.4(4.4)
4Me-py	15.6(15.5)	2.1(2.1)	2.3(2.3)
3,5Me$_2$-py	16.9(17.0)	2.3(2.4)	2.2(2.2)

* Calculated values are given in parentheses.

The Pt-H coupling constants for the *trans* isomers of [Pt(Xpy)$_2$Cl$_2$] and [Pt(Xpy)$_2$I$_2$] (X = H or Me) were 34 and 33 Hz respectively, and for *trans*-[Pt(py)(CO)X$_2$](X = Cl or Br), 30 and 29 Hz[15] while for the corresponding *cis* isomers the values were 42 Hz. Thus, the coupling constant seems to depend primarily on the geometry of the complex and suggests that the complexes [Pt(Xpy)(dmso)I$_2$] are *trans*.

In order to verify the geometry of these complexes, the *X*-ray crystal structure of the 3,5-dimethylpyridine derivative was determined (Table 4).

The Structure of [Pt(3,5Me$_2$-py)(dmso)I$_2$].—The atomic co-ordinates for the complex are given in Table 5 and the inter-atomic distances and bond angles in Table 6. A perspective view of the molecule with the atom labelling is given in the Figure.

The complex [Pt(3,5Me$_2$-py)(dmso)I$_2$] has the *trans* configuration. The co-ordination about the platinum is square planar as expected. The weighted best plane was calculated through the five atoms. The deviations from this plane are Pt −0.030, N −0.028, I(1) 0.025, I(2) 0.026, and S −0.023 Å. In addition, C(8) of the dmso ligand is −0.202 Å from the plane and this in turn may have an effect on the bond angles (see below).

The dmso molecule is bonded to platinum through the sulphur atom. The Pt-S bond distance [2.233(5) Å] is slightly longer than those reported for platinum complexes with a dmso *trans* to a pyridine ligand {*trans*-[Pt(py)(dmso)Cl$_2$] 2.224(2), 2.225(3),[16] *trans*-[Pt(2Me-py)(dmso)Cl$_2$] 2.212(3) Å[17]}. Values of 2.17—2.24 Å have been reported for the Pt-S distance for the dmso ligand and the variation does not seem to depend on the *trans* influence of the opposite ligand, *e.g. trans*-(S,O)-[Pt(pyca)(dmso)Cl] 2.174(2) (pyca = pyridine-2-carboxylate),[18] *cis*-[Pt(NH$_3$)(dmso)Cl$_2$] 2.186(4),[19] *cis*-[Pt(2Me-py)(dmso)Cl$_2$] 2.200(3),[20] [{Pt(dmso)$_2$(μ-OH)}$_2$]$^{2+}$ 2.203(2), 2.223(3),[21] and *cis*-[Pt(dmso)$_2$Cl$_2$] 2.229(2), 2.244(2) Å.[22] The geometry of the co-ordinated dmso is approximately tetrahedral with angles ranging from 109 to 117°. The S-O bond distance is 1.45(2) Å and the S-C bond distance is 1.82(2) Å. In the complexes cited above the range of S-O distances is 1.46—1.49 Å and for the S-C distances 1.75—1.79 Å.

The Pt-N bond distance is 2.08(2) Å. In complexes without dmso, *e.g. cis*-[Pt(vpy)$_2$Cl$_2$] (vpy = 4-vinylpyridine), [{Pt(2,6-

Table 2. I.r. absorptions (cm^{-1}) for the *trans*-[Pt(Xpy)(dmso)I$_2$] complexes*

Xpy	v(S-O)	dmso ligand	Xpy bands	Other peaks
py	1 125s 1 112m	441m, 385m	1 608m, 766s, 703m	1 013m
4Cl-py	1 133m	440w, 383w	1 598m, 1 127m, 743m	1 133m, 1 019m, 845s
4CN-py	1 120s	445m, 382m	1 614m, 842s, 721s	1 026s
4Me-py	1 138s	441s, 387m	1 621m, 1 017m, 830s, 733m, 726m, 510m	690w
3,5Me$_2$-py	1 126s	440m, 377m	730m, 723m, 693m	1 015m, 502w

* s = Strong, m = medium, w = weak.

Table 3. Proton n.m.r. data* of *trans*-[Pt(Xpy)(dmso)I$_2$] complexes

	Ring protons					
Xpy	C(2)-H C(6)-H	C(3)-H C(5)-H	C(4)-H	C(4)-Me	C(3)-Me C(5)-Me	(CH$_3$)$_2$SO
py	8.716	7.378	7.785			3.861
	[d, *J* 6.4, *J*(Pt-H) 33]	[t, *J* 7.1]	[t, *J* 7.7]			[s, *J*(Pt-H) 21.9]
4Cl-py	8.644	7.384				3.861
	[d, *J* 6.8, *J*(Pt-H) 32.5]	[d, *J* 7.0]				[s, *J*(Pt-H) 22.3]
4CN-py	8.990	7.617				3.876
	[d, *J* 6.9, *J*(Pt-H) 34]	[d, *J* 6.7]				[s, *J*(Pt-H) 22.8]
4Me-py	8.521	7.172		2.434(s)		3.846
	[d, *J* 6.7 *J*(Pt-H) 33]	[d, *J* 6.1]				[s, *J*(Pt-H) 21.6]
3,5Me$_2$-py	8.313		7.348(s)		2.304(s)	3.841
	[s, *J*(Pt-H) 33.5]					[s, *J*(Pt-H) 21.5]

* In CDCl$_3$. Chemical shifts were measured with respect to the CHCl$_3$ signal at δ 7.25. s = Singlet, d = doublet, and t = triplet; coupling constants in Hz, *J* = H-H coupling constant.

Table 4. Crystallographic data for *trans*-[Pt(3,5Me$_2$-py)(dmso)I$_2$]

Crystal system	Orthorhombic
M	634.188
a/Å	10.617(9)
b/Å	17.052(6)
c/Å	16.951(6)
U/Å^3	3 068(2)
Z	8
D_c/g cm^{-3}	2.745
F(000)	2 272
Crystal dimensions/mm	2 × 0.06 × 0.05
Scan	
type	θ—2θ
speed/°min^{-1}	20
width	0.85 tanθ
Radiation	Mo-K_α(λ = 0.7107 Å)
2θ Range/°	1—30°
Reflections measured	h,k,l

Table 5. Fractional atomic co-ordinates (e.s.d.s) for [Pt(3,5Me$_2$-py)-(dmso)I$_2$]

Atom	x	y	z
Pt	0.737 37(8)	0.192 64(4)	0.155 17(5)
I(1)	0.603 1(2)	0.265 3(1)	0.050 0(1)
I(2)	0.880 5(2)	0.109 4(1)	0.248 6(1)
S	0.749 4(6)	0.292 9(3)	0.239 6(4)
O	0.878(2)	0.317 1(9)	0.257(1)
N	0.734(2)	0.095 4(9)	0.082(1)
C(1)	0.648(2)	0.039(1)	0.102(2)
C(2)	0.644(3)	−0.028(1)	0.053(2)
C(3)	0.720(3)	−0.035(1)	−0.013(2)
C(4)	0.806(3)	0.026(1)	−0.031(2)
C(5)	0.808(2)	0.093(1)	0.016(2)
C(6)	0.549(3)	−0.096(1)	0.077(2)
C(7)	0.891(3)	0.020(2)	−0.101(2)
C(8)	0.654(3)	0.378(1)	0.217(2)
C(9)	0.675(3)	0.264(2)	0.332(2)

Table 6. Bond distances (Å) and angles (°) with e.s.d.s. in parentheses for [Pt(3,5Me$_2$-py)(dmso)I$_2$]

Pt–I(1)	2.598(2)	N–C(1)	1.37(4)
Pt–I(2)	2.613(2)	N–C(5)	1.36(3)
Pt–S	2.233(5)	C(4)–C(5)	1.40(3)
Pt–N	2.08(2)	C(1)–C(2)	1.40(3)
S–O	1.45(2)	C(2)–C(3)	1.38(4)
S–C(8)	1.82(2)	C(2)–C(6)	1.60(4)
S–C(9)	1.82(4)	C(4)–C(7)	1.50(4)
C(3)–C(4)	1.41(4)		
I(1)–Pt–I(2)	173.76(7)	Pt–N–C(1)	115(2)
I(1)–Pt–S	96.1(2)	Pt–N–C(5)	120(1)
I(1)–Pt–N	87.8(5)	C(1)–N–C(5)	124(2)
I(2)–Pt–S	89.7(2)	N–C(1)–C(2)	117(2)
I(2)–Pt–N	86.5(5)	C(1)–C(2)–C(3)	121(2)
S–Pt–N	176.2(6)	C(1)–C(2)–C(6)	117(2)
Pt–S–O	113.6(8)	C(3)–C(2)–C(6)	121(2)
Pt–S–C(8)	116.7(9)	C(2)–C(3)–C(4)	120(2)
Pt–S–C(9)	108(1)	C(3)–C(4)–C(5)	120(2)
O–S–C(8)	110(2)	C(3)–C(4)–C(7)	122(2)
O–S–C(9)	109(1)	C(5)–C(4)–C(7)	119(2)
C(8)–S–C(9)	99(1)	N–C(5)–C(4)	119(3)

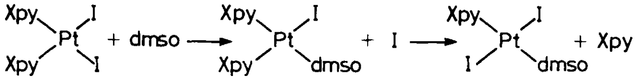
Me$_2$-py)Cl$_2$}$_2$], and *trans*-[Pt(2,6Me$_2$-py)(dmf)Cl$_2$](dmf = dimethylformamide), the Pt–N bond distances are 1.969(19) and 1.988(23) Å,[23] 2.020(10),[24] and 2.013(6)[25] respectively. In *cis*-[Pt(2Me-py)(dmso)Cl$_2$] the Pt–N distance is 2.062(10) Å, while for the *trans* isomer the value is 2.046(10) Å compared with 2.052(6) Å for *trans*-[Pt(py)(dmso)Cl$_2$]. Thus, there is no obvious lengthening of the Pt–N bond *trans* to the dmso ligand. The Pt–I bond distances are 2.598(2) and 2.613(2) Å respectively. The analogous distances for *cis*-[Pt(NH$_3$)$_2$I$_2$] are 2.577(1) and 2.595(1) Å.[26]

The bond lengths in the 3,5-dimethylpyridine ring average 1.37(4) and 1.40(4) Å for C–N and C–C respectively and the angles are close to 120° except about N(1). The 3,5-dimethylpyridine ring is planar with deviations from the plane of $\leqslant$0.027 Å and the angle between the co-ordination plane and the aromatic ring is 100.6(5)°. The dihedral angle I(2)–Pt–S–O is 56.0(9)°.

The bond angles about the platinum show deviations from regular square-planar co-ordination. The I(2)–Pt–S angle is normal [89.7(2)°] while I(1)–Pt–S is 96.1(2)° giving I(1)–Pt–I(2) 173.8(7)°. This difference would appear to arise from the steric interactions between the iodo ligands and the dmso molecule, since the dihedral angle I(1)–Pt–S–C(8) is only 7.7(1.0)° while I(2)–Pt–S–C(9) is −64.1(11)°. Consequently, C(8) is only −0.202 Å from the co-ordination plane, while C(9) and O are −1.556 and 1.10 Å from the plane. If so, this difference in bond angles should depend on the dihedral angle and should also be seen, although perhaps to a lesser extent, in the analogous chloro complexes. The Cl–Pt–Cl angles are for *trans*-[Pt(py)-(dmso)Cl$_2$] 175.8(1)°, *trans*-[Pt(2Me-py)(dmso)Cl$_2$] 174.2(1), and *trans*-[Pt(NH$_2$Pr^i)(dmso)Cl$_2$] 175.80(9)°.[27] The I–Pt–N angle is in turn affected, being less than 90°, while the N–Pt–S angle is 176.2(6)°.

Reaction Mechanism.—We have shown that the products of the solvolysis of *cis*-[Pt(Xpy)$_2$I$_2$] in dmso are *trans*-[Pt(Xpy)-(dmso)I$_2$]. The observed isomerization requires the substitution of two ligands. Iodide and pyridine have similar *trans* effects. At the same time the Pt–N bond is considered to be strong and this can override the *trans* effect.[28] This raises the interesting question of which is the first ligand to be displaced by the dmso.

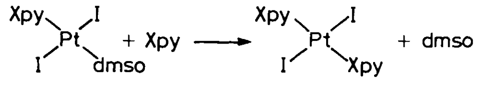
If the dmso substitutes an Xpy giving *cis*-[Pt(Xpy)(dmso)I$_2$], it is difficult to see how this can rearrange rapidly to the *trans* isomer under the mild conditions of the n.m.r. experiment. On the other hand, substitution of iodide to give *cis*-[Pt(Xpy)$_2$-(dmso)I] followed by a rapid attack by iodide easily leads to a *trans* product (Scheme).



Scheme.

It may be that the two *cis*-iodo ligands result in a mutual labilization similar to that observed by Lanza *et al.*[29] for [Pt(en)(dmso)$_2$]$^{2+}$ (en = ethylenediamine), while for step 2 it is known that the reactivity of iodide with respect to platinum(II) is high.[30]

When an excess of Xpy (10-fold molar excess) was added to the solution of *cis*-[Pt(Xpy)$_2$I$_2$], in deuteriated dmso, the n.m.r. spectrum of the mixture showed that the dmso complex, *trans*-[Pt(Xpy)(dmso)I$_2$], disappeared while *trans*-[Pt(Xpy)$_2$I$_2$] increased, suggesting that reaction (3) occurred.



(3)

In a separate n.m.r. experiment it was found that *trans*-[Pt(Xpy)$_2$I$_2$] (X = H or Me) does not react to any significant extent with dmso.

Experimental

Preparation of the Complexes.—The complexes *cis*- and *trans*-$[Pt(Xpy)Cl_2]$ (Xpy = pyridine or 4-methylpyridine) were prepared from $K_2[PtCl_4]$ by well established methods;[31,32] *trans*-$[Pt(Xpy)_2I_2]$ were prepared according to Souchard *et al.*[33] *cis*-Di-iodobis(pyridine)platinum and analogues were prepared by a variation of the previously described method:[11] $K_2[PtCl_4]$ (100 mg, 0.24 mmol) was dissolved in water (1.5 cm^3) and added to a KI solution (240 mg, 1.44 mmol) in water (1.5 cm^3). The dark solution obtained after 10 min was filtered and the filtrate was added with stirring to 50% excess of pyridine (or substituted pyridines) (0.72 mmol) in water and the mixture was stirred for 30 min. The yellow precipitate was filtered off, washed with water and ethanol, and dried under vacuum (130 mg, 91%).

trans-*(Dimethyl sulphoxide)di-iodo(pyridine)platinum.* *cis*-Di-iodobis(pyridine)platinum (61 mg, 0.1 mmol) was dissolved in dmso (0.3 cm^3, 4.2 mmol). An orange solid was precipitated by addition of diethyl ether, filtered off, washed with diethyl ether, and dried under vacuum (45 mg, 74%).

trans-*(4-Chloropyridine)(dimethyl sulphoxide)di-iodoplatinum.* *cis*-Bis(4-chloropyridine)di-iodoplatinum (101 mg, 0.15 mmol) was dissolved in dmso (4 cm^3, 55.7 mmol). Excess of dmso and unreacted starting material were removed by multiple extractions with diethyl ether. The orange precipitate was filtered off, washed with diethyl ether, and dried under vacuum (24 mg, 25%).

trans-*(4-Cyanopyridine)(dimethyl sulphoxide)di-iodoplatinum.* *cis*-Bis(4-cyanopyridine)di-iodoplatinum (99 mg, 0.15 mmol) was dissolved in dmso (1 cm^3, 13.9 mmol). Excess of dmso and unreacted starting material were removed by multiple extractions with diethyl ether. The orange precipitate was filtered off, washed with diethyl ether, and dried under vacuum (26 mg, 27%).

trans-*(Dimethyl sulphoxide)di-iodo(4-methylpyridine)platinum.* *cis*-Di-iodobis(4-methylpyridine)platinum (63 mg, 0.1 mmol) was dissolved in dmso (32 cm^3, 446 mmol). Excess of dmso and 4-methylpyridine were removed by distillation under vacuum. The dried residue was recrystallized with chloroform and gave orange crystals (53 mg, 85%).

trans-*(3,5-Dimethylpyridine)(dimethyl sulphoxide)di-iodoplatinum.* *cis*-Di-iodobis(3,5-dimethylpyridine)platinum (66 mg, 0.1 mmol) was dissolved in dmso (33 cm^3, 460 mmol). Excess of dmso and 3,5-dimethylpyridine were removed by distillation under vacuum. The dried residue was dissolved in a minimum of dmso (0.3 cm^3) and left overnight. Orange crystals precipitated which were filtered off, washed with diethyl ether, and dried under vacuum (39 mg, 62%).

Spectral Measurements.—Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer as Nujol mulls (CsI plates), n.m.r. spectra on a Bruker 250–MHz spectrometer.

X-Ray Measurements.—Slow crystallization of *trans*-$[Pt(3,5Me_2\text{-}py)(dmso)I_2]$ from either dmso or dmso-diethyl ether at room temperature gave orange-red rods of the complex.

Data collection. An orange-red flat crystal of $C_9H_{15}I_2NOPtS$ was mounted on a glass fibre in a random orientation. Preliminary examination and data collection were performed on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal, incident-beam monochromator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of 25 reflections in the range $9 < \theta < 13°$. The cell parameters and calculated volume are given in Table 4. The systematic absences of: $hk0$ $h = 2n$, $h0l$ $l = 2n$, and $0kl$ $k = 2n$ allow the determination of the space group *Pbca* (no. 61). The data were collected at room temperature (20 °C). Data collection parameters are given in Table 4.

Data reduction. A total of 4 817 reflections were collected, of which 4 439 were unique and not systematically absent. As a check on crystal stability three representative reflections were measured every h. The intensities of these standards remained constant and no decay correction was applied. Lorentz and polarization corrections were applied. The linear absorption coefficient was 133.3 cm^{-1} for Mo-K_α radiation and a numerical absorption correction was made.

Structure and refinement. The structure was solved using the Patterson heavy-atom method which revealed the position of the platinum atom. The remaining atoms were located in succeeding Fourier difference syntheses. Hydrogen atoms were located and added to the structure-factor calculations but their positions were not refined. Scattering factors were taken from Cromer and Waber.[34] Anomalous dispersion effects were included in F_c.[35] The values of f' and f'' were those of Cromer.[36] Only the 2 848 reflections having intensities $I > 3\sigma(I)$ were used in the refinement.

The final cycle of refinement included 137 variable parameters with an agreement R factor of 0.065 and R' of 0.087 [weighting scheme $w = 1/\sigma^2(F)$]. All calculations were performed on a VAX 730 computer using the Structure Determination Package of Enraf Nonius.[37]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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