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Second-order paramagnetic rhenium(III) complexes: solid-state structure and assignment of the carbon-13 magnetic resonance spectra in solution

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Single-crystal X-ray diffraction of *trans,mer*-[$ReCl_3(PEt_2Ph)_3$] has confirmed the structure derived from ^1H and ^{13}C NMR spectroscopy: space group *Pbca*, $a = 15.122(3)$, $b = 20.019(4)$, $c = 21.689(4)$ Å, $z = 8$. The carbon-13 NMR spectra of [$ReCl_3(PEt_2Ph)_3$] and [$ReCl_3(PPr^n{}_2Ph)_3$] have been assigned on the basis of the known proton assignments by ^{13}C–^1H correlation spectroscopy experiments. The spectra show no couplings between ^{13}C and ^{31}P. The C^1 carbon resonances for the aryl groups, unlike the C_α resonances of the alkyl groups, are too broad for detection. The proton relaxation rates T_1^{-1} and T_2^{-1} as well as the linewidths in three different magnetic fields, corresponding to proton frequencies of 250, 400 and 600 MHz, show an increase with field strength.

Numerous investigations have been carried out on rhenium phosphine complexes,[1–10] but no work has been done on their ^{13}C NMR spectra and very little on their structure.[7] The complexes of the type [$ReX_3(PR_2Ph)_3$], where X = Cl or Br and R = Me, Et, Pr^n or Bu^n, are of especial interest since they have unusual proton resonance spectra.[2–5] Although the solutions are paramagnetic, the spectra have narrow lines (≈1 Hz) at low field, exhibit no ^{31}P–H splittings and there are very large differences in chemical shifts between geminal methylene protons because of the low symmetry at the phosphorus.[4,5]

Here we report the ^{13}C NMR spectra of the d^4 neutral, paramagnetic complexes [$ReCl_3(PEt_2Ph)_3$] and [$ReCl_3(PPr^n{}_2Ph)_3$]. They display sharp and broad lines, shifted relative to those of diamagnetic analogues or free phosphines by several parts per million. The spectra have been completely assigned by ^{13}C–^1H correlation spectroscopy from the known ^1H assignments, and with the aid of measurements of ^1H and ^{13}C relaxation times.

The structure of [$ReCl_3(PEt_2Ph)_3$] has been determined by single-crystal X-ray diffraction, and the chemical shifts of the ^{13}C NMR spectra in solution have been compared with the corresponding bond distances in the solid state.

Results and Discussion

Crystal structure of *mer*-[$ReCl_3(PPr^n{}_2Ph)_3$]

The structures[7] of a series of complexes [$MCl_3(PMe_2Ph)_3$] have been described in preliminary form for Re^{III}, Os^{III} and Ir^{III}. Subsequently two papers with complete descriptions of the structures of *mer*-[$IrCl_3(PMe_2Ph)_3$][11] and *mer*-[$WCl_3(PMe_2Ph)_3$][12] were published, but the data for Re and Os have never been expanded. The structure of *mer*-[$ReCl_3(PEt_2Ph)_3$] is actually the first one of this type to be described thoroughly. It is shown in Fig. 1.

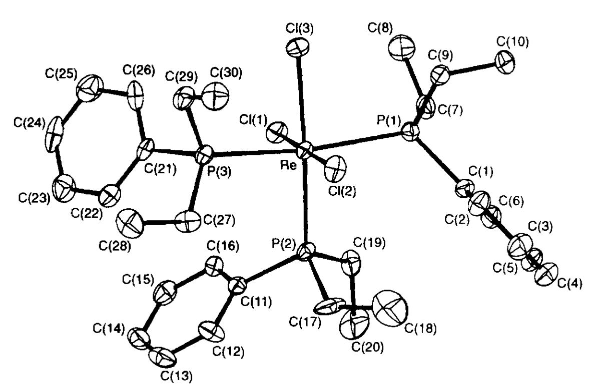


Fig. 1 Crystal structure of [$ReCl_3(PEt_2Ph)_3$]

This compound has *trans* meridional arrangements of phosphine and chloride ligands in the solid. This symmetry is the same as that derived from ^1H NMR[5] studies on solutions. Selected bond lengths and angles are given in Table 1. Intermolecular approaches, shorter than the appropriate van der Waals contacts, have not been observed. It is noteworthy that all three Re–Cl bond lengths are different (Table 1) {in contrast with the results for [$ReCl_3(PMe_2Ph)_3$][7]} by as much as 0.11 Å. The shortest one, Re–Cl(1), is for a bond *trans* to a chloride. This effect is most probably due to crystal-packing forces rather than to an intramolecular electronic effect. The three Re–P bonds also differ in length but only by 0.06 Å from each other and are of the expected magnitudes. The unique axial bond opposite to chloride is slightly shorter than the other two equatorial ones. In solution the equatorial ligands are equivalent in their NMR behaviour, so that again the small inequivalence (0.03 Å) in the solid must be due to crystal-packing forces.

The angles about rhenium do not differ much from the ideal 90°, however the equatorial phosphorus atoms P(1) and P(3) are bent towards the axial Cl(3). Also the angles in the phosphine ligand that is *trans* to chloride are slightly smaller than the angles in the other two phosphine ligands. These distortions could be related to ligand bulk.

Assignments of the ^{13}C NMR spectra of trichlorotris(diethylphenylphosphine) and trichlorotris(phenyldi-*n*-propylphosphine) complexes of Re^{III}

Chemical shifts for the rhenium(III) complexes and the free phosphines are given in Table 2. The numbering of the carbon atoms is shown in **I**.

The ^1H NMR spectra have been assigned previously.[4,5] The assignments of the ^{13}C spectra were derived by one-bond ^{13}C–^1H correlation spectroscopy (H,C-COSY) and by the use of ^1H and ^{13}C relaxation times (T_1).

The ^{13}C NMR spectra exhibit no ^{31}P–^{13}C coupling. This behaviour is consistent with previous results for ^1H spectra.[4] It

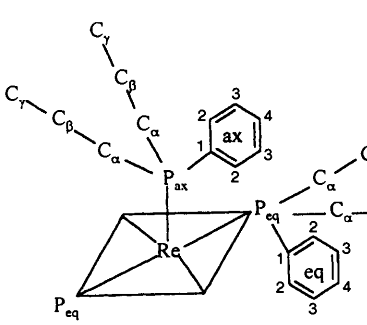
Table 1 Selected molecular dimensions (lengths in Å, angles in °) in *mer*-[$\mathrm{ReCl_3(PEt_2Ph)_3}$] with estimated standard deviations in parentheses

(*a*) In the rhenium co-ordination sphere

Re–Cl(1)	2.346(2)	Re–P(1)	2.494(2)
Re–Cl(2)	2.352(2)	Re–P(2)	2.432(2)
Re–Cl(3)	2.459(2)	Re–P(3)	2.462(2)
Cl(1)–Re–Cl(2)	178.53(7)	Cl(2)–Re–P(3)	86.61(8)
Cl(1)–Re–P(2)	84.86(7)	Cl(2)–Re–P(1)	85.56(8)
Cl(1)–Re–Cl(3)	87.22(8)	Cl(2)–Re–P(1)	85.56(8)
Cl(1)–Re–P(3)	94.83(7)	Cl(3)–Re–P(3)	85.61(7)
Cl(1)–Re–P(1)	93.08(7)	Cl(3)–Re–P(1)	85.39(7)
Cl(2)–Re–P(2)	94.73(8)	P(2)–Re–P(3)	94.33(7)
Cl(2)–Re–P(3)	86.61(8)	P(2)–Re–P(1)	95.73(7)
Cl(2)–Re–Cl(3)	93.20(8)	P(3)–Re–P(1)	167.71(7)
P(2)–Re–Cl(3)	172.06(8)		

(*b*) In the phosphine ligands

P(1)–C(9)	1.833(8)	C(7)–C(8)	1.529(11)
P(1)–C(7)	1.845(8)	C(9)–C(10)	1.527(12)
P(1)–C(1)	1.847(4)	C(17)–C(18)	1.03(2)
P(2)–C(17)	1.805(10)		
P(2)–C(19)	1.822(9)	C(19)–C(20)	1.531(13)
P(2)–C(11)	1.858(4)	C(27)–C(28)	1.519(12)
P(3)–C(21)	1.823(5)	C(27)–C(28)	1.519(12)
P(3)–C(29)	1.831(8)	C(29)–C(30)	1.496(12)
P(3)–C(27)	1.831(8)		
C(9)–P(1)–C(7)	104.5(4)	C(21)–P(3)–C(29)	100.3(4)
C(9)–P(1)–C(1)	100.0(3)	C(21)–P(3)–C(27)	105.2(4)
C(7)–P(1)–C(1)	103.9(3)	C(29)–P(3)–C(27)	103.1(4)
C(9)–P(1)–Re	112.3(3)	C(21)–P(3)–Re	116.9(2)
C(7)–P(1)–Re	114.4(3)	C(29)–P(3)–Re	115.7(3)
C(1)–P(1)–Re	119.8(2)	C(27)–P(3)–Re	113.8(3)
C(17)–P(2)–C(19)	103.3(6)	C(2)–C(1)–P(1)	119.2(3)
C(17)–P(2)–C(11)	101.3(5)	C(6)–C(1)–P(1)	120.8(3)
C(19)–P(2)–C(11)	98.9(3)	C(8)–C(7)–P(1)	113.9(6)
C(17)–P(2)–Re	119.0(4)	P(1)–C(7)–H(7A)	108.8(3)
C(19)–P(2)–Re	112.5(3)	P(1)–C(7)–H(7B)	108.8(3)
C(11)–P(2)–Re	118.9(2)	C(12)–C(11)–P(2)	122.3(3)
C(18)–C(17)–P(2)	141(2)	C(22)–C(21)–P(3)	122.5(4)



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can be ascribed to fast relaxation of the ^{31}P nuclei which leads to decoupling of phosphorus from *both* the ^{1}H and the ^{13}C nuclei. The shift behaviour of alkyl carbons in these compounds is quite complex. The lines for the α-carbon atoms appear at lowest field followed by γ-carbons to higher field and β-carbons at highest field. Also it seems that the effect is larger on the axial phosphine ligand than on the equatorial ones. The most noteworthy result in the ^{13}C NMR spectra (Table 2) is that there is no evidence of lines for the C^1 carbons bonded to phosphorus in either the equatorial or the axial positions. Evidently the relaxation times of the carbon close to the paramagnetic rhenium centre are too short and lead to lines too broad for observation, as we have deduced for the even closer phosphorus nuclei. However the X-ray data for the solid give distances for the alkyl α-carbons about the same as for the C^1 aryl. For first-order paramagnetics in such a case one could invoke the Fermi-contact relaxation effects for the aryl groups, which are absent for the alkyl, but the logic rules this argument out.

The phenyl regions of the spectra therefore consist of only three areas of resonance due to C_{ortho} (C^2), C_{meta} (C^3) and C_{para} (C^4). The shifts of the phenyl carbons in these complexes follow a general pattern: the *o*-carbons are at lowest field followed by the *m*- and *p*-carbons at highest field. This pattern is slightly different from the one for the aryl protons in similar compounds,[5] where the series is *o*-, *p*- and *m*-protons at highest field. It is nevertheless consistent with a mechanism which is distance dependent, unlike the Fermi-contact mechanism.

The shifts are influenced by the position of the phosphine ligand. If we compare the distances between the axial and the equatorial ligand (Table 1, Re–P_{ax} 2.43, Re–P_{eq} 2.49 and 2.46 Å) we see that the equatorial ligands are closer to the anisotropic centre (Re^{III}) than is the axial one. This results in larger interactions between the paramagnetic dipole and the magnetic moments of the carbon nuclei of the equatorial ligand relative to the axial one. Thus the signal of the C_α carbon of the axial ligand in the diethyl case is shifted 148.4 ppm relative to the free phosphine, whereas the corresponding shift for the equatorial ligand is less at 120.4 ppm. The corresponding figures for the di-*n*-propyl case are 142.4 and 93.1 ppm respectively. This analysis however ignores the angular dependency of the shift.

Temperature effects. Table 3 shows the temperature dependence of the chemical shifts of carbon atoms of *mer*-[$\mathrm{ReCl_3(PPr^n{}_2Ph)_3}$]. The temperature dependence becomes less important as the carbons on the alkyl chain become further removed from the metal (Table 3). However the magnitude of the chemical shifts does not decrease regularly along the alkyl chain, but reaches a maximum at the β-carbon atom.

A simple linear equation (1) that permits the calculation

$$\delta(^{13}\mathrm{C}) = aT + b \qquad (1)$$

of the chemical shifts in different temperatures has been found. The data for *a* and *b* are given in Table 3. This equation can be used for the ^{1}H chemical shifts as well, of course with different coefficients. Our numerical analysis revealed that equation (1) provides much better fitting of the observed data than the inverse Curie model (2), which requires that the shift mechanism be of the Fermi-contact type.

$$\delta(^{13}\mathrm{C}) = a(1/T) + b \qquad (2)$$

The direct dependence of the methyl and methylene carbon shifts on temperature immediately confirms that the shift mechanism is not of the Fermi-contact type, which is in concordance with previous results for the proton spectra.[5] According to the alternative model the rhenium(III) complexes show a second-order (Van Fleck) paramagnetic effect arising from the mixing of the ground state (A_{1g}) ($J = 0$) with an excited state (T_{1g}) ($J = 1$) in the presence of a magnetic field.[13] The shift mechanism in second-order paramagnetic situations can be simply described as a direct interaction between an electron magnetic dipole (arising from an anisotropic susceptibility) and the nuclear dipoles. The form of the shift equation contains two angular terms (one if the symmetry is high enough) and an r^{-3} term, where *r* is the distance of the nucleus from the paramagnetic rhenium centre. The relaxation effect should have no angular dependence and should vary as r^{-6}.

Proton and ^{13}C relaxation times for *mer*-[$\mathrm{ReCl_3(PPr^n{}_2Ph)_3}$] and linewidths

An added complication arises if the molecules are not isotropically oriented. In very high magnetic fields molecules with anisotropic susceptibility tensors can become slightly oriented.[14,15] Since paramagnetic susceptibilities are usually much larger than diamagnetic susceptibilities, it is not surprising that the

Table 2 Carbon-13 chemical shifts of $[ReCl_3(PEt_2Ph)_3]$, $[ReCl_3(PPr^n{}_2Ph)_3]$ and the free tertiary phosphines in $CDCl_3$ solution (ppm with respect to $SiMe_4$) at 295 K

	Carbon	$[ReCl_3(PEt_2Ph)_3]$	PEt_2Ph[a]	$[ReCl_3(PPr^n{}_2Ph)_3]$	$PPr^n{}_2Ph$[a]
Alkyl	$C_{\alpha ax}$	−169.352	−20.9	−174.230	−31.7
	$C_{\alpha eq}$	−121.502		−124.833	
	$C_{\beta ax}$	+11.265	−10.0	+1.850	−20.1
	$C_{\beta eq}$	*b*		+0.561	
	$C_{\gamma ax}$	—	—	−24.177	−16.1
	$C_{\gamma eq}$	—	—	−39.865	
Aryl	$C^1{}_{eq}$	*c*	−139.8	*c*	−140.4
	$C^1{}_{ax}$	*c*		*c*	
	$C^2{}_{eq}$	−144.197	−132.7	−143.966	−132.8
	$C^2{}_{ax}$	−132.233		−133.064	
	$C^3{}_{eq}$	−136.079	−128.6	−135.952	−128.6
	$C^3{}_{ax}$	−128.639		−132.325	
	$C^4{}_{eq}$	−123.937	−128.7	−123.880	−128.7
	$C^4{}_{ax}$	−121.502		−121.315	

[a] Ref. 6. [b] Not assigned. [c] Not observed.

Table 3 Temperature dependence of the ^{13}C chemical shifts of $[ReCl_3(PPr^n{}_2Ph)_3]$ and coefficients for equation (1) (ppm with respect to $SiMe_4$)

		T/K					
		298	278	258	248	*a*	*b*
Alkyl	$C_{\alpha ax}$	−174.230		broadens			
	$C_{\alpha eq}$	−124.833		broadens			
	$C_{\beta ax}$	1.850	3.204	4.319	4.872	0.0601	−3.411
	$C_{\beta eq}$	0.561	0.867		broadens	0.0153	−0.943
	$C_{\gamma ax}$	−24.177	−24.026	−23.937	−23.922	0.0052	24.028
	$C_{\gamma eq}$	−39.865	−41.370	−42.951	−43.721	−0.0773	41.783
Aryl	$C^2{}_{eq}$	−143.996	−143.667	−143.205	−142.952	0.0210	143.507
	$C^2{}_{ax}$	−133.064	−132.164	−130.996	−130.519	0.0518	131.815
	$C^3{}_{eq}$	−135.952	−135.997	−136.008	−136.006	−0.0011	135.988
	$C^3{}_{ax}$	−132.325	−132.164	−131.987	−131.900	0.0085	132.115
	$C^4{}_{eq}$	−123.880	−123.740	−123.617	−123.565	0.0063	123.716
	$C^4{}_{ax}$	−121.315	−121.227	−121.060	−121.082	0.0053	121.184

Table 4 Proton 'linewidths', Δ, for $[ReCl_3(PPr^n{}_2Ph)_3]$

		Δ/Hz			
Proton	$\delta(^1H)$	600	400	250 MHz	Expected multiplicity
o_{eq}	11.75	14.57	11.91	11.4	d
p_{eq}	10.21	2.77	2.24	2.10	t
p_{ax}	10.19	2.77	2.24	1.50	t
o_{ax}	8.50	14.22	13.43	12.18	d
m_{eq}	8.34	2.77	2.24	2.11	t
β_{eq}	8.33	3.81	3.15	3.02	dt
m_{ax}	8.24	24.68	22.10	20.52	t
β_{eq}*	7.43	37.24	32.94	28.05	dt
$CHCl_3$	7.24	1.04	0.95	1.18	
α_{eq}	7.18	31.95	30.45	30.07	t
β_{ax}*	5.91	29.82	26.15	23.46	dt
β_{ax}	5.15	27.86	26.11	24.52	dt
α_{eq}*	4.49	37.45	32.67	31.40	t
α_{ax}*	2.57	60.00	42.63	32.62	t
γ_{ax}	2.35	3.12	2.24	1.80	t
γ_{eq}	2.33	2.43	1.95	1.80	t
α_{ax}	−2.62	31.21	30.70	30.08	t

Δ is the total frequency spread across the multiplet. * Inequivalent methylene protons.

anisotropies of the paramagnetic susceptibilities are also much larger, and the degree of alignment correspondingly greater.

Table 4 shows the ^1H 'linewidths' in three different magnetic fields (5.9, 9.4 and 14.1 T) corresponding to ^1H resonance frequencies of 250, 400 and 600 MHz. In general the lines become broader as the field becomes higher, and therefore in some cases the multiplet resolution is lost (Table 4), so that the doublet or triplet bands coalesce into broad singlets. The table lists the total spread, Δ, across the multiplet.

The ^{13}C linewidths and spin–spin relaxation times (T_2) also indicate partial orientation (Table 5), and the influence of the field is larger than that for the ^1H spectra. The ^{13}C linewidth is at least double at 14.1 T than at 5.9 T, and for some carbons the increase is even greater (*e.g.* $C_{\alpha 1}$: 0.82 Hz at 250 MHz to 13.36 Hz for 600 MHz). These observations, as well as the fact that we could not obtain observable ^{31}P NMR spectra within ±4500 ppm of phosphoric acid, at 5.9 and 14.1 T, indicate that the closer a nucleus is to the centre of anisotropy (Re^{III}) the broader is the line and the larger the shift.

The absence of any observable ^{31}P NMR signal for these complexes at high field is most probably a result of the very fast relaxation, which also produces an absence of phosphorus–carbon or -proton coupling.

Only once has an observable ^{31}P NMR signal for rhenium(III) complexes of this type been reported and then only briefly.[16] The compound was $[ReCl_3(PMe_2Ph)_3]$, in chloroform at low field, 1.76 T, with a ^{31}P resonance frequency of 30 MHz. There were two chemically shifted resonances in the ratio of 2:1, with a chemical shift difference of 792 ± 2 ppm, indicating that the compound has C_{2v} symmetry. The chemical shifts were δ 3420 ± 20 and 4212 ± 20 for the equatorial and axial phosphorus nuclei, respectively, to high field relative to the free phosphine as external reference.[16] These very large shieldings compared to the diamagnetic complexes confirm the paramagnetic nature of the complexes, and the ^{13}C and ^1H NMR results.

Since the ^{31}P spin–lattice relaxation time is of the order of a few milliseconds the lines are broad and the signals are very weak.[16] The lines are expected to become broader as the magnetic field becomes higher, since the anisotropy increases linearly with field. This would account for our failure to

Table 5 Carbon-13 spin–spin relaxation times T_2 for $[ReCl_3(PPr^n{}_2Ph)_3]$ and linewidths

				Linewidth/Hz			
Carbon	$\delta(^{13}C)$	T_2/ms (600 MHz)	10^{-1} Standard deviation	$1/\pi T_2$	600	400	250
$C^2{}_{eq}$	143.88	192.678	1.710	1.65	1.63	1.14	0.80
$C^3{}_{eq}$	135.73	178.691	0.836	1.78	2.68	1.64	1.20
$C^2{}_{ax}$	133.33	128.848	1.742	2.47	2.68	1.86	0.75
$C^3{}_{ax}$	132.10	149.018	1.038	2.13	1.16	1.02	0.65
$C_{\alpha eq}$	124.18	350.397	1.397	9.09	13.36	1.86	0.82
$C_{\gamma ax}$	40.18	114.854	1.627	2.77	5.73	3.77	1.30
$C_{\gamma eq}$	23.96	164.617	1.208	1.93	2.68	1.24	0.90
$C_{\beta ax}$	−0.22				9.78	2.81	0.96
$C_{\beta eq}$	−2.22	41.911	1.739	7.60	10.95	4.77	1.52

The ^{13}C nuclei are decoupled from the protons.

detect the ^{31}P NMR signals at higher fields such as 14.1 T (243 MHz).

Experimental

Proton and ^{13}C NMR spectra were obtained at 5.9, 9.7 and 14.1 T with Bruker AM-250, AM-400 and 600-AMX spectrometers, respectively. The sample temperatures were controlled by B-VT 2000 Bruker temperature units. Deuteriochloroform was used as solvent and tetramethylsilane as internal reference.

The complexes were prepared by the literature method.[1]

Trichlorotris(diethylphenylphosphine)rhenium(III)

Concentrated hydrochloric acid (40 cm^3) and diethylphenylphosphine (36 g) were added to a solution of sodium perrhenate (9 g) in ethanol (500 cm^3) under nitrogen. The mixture was boiled for 3–5 h, evaporated to a quarter of its original volume, and allowed to cool. The solid was removed and washed successively with ethanol, water, ethanol and then dried *in vacuo*. The violet mother-liquor was concentrated to one-fifth of its volume and an equal volume of light petroleum (b.p. 40–60 °C) was added to precipitate a violet solid (9.0 g) recrystallized from benzene–light petroleum as violet needles (8.6 g, m.p. 164–166 °C). A solution of the violet complex (2.0 g) and diethylphosphine (10.5 g) in ethanol (200 cm^3) was refluxed under nitrogen for 5 h and allowed to cool. The orange solid (0.9 g) precipitated was recrystallized from ethanol as yellow-orange needles (0.9 g, m.p. 162–164 °C).

Trichlorotris(phenyldi-*n*-propylphosphine)rhenium(III)

This complex was prepared exactly analogously to the diethylphenylphosphine complex. The product was orange-yellow needles (1.0 g, m.p. 170–173 °C) (Found: C, 48.6; H, 6.75; Cl, 12.4; P, 10.4. $C_{36}H_{57}Cl_3P_3Re$ requires C, 49.4; H, 6.50; Cl, 12.2; P, 10.65%).

Crystallography

Crystal data for *mer*-$[ReCl(PEt_2Ph)_3]$. $C_{30}H_{45}Cl_3P_3Re$, $M = 791.12$, orthorhombic, space group *Pbca*, $a = 15.122(3)$, $b = 20.019(4)$, $c = 21.689(4)$ Å, $U = 6566(2)$ Å^3, $Z = 8$, $D_c = 1.601$ g cm^{-3}, $F(000) = 3168$, μ(Mo-Kα) = 41.11 cm^{-1}, λ(Mo-Kα) = 0.710 73 Å.

The intensity data were collected by a CAD4 diffractometer using ω–2θ scans. 5755 Unique reflections [R(int) = 0.04, $T \approx 295$ K, $2\theta_{max} = 49.94$, crystal dimensions 0.30 × 0.35 × 0.20 mm] were collected of which 3285 [$I > 2\sigma(I)$] were considered 'observed'. The unit-cell parameters were determined by a least-squares refinement on diffractometer angles for 25 automatically centred reflections having $10 \leqslant \theta \leqslant 13°$. The structure was solved by heavy-atom methods using the SHELXS 86 program package,[17] and refined anisotropically by full-matrix least squares on F^2 using SHELXL 93).[18] All hydrogen atoms were calculated geometrically (riding model) by using the AFIX command in the SHELXL 93 program. Empirical absorption correction applied, using ψ scans of three reflections: minimum and maximum transmission factors 0.70, 0.99.[19] Final R indices (on observed reflections) were $R1 = 0.0457$, $wR2 = 0.0984$, where $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_c|$ and $wR2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{\frac{1}{2}}$ and $w = 1/\sigma^2(F_o{}^2) + (0.1481P)^2 + 0.0000P$, where $P = (F_o{}^2 + 2F_c{}^2)/3$. The program SNOOPI[20] was used for drawing the molecular structures.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/266.

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