Synthesis of New Cobalt–Osmium Mixed-metal Clusters using a Novel Reactive Cobalt Species; *X*-Ray Crystal Structure of $[Os_3Co(CO)_{10}(C_5Me_4Et)H_2]$ †

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Thermal decomposition of the known complex $[Co(C_5Me_4Et)(C_2H_4)Me_2]$ gives the intermediate species ' $Co(C_5Me_4Et)$ ' which reacts with $[Os_3(CO)_{10}H_2]$ to produce $[Os_3Co(CO)_{10}(C_5Me_4Et)H_2]$. This complex crystallises in the triclinic space group $P\bar{1}$ with a = 9.072(4), b = 10.477(5), c = 13.921(7) Å, α = 95.80(3), β = 93.54(3), γ = 102.48(3)°, and Z = 2. The structure was solved by a combination of direct methods and Fourier-difference techniques and refined by blocked-cascade least squares to R = 0.039 for 3 084 diffractometer data. The $Co(C_5Me_4Et)$ fragment caps the Os_3 triangle. Each Os atom is also co-ordinated to three terminal carbonyl groups while the tenth carbonyl bridges an Os–Co bond. The complex $[Os_3Co(CO)_{10}(C_5Me_4Et)H_2]$ reacts with hydrogen to give $[Os_3Co(CO)_9(C_5Me_4Et)H_4]$, and both clusters react with carbon monoxide under fairly mild conditions to yield $[Os_3(CO)_{12}]$ and $[Co(CO)_2(C_5Me_4Et)]$.

THERE has been a recent increase in interest in the synthesis and reactivity of clusters containing several different types of metal atoms. Inherent polarity in mixed-metal bonds should induce greater reactivity than that observed in analogous homonuclear clusters.

Relatively few mixed cobalt–osmium clusters have been reported and structural information is available on only one of them.[1] Recently, Shore and co-workers [2] reported the complex $[Os_3Co(CO)_{10}(C_5H_5)H_2]$ and it is of interest to determine what effect a more bulky cyclopentadienyl group would have on the distribution of the carbonyl ligands in such a system. We now report the preparation and characterisation of two new mixed-metal clusters $[Os_3Co(CO)_{10}(C_5Me_4Et)H_2]$ (1) and $[Os_3Co(CO)_9(C_5Me_4Et)H_4]$ (2).

RESULTS AND DISCUSSION

Previous work has led to the preparation of the thermally unstable complex $[Co(C_5Me_4Et)(C_2H_4)Me_2]$, which decomposes above 0 °C with the loss of the olefin and alkyl ligands. The resulting species ' $Co(C_5Me_4Et)$ ' can either polymerise or insert into chemical bonds. With $[Os_3(CO)_{10}H_2]$, the air-stable red-brown cluster (1) is formed in 40% yield, together with $[\{Co(CO)(C_5Me_4Et)\}_2]$. Both these complexes appear to be the products of insertion into Os–Os or Os–CO bonds respectively. In order to obtain a reasonable yield of (1) it is necessary to use a two-fold excess of $Co(C_5Me_4Et)$.

The complex (1) was characterised by analytical, i.r., ^1H n.m.r., and mass spectroscopic techniques. The analytical data (Found: C, 23.9; H, 2.0; Co, 5.2. Calc. C, 24.1; H, 2.0; Co, 5.6%) and m/e (M^+) of 1 066 (for $^{59}Co^{192}Os_3{}^{12}C_{21}{}^1H_{19}{}^{16}O_{10}$) give the molecular formula. The i.r. spectrum in hexane showed 13 bands in the ν(CO) region at 2 084s, 2 064m, 2 054s, 2 039(sh), 2 035s, 2 009s, 2 000m, 1 995m, 1 986s, 1 963br, m, 1 807w, 1 793m, and 1 778m cm^{-1}. The solid-state i.r. spectrum, obtained by using a KBr disc, exhibited nine bands at 2 080s, 2 050s, 2 022(sh), 2 016s, 1 998m, 1 975s, 1 955m, 1 951m, and 1 778m cm^{-1}. The 80-MHz Fourier-transform ^1H n.m.r. spectrum in $CDCl_3$ showed resonances from the C_5Me_4Et group (δ 2.4, quartet, J = 7.2, CH_2 of Et; 1.83, s, Me; 0.97, t, J = 7.2 Hz, CH_3 of Et) together with a slightly broadened singlet at δ −21.4 corresponding to the hydridic protons. Cooling the sample to −50 °C did not alter the linewidth.

The large number of bands in the solution i.r. spectrum of (1) together with the reduction in the number in the solid is indicative of the presence of isomers in solution. The broad singlet in the hydride region is consistent with the existence of fluxional processes even at lower temperatures. The i.r. spectrum of (1) is more complex than that of $[Os_3Co(CO)_{10}(C_5H_5)H_2]$ [2] where only seven bands are observed. This may suggest that there are isomers of (1) which exhibit different structures to that proposed for $[Os_3Co(CO)_{10}(C_5H_5)H_2]$.[2] Also, (1) is isolated as a red-brown solid while the unsubstituted cyclopentadienyl cluster is black-green. An *X*-ray analysis of (1) was undertaken to establish the structure and assess whether the presence of the bulky cyclopentadienyl ring has any effect on the geometry of the cluster.

The molecular structure of (1) is shown in Figure 1 which includes the atom-numbering scheme adopted. Selected bond lengths and interbond angles are displayed in Table 1. There are no intermolecular contacts shorter than the sum of the van der Waals radii.

The four metal atoms define a distorted tetrahedron. The metal core may also be viewed as an Os_3 triangle asymmetrically capped by the $Co(C_5Me_4Et)$ unit, with the Co atom positioned 2.179 Å above the metal triangle. The Co atom lies significantly closer to the Os(1)–Os(3) edge than to the Os(2) atom. The Co(1)–Os(1) and Co(1)–Os(3) bond lengths are similar to the average value of 2.694(3) Å in $[Os_3Co(CO)_{12}H_3]$,[1] although in (1) the former bond is asymmetrically bridged by a carbonyl ligand. The Co(1)–Os(2) bond is *ca.* 0.15 Å longer than the other two Co–Os bonds. Potential-energy calculations [3] indicate that this Co(1)–Os(2) edge is bridged by a hydride ligand. The Os–Os distances in (1) range from

† 1,2-μ-Carbonyl-2,2,2,3,3,3,4,4,4-nonacarbonyl-1-(1′—5′-η-ethyltetramethylcyclopentadienyl)-di-μ-hydrido-*tetrahedro*-cobalttriosmium.

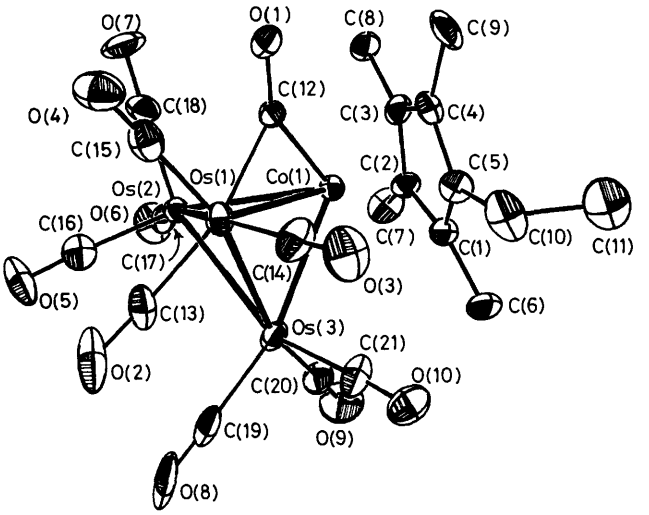


FIGURE 1 The molecular structure of $[Os_3Co(CO)_{10}(C_5Me_5Et)H_2]$ showing the atom-numbering scheme

2.781(1) to 2.897(1) Å, all of which are shorter than the average value of 2.901(3) Å for the Os–Os bonds in $[Os_3Co(CO)_{12}H_3]$ [1] where these bonds are considered to be bridged by hydrides. Again potential-energy calculations [3] indicate that the longest edge, Os(2)–Os(3), is bridged by a hydride, although neither hydride was located directly in the structure analysis.

TABLE 1

Bond parameters for $[Os_3Co(CO)_{10}(C_5Me_4Et)H_2]$

Distances (Å)

Os(1)–Os(2)	2.834(1)	Co(1)–Os(1)	2.669(2)
Os(1)–Os(3)	2.781(1)	Co(1)–Os(2)	2.827(1)
Os(2)–Os(3)	2.897(1)	Co(1)–Os(3)	2.689(1)
Co(1)–C(12)	1.918(11)	Co(1)–C(1)	2.154(12)
Os(1)–C(12)	2.071(11)	Co(1)–C(2)	2.087(12)
Os(1)–C(13)	1.889(13)	Co(1)–C(3)	2.091(12)
Os(1)–C(14)	1.907(13)	Co(1)–C(4)	2.105(10)
Os(1)–C(15)	1.883(16)	Co(1)–C(5)	2.110(11)
Os(2)–C(16)	1.896(14)	Os(3)–C(19)	1.896(15)
Os(2)–C(17)	1.928(12)	Os(3)–C(20)	1.901(14)
Os(2)–C(18)	1.892(14)	Os(3)–C(21)	1.901(14)

Angles (°)

Os(2)–Os(1)–Os(3)	62.1(1)	Os(1)–Co(1)–Os(2)	62.0(1)
Os(1)–Os(2)–Os(3)	58.0(1)	Os(1)–Co(1)–Os(3)	62.5(1)
Os(1)–Os(3)–Os(3)	59.8(1)	Os(2)–Co(1)–Os(3)	63.3(1)
Os(1)–Co(1)–C(12)	50.5(3)	Co(1)–Os(1)–C(12)	45.6(3)
Os(1)–C(12)–Co(1)	83.9(4)		

Each Os atom is co-ordinated to three terminal carbonyl groups, two of which lie close to the plane of the Os_3 triangle and the third in a pseudo-axial position. This geometry is adopted in many trinuclear clusters where one side of the metal triangle is capped by a donor ligand. The average Os–C and C–O distances for these groups are 1.90(2) and 1.15(3) Å, respectively; the average Os–C–O angle is 178(2)°. The tenth carbonyl group bridges the Os(1)–Co(1) bond. The formation of bridging carbonyl groups in osmium clusters is relatively uncommon but is well established in the cobalt carbonyl $[Co_4(CO)_{12}]$ [4] and related species. With the observed ligand distribution each metal atom obeys the '18-electron' rule.

The substituted cyclopentadienyl ring is η^5-bound to the Co(1) atom with a Co(1)–cp(centroid) distance of 1.729(13) Å. The Co–C distances lie in the range 2.087(12)—2.154(12) Å which is similar to the values in a number of clusters containing the Co–cp unit.[5] The plane of the cyclopentadienyl ring makes an angle of 16.6° with that of the Os_3 triangle. The bond parameters within the cyclopentadienyl ring lie in the expected range for this system and the ethyl substituent group is orientated away from the cluster core. There are no intramolecular contacts significantly shorter than the sum of the van der Waals radii between the atoms of the cyclopentadiene group and the carbonyl ligands.

Although the presence of the bulky, substituted cyclopentadienyl ring appears to have little effect on the geometry of (1) it is interesting to note that this isomer, isolated in the solid state, does not have the same structure as that determined by spectroscopic techniques for $[Os_3Co(CO)_{10}(C_5H_5)H_2]$.[2] In the latter complex the two hydride ligands bridge Os–Os bonds. It may be that the presence of the more bulky and electron-donating C_5Me_4Et ligand in (1) stabilises another isomer, and

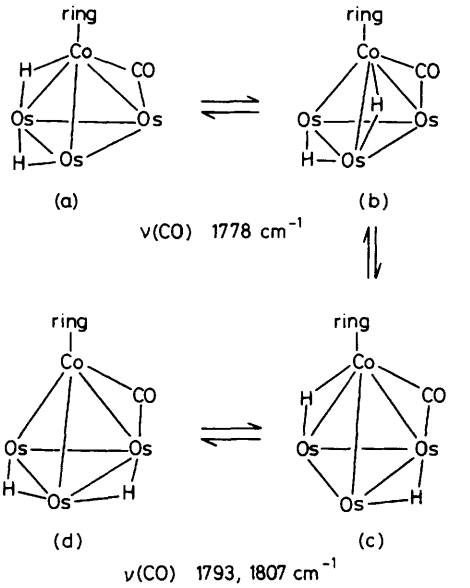


FIGURE 2 Possible isomeric structures of (1)

perhaps facilitates hydride site exchange. This is consistent with the more complex solution i.r. spectrum of (1), and possible isomeric structures in keeping with this spectrum are illustrated in Figure 2. Isomer (b) is that observed in the solid while isomer (d) has a similar structure to that of $[Os_3Co(CO)_{10}(C_5H_5)H_2]$.[2,*]

Reactions of (1) *with Hydrogen.*—Solutions of (1) in hexane were treated with hydrogen (50 bar) † in a high-pressure i.r. cell and the i.r. spectrum observed as a

† Throughout this paper: 1 bar = 10^5 Pa.

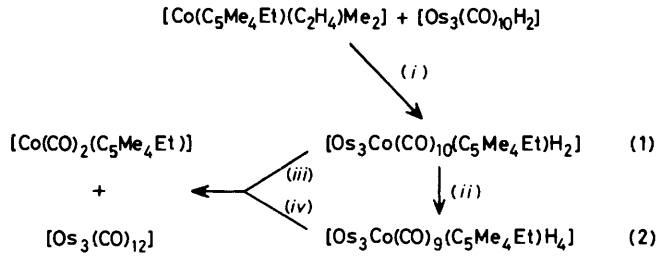
* *Note added in proof*: A recent *X*-ray analysis of $[Os_3Co(CO)_{10}(C_5H_5)H_2]$ (M. R. Churchill, C. Bueno, S. Kennedy, J. C. Bricker, J. S. Platkin, and S. G. Shore, *Inorg. Chem.*, 1982, **21**, 627) confirms the solid-state structure to be that shown in Figure 2(d).

function of temperature. It was found that at 80 °C an air-stable green-brown product, (2), was obtained almost quantitatively.

Analysis (Found: C, 23.2; H, 2.2. Calc.: C, 23.2; H, 2.0%) and mass spectrum *m/e* (M^+) 1 040 (for $^{59}Co^{192}Os_3{}^{12}C_{20}{}^{1}H_{21}{}^{16}O_9$) both indicate a formula of $Os_3Co(CO)_9(C_5Me_4Et)H_4$. The 80-MHz Fourier-transform ^1H n.m.r. spectrum ($CDCl_3$) shows resonances due to C_5Me_4Et (2.55, quartet $J = 7.5$, CH_2 of Et; 2.0, s, Me; 1.07, t, $J = 7.5$ Hz, CH_3 of Et) and a singlet at δ −17.9 due to hydride protons. Cooling solutions of (2) in CD_2Cl_2 to −60 °C resulted in some broadening of the hydridic resonance. The i.r. spectrum of (2) shows the following bands: 2 084m, 2 054s, 2 047s, 2 007s, 1 992m, 1 984s, and 1 972w cm^{-1}. There are thus no bridging carbonyl ligands.

Pyrolysis of (1) in refluxing octane also gave (2), but in very low yield.

Reactions of (1) *and* (2) *with Carbon Monoxide.*—Using the high-pressure i.r. cell, it was found that (1) and (2) show differing reactivity towards carbon monoxide. In each case fragmentation occurs giving $[Co(CO)_2(C_5Me_4Et)]$, and $[Os_3(CO)_{12}]$, but (1) reacts at 50 °C while (2) reacts at 150 °C. In each case 50 bar pressure and hexane solvent were used. No intermediates were seen by i.r. spectroscopy and no organic products were detected by gas chromatography (g.c.). Similar results were found when (1) was heated at 80 °C for 4 h under 50 bar hydrogen–carbon monoxide (1 : 1) in hexane. The reactions are summarised in the Scheme.



SCHEME (*i*) 0 °C, 24 h, in Et_2O; (*ii*) H_2, 50 bar, 80 °C, 4 h, in hexane; (*iii*) CO, 50 bar, 50 °C, 2 h, in hexane; (*iv*) CO, 50 bar, 150 °C, 4 h, in hexane

Thus replacement of carbon monoxide by two hydrides appears to stabilise the cluster framework, although the presence of a cobalt atom labilises the systems in comparison with the all-osmium systems.

EXPERIMENTAL

All reactions were carried out under nitrogen using dry, distilled solvents. Thin-layer chromatography (t.l.c.) and subsequent procedures were carried out in air. The compound $[Co(C_5Me_4Et)(C_2H_4)Me_2]$ was prepared as previously described.[6]

$[Os_3Co(CO)_{10}(C_5Me_4Et)H_2]$ (1).—The compound $[Os_3(CO)_{10}H_2]$ (400 mg, 0.47 mmol) and hexane (10 cm^3) were cooled to 0 °C. A solution of $[Co(C_5Me_4Et)(C_2H_4)Me_2]$ (*ca.* 1 mmol) in diethyl ether (80 cm^3) at −78 °C was added and the mixture stirred in an ice-bath which slowly warmed to room temperature over 24 h. The resulting green, air-sensitive solution was evaporated to dryness under reduced pressure and dissolved in hexane (30 cm^3). The solution was eluted from a column of Kieselgel 60 first with hexane, to remove traces of $[Os_3(CO)_{10}H_2]$, and then with 30% dichloromethane in hexane. An intense green band then eluted ($[\{Co(CO)(C_5Me_4Et)\}_2]$, ν(CO) 1 750 cm^{-1}, *ca.* 140 mg) followed by the red-brown product, which was purified by t.l.c. using 30% dichloromethane in hexane, $R_f = 0.16$ in pure hexane, *ca.* 200 mg (40%).

$[Os_3Co(CO)_9(C_5Me_4Et)H_4]$ (2).—The compound $[Os_3Co(CO)_{10}(C_5Me_4Et)H_2]$ (12 mg, 0.011 mmol) in hexane (5 cm^3) was stirred in a glass-lined autoclave (100 cm^3) under hydrogen (50 bar) at 80 °C for 4 h. The resulting green-brown solution was purified by t.l.c. in hexane, $R_f = 0.6$, 10 mg (85%).

Reactions of (1) *and* (2) *with Carbon Monoxide.*—The complex (*ca.* 10 mg) in hexane was put into a high-pressure i.r. cell under carbon monoxide (50 bar). The temperature was then increased at 10° h^{-1} until the i.r. spectrum began to alter. In each case $[Os_3(CO)_{12}]$, ν(CO) 2 067m, 2 035m, 2 021w, and 2 003w, cm^{-1} and $[Co(CO)_2(C_5Me_4Et)]$, ν(CO) 2 008s and 1 947s cm^{-1}, were observed with no intermediates.

Pyrolysis of (1).—Compound (1) (20 mg, 0.019 mmol) was refluxed in octane (10 cm^3) for 10 h. The solvent was removed under reduced pressure and the solid extracted with dichloromethane. Most of the product is insoluble, but the extract was applied to t.l.c. plates and eluted with 20% dichloromethane in hexane. Two main bands were formed of (1) (*ca.* 2 mg) and (2) (*ca.* 1 mg) respectively, which were identified by their i.r. spectra.

Structure Determination of (1).—Crystals of $[Os_3Co(CO)_{10}(C_5Me_4Et)H_2]$ were obtained as dark red-black blocks from hexane solution. A single crystal (*ca.* 0.19 × 0.19 × 0.12 mm) was mounted on a glass fibre and unit-cell dimensions and the space group determined *via* Weissenberg *X*-ray photography.

The crystal was mounted on a Stoe four-circle diffractometer, and accurate cell dimensions obtained by centering 20 strong reflections ($15.0 < 2\theta < 25°$). 4 797 Intensities were measured in the range $3.0 < 2\theta < 55.0°$, using graphite-monochromated Mo-K_α radiation and a 140-step ω—θ scan procedure; each reflection was subjected to a 1-s prescan, those with a measured intensity of <7 counts s^{-1} not being remeasured. Two check reflections were monitored periodically throughout data collection and showed no significant variation.

A semi-empirical absorption correction based on a pseudo-ellipsoid model and 423 azimuthal scan data from 42 independent reflections was applied. Transmission factors ranged from 0.66 to 0.97 for the full data set. Lorentz and polarisation corrections were applied and equivalent reflections averaged to give 3 084 unique observed reflections [$F > 3\sigma(F)$].

Crystal data. $C_{21}H_{20}CoO_{10}Os_3$, $M = 1\,061.90$, Triclinic, $a = 9.072(4)$, $b = 10.477(5)$, $c = 13.921(7)$ Å, $\alpha = 95.80(3)$, $\beta = 93.54(3)$, $\gamma = 102.48(3)°$, $U = 1\,280.5$ Å^3, D_m = not measured, $Z = 2$, $D_c = 2.75$ g cm^{-3}, $F(000) = 959.68$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 155.11 cm^{-1}, space group $P\bar{1}$ from successful refinement.

The positions of the three Os and the Co atom were located by multisolution Σ_2 sign expansion, and all the remaining non-hydrogen atoms from a subsequent electron-density difference synthesis. All these atoms were refined by blocked-cascade least squares having been assigned anisotropic thermal parameters. The methyl and ethyl H

TABLE 2

Atom co-ordinates ($\times 10^4$)

Atom	X/a	Y/b	Z/c
Os(1)	3 382(1)	1 478(1)	3 353(1)
Os(2)	238(1)	918(1)	2 772(1)
Os(3)	2 504(1)	1 409(1)	1 395(1)
Co(1)	2 213(2)	3 391(1)	2 704(1)
C(1)	2 676(14)	4 757(10)	1 645(8)
C(2)	1 217(12)	4 670(10)	1 966(8)
C(3)	1 390(14)	5 092(11)	3 001(9)
C(4)	2 910(13)	5 382(10)	3 286(9)
C(5)	3 773(12)	5 124(11)	2 484(9)
C(6)	3 036(17)	4 808(12)	605(10)
C(7)	−258(15)	4 347(14)	1 349(10)
C(8)	104(16)	5 198(12)	3 614(10)
C(9)	3 652(19)	6 058(12)	4 296(10)
C(10)	5 457(14)	5 417(13)	2 449(14)
C(11)	6 125(18)	6 861(16)	2 238(17)
C(12)	2 553(13)	3 011(10)	4 008(7)
O(1)	2 329(11)	3 462(8)	4 792(6)
C(13)	3 550(17)	−227(12)	2 860(11)
O(2)	3 714(15)	−1 279(10)	2 617(10)
C(14)	5 475(15)	2 306(14)	3 372(10)
O(3)	6 742(11)	2 814(10)	3 381(9)
C(15)	3 458(15)	1 015(12)	4 625(12)
O(4)	3 527(13)	730(11)	5 405(8)
C(16)	223(15)	−882(13)	2 840(10)
O(5)	177(14)	−1 977(9)	2 838(9)
C(17)	−1 785(13)	643(11)	2 154(9)
O(6)	−2 984(10)	398(10)	1 813(9)
C(18)	−337(15)	1 221(12)	4 044(10)
O(7)	−689(13)	1 419(11)	4 828(7)
C(19)	2 679(20)	−253(14)	797(11)
O(8)	2 773(19)	−1 271(12)	449(10)
C(20)	1 544(17)	1 765(13)	230(9)
O(9)	972(14)	1 954(12)	−475(8)
C(21)	4 508(16)	2 247(13)	1 168(10)
O(10)	5 726(12)	2 725(10)	1 007(9)

atoms were placed in idealised positions and constrained to ride 1.08 Å from the relevant C atom; the methyl groups were refined as rigid groups. All the H atoms were assigned a common isotropic thermal parameter which refined to 0.10(1) Å^2. The hydride atoms were not located directly and the positions derived from the potential-energy calculations [3] were not included in the refinement. At this stage 11 strong low-angle reflections, which were considered to be suffering severely from extinction, were zero weighted and a weighting scheme of the form $w = [\sigma^2(F) + 0.0003|F|^2]^{-1}$ introduced; this minimised the dependence of $w\Delta^2$ on $|F|$ and sin θ. Refinement continued until the shift/estimated standard deviation (e.s.d.) for any parameter did not exceed 0.03. The final residuals for the 3 084 reflections were $R = 0.039$ and $R' = [\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F|] = 0.038$, and a final difference map showed no regions of significant electron density.

Complex neutral-atom scattering factors were employed throughout.[7] All the computing was performed on the University of Cambridge IBM 370/165 computer, using programs written by Professor G. M. Sheldrick. The atomic fractional co-ordinates for the non-hydrogen atoms are given in Table 2, while lists of thermal parameters, full details of bond parameters, hydrogen-atom co-ordinates, observed and calculated structure factors, and details of least-squares planes have been deposited as Supplementary Publication No. SUP 23306 (31 pp.).*

R. B. A. P. wishes to thank the S.E.R.C. for a Postdoctoral Research Fellowship.

[1/1992 *Received*, 30*th December*, 1981]

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

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