Chemistry of the Metal Carbonyls. Part 80.[1] Diosmiumdiplatinum Carbonyl Complexes derived from Tetracarbonyldihydrido-osmium. *X*-Ray Crystal Structure of $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$*

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The complexes $[Pt(C_2H_4)_2(PR_3)]$ react at room temperature with $[OsH_2(CO)_4]$ in light petroleum to give diosmiumdiplatinum compounds $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PR_3)_2]$ (R = Ph, cyclo-C_6H_{11}, or Me), the spectroscopic properties of which are reported. The molecular structure of the triphenylphosphine derivative was established by an *X*-ray diffraction study. The four metal atoms form a ' butterfly ' cluster with the two osmium atoms at the ' hinge ' (Os–Os = 2.781$_4$ Å) and the two platinum atoms at the ' wingtips ' (Pt $\cdots$ Pt = 3.206$_0$ Å). The molecule has two-fold rotational symmetry crystallographically imposed, the two Os–Pt distances being 2.862$_9$ and 2.708$_9$ Å; the longer bonds are hydrido-bridged. The platinum atoms each carry one carbonyl group and a triphenylphosphine ligand. Crystals of $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ are monoclinic, a = 15.488(4), b = 12.949(3), c = 21.364(5) Å, β = 93.71(2)°, space group $C2/c$. The structure was solved by heavy-atom methods and has been refined to R 0.031 (R' 0.028) for 4 192 reflections.

THE sub-group 8 metals readily form mixed-metal clusters with carbonyl, tertiary phosphine, or tertiary phosphite ligands.[2] An early synthetic route to several platinum–iron and –ruthenium species [3,4] involved reactions of the Malatesta and Cenini [5] compounds $[Pt(PR_3)_n]$ (n = 3 or 4) with $[Fe(CO)_5]$ or $[Ru_3(CO)_{12}]$. However, extension of this method to $[Os_3(CO)_{12}]$ failed to give complexes with platinum–osmium bonds.[4] Instead, the stability of the metal–metal bonds in $[Os_3(CO)_{12}]$, coupled with the ready dissociation of PR_3 groups from the platinum reagents, led to the preferential formation of phosphine derivatives of dodecacarbonyltriosmium, $[Os_3(CO)_{12-n}(PR_3)_n]$ (n = 1 or 2). Nevertheless, by employing the mononuclear osmium complex $[OsH_2(CO)_4]$ in reactions with the two platinum reagents $[Pt(PMePh_2)_4]$ and $[Pt(C_2H_4)(PPh_3)_2]$, it was possible to obtain the mixed-metal complexes $[Os_2Pt_2H_2(CO)_8(PPh_3)_2]$, $[OsPt_2(CO)_5(PPh_3)_3]$, and $[Os_2Pt(CO)_7(PMePh_2)_3]$.[4] However, yields of these mixed-metal compounds were low; the major products were phosphine-substituted mononuclear osmium derivatives, *e.g.* $[OsH_2(CO)_3(PPh_3)]$.

A more favourable route to platinum–osmium compounds became available with the discovery of the complexes $[Pt(C_2H_4)_2(PR_3)]$.[6] The latter readily react with CO to the extent of being able to abstract carbonyl ligands from co-ordinatively saturated compounds, thereby providing a vacant site for occupation by a Pt(CO)(PR_3) group.[1] It thus seemed likely that the species $[Pt(C_2H_4)_2(PR_3)]$ would react with $[OsH_2(CO)_4]$ to give platinum–osmium complexes without the occurrence of side reactions leading to $[OsH_2(CO)_{4-n}(PR_3)_n]$ (n = 1 or 2) observed previously.[4] It was for this reason that the work described in this paper was carried out.[7]

RESULTS AND DISCUSSION

The complexes $[Pt(C_2H_4)_2(PR_3)]$ react readily in light petroleum at room temperature with $[OsH_2(CO)_4]$ to give orange crystalline compounds $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PR_3)_2]$ (1, R = Ph; 2, R = cyclo-C_6H_{11}; 3, R = Me) in good yield. The similarity of the i.r. spectra of all three compounds in the carbonyl region showed that they were of analogous structure. Moreover, the spectrum of (1) was identical with that reported [4] for the compound prepared by reacting $[OsH_2(CO)_4]$ with $[Pt(C_2H_4)(PPh_3)_2]$, but isolated previously in only 8% yield.

The ^1H n.m.r. spectrum of (1) showed, from −50 to 25 °C, a high-field hydrido-ligand signal at τ 17.72. This resonance was a complex doublet of doublets [J(PH) 20 and 2 Hz] displaying second-order effects, with J(PtH) 520 Hz. On warming to 50 °C the resonance collapsed to a triplet, but the coalescence temperature could not be clearly observed. The magnitude (260 Hz) of J(PtH) at higher temperature is consistent with rapid site exchange on the n.m.r. time scale of the hydrido-ligands between two platinum atoms bearing phosphine ligands. The trimethylphosphine derivative (3) was evidently more dynamic since at ambient temperature the ^1H n.m.r. spectrum showed the high-field signal (τ 18.94) as a triplet [J(PH) 10 Hz]. On cooling to −50 °C the same pattern was obtained as observed with (1) at this temperature.

Confirmation that the complexes (1)—(3) contained two equivalent $PtPR_3$ groups came from the ^{31}P n.m.r. spectra which were in essence identical for the three species. The spectrum of compound (2) showed a singlet at −53.3 p.p.m. with two sets of ^{195}Pt satellites [J(PPt) 2 678 and 49 Hz]. Further analysis of the double satellites (molecules with two ^{195}Pt nuclei) yielded values of ^3J(PP) 0 and ^1J(PtPt) 1 542 Hz. The complexes were not sufficiently soluble to obtain satisfactory ^{13}C n.m.r. spectra.

It thus appeared from the spectroscopic data that compounds (1)—(3) were probably osmium analogues of the iron compound $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$.[1] In order to establish whether this was true a single-crystal *X*-ray diffraction study was carried out on complex (1).

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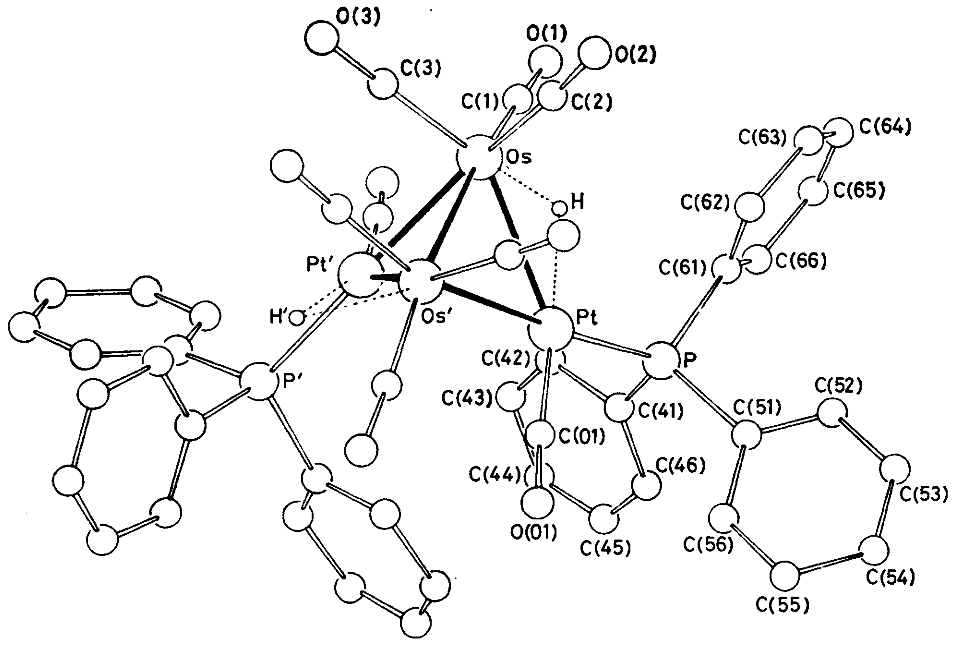
* 1,2,2,2,3,4,4,4-Octacarbonyl-1,2; 3,4-di-μ-hydrido-1,3-bis(tri-phenylphosphine)-*tetrahedro*-diplatinumdiosmium (4*Pt–Os*)-(*Os–Os*).



Molecular structure of the complex $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$, (1)

The results of this study are summarised in Tables 1 and 2, and the molecular structure is shown in the Figure, together with the atomic numbering scheme.

The molecular structure of (1) is indeed closely similar to that of $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$,[1] with the platinum atoms forming the wing-tips of a ' butterfly ', each Pt atom carrying one CO and one PPh_3 ligand. However, the compounds are not isostructural since complex (1) crystallises in the space group *C*2/*c* while that for the di-iron compound is $P2_1/c$. Molecules of (1) lie across a crystallographic two-fold axis, whereas in the iron compound there is an approximate two-fold axis but it is not a crystallographically defined one. Overall, however, the structures of the two compounds are alike except in the relative orientations of the phenyl rings of the phosphine ligands.*

TABLE 1

Atomic positional parameters (fractional co-ordinates) with estimated standard deviations in parentheses for complex (1)

Atom	*x*	*y*	*z*
Pt	−0.059 55(2)	0.206 11(2)	0.185 75(1)
Os	−0.078 30(2)	0.066 63(2)	0.221 61(1)
C(01)	−0.168 6(6)	0.247 7(6)	0.205 2(4)
O(01)	−0.238 1(4)	0.274 6(5)	0.215 0(3)
C(1)	0.183 0(6)	0.108 0(6)	0.184 4(4)
O(1)	0.244 0(4)	0.129 3(5)	0.161 1(3)
C(2)	0.053 7(5)	−0.046 6(6)	0.166 3(4)
O(2)	0.040 8(4)	−0.115 1(4)	0.134 2(3)
C(3)	0.130 1(6)	−0.019 5(6)	0.286 5(4)
O(3)	0.162 2(4)	−0.069 2(5)	0.324 8(3)
P	−0.033 66(12)	0.321 68(13)	0.106 14(8)
C(41)	0.012 0(5)	0.441 3(5)	0.139 6(3)
C(42)	0.082 4(5)	0.432 9(6)	0.182 3(4)
C(43)	0.119 9(6)	0.521 1(8)	0.211 5(4)
C(44)	0.083 9(6)	0.616 8(7)	0.197 9(4)
C(45)	0.013 9(6)	0.625 9(6)	0.154 9(4)
C(46)	−0.023 7(5)	0.538 1(5)	0.125 1(4)
C(51)	−0.126 7(5)	0.360 0(5)	0.054 4(3)
C(52)	−0.129 0(5)	0.343 6(6)	−0.010 4(3)
C(53)	−0.201 6(5)	0.365 5(6)	−0.048 7(4)
C(54)	−0.273 5(5)	0.408 9(6)	−0.022 9(3)
C(55)	−0.272 1(5)	0.427 1(6)	0.041 6(3)
C(56)	−0.200 8(5)	0.401 7(6)	0.079 5(4)
C(61)	0.043 6(5)	0.277 4(5)	0.051 3(3)
C(62)	0.037 7(5)	0.175 5(6)	0.030 9(4)
C(63)	0.089 6(6)	0.142 4(6)	−0.016 0(4)
C(64)	0.146 2(6)	0.208 1(7)	−0.041 5(4)
C(65)	0.153 9(5)	0.309 6(6)	−0.020 7(4)
C(66)	0.102 5(5)	0.343 8(6)	0.025 2(3)

There is good evidence that the hydrido-ligands bridge the Pt–Os and Pt'–Os' edges of the cluster. Thus these edges are *ca.* 0.15 Å longer than the other pair of osmium–platinum separations. Moreover, the longer Pt–Os (Pt'–Os') distance is associated with a widening of the *cis* angles C(1)–Os–Pt and C(2)–Os–Pt (Table 2), while a projection of the molecule onto the Pt·Os'·Pt' plane reveals that the CO ligands on Os are staggered relative to the M–M vectors.[8,9] Further evidence for location of the hydrido-ligands on the two Pt–Os (Pt'–Os') edges comes from Fourier synthesis of residual electron density, and from calculations[10] based on potential-energy minima. It is interesting that the relatively low chemical shift (τ 17.72) for the hydrido-protons in (1) is similar to that found in other compounds containing Os(μ-H)Pt groups.[11]

The Pt–Pt' separation [3.206(1) Å] is *ca.* 0.2 Å longer than that measured in $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$.[4] Presumably this is due to the general expansion of the cluster by the incorporation of the larger osmium atoms in place of iron. The greater Pt–Pt' separation is also reflected in a larger ' butterfly ' angle of 82.9°, compared

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* The orientations of the phenyl rings in the phosphine ligands are most readily characterised by the angle between the plane of the ring and the plane defined by Pt–P–C(1). For the three rings C(41)—(46), C(51)—(56), and C(61)—(66) these are 52, 57, and 41°, respectively.

TABLE 2

Important interatomic distances (Å) and bond angles (°) for $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$, (1), with estimated standard deviations in parentheses

(*a*) Distances			
Pt–Pt′	3.206 0(10)	C(01)–O(01)	1.16(1)
Pt–Os	2.862 8(7)	C(1)–O(1)	1.13(1)
Pt–Os′	2.708 9(6)	C(2)–O(2)	1.13(1)
Os–Os′	2.781 3(9)	C(3)–O(3)	1.13(1)
Pt–C(01)	1.843(9)	Pt–P	2.320(2)
Os–C(1)	1.926(9)	P–C(41)	1.829(7)
Os–C(2)	1.905(8)	P–C(51)	1.827(7)
Os–C(3)	1.913(8)	P–C(61)	1.821(7)
(*b*) Angles			
Os–Pt–Os′	59.82(1)	Pt–C(01)–O(01)	177.5(7)
Os′–Pt–Pt′	57.15(1)	Os–C(1)–O(1)	177.5(7)
Pt–Os–Os′	57.34(2)	Os–C(2)–O(2)	178.4(7)
Os–Pt–Pt′	52.64(1)	Os–C(3)–O(3)	178.5(8)
Pt–Os–Pt′	70.21(2)	Pt–P–C(41)	109.9(2)
Pt′–Os–Os′	62.84(1)	Pt–P–C(51)	116.9(2)
Pt′–Os–C(3)	85.4(2)	Pt–P–C(61)	114.9(2)
Os′–Os–C(3)	91.2(3)	C(41)–P–C(51)	106.1(3)
Os′–Pt–C(01)	83.6(2)	C(41)–P–C(61)	105.3(3)
Pt′–Pt–C(01)	106.8(3)	C(51)–P–C(61)	102.8(3)
Pt–Os–C(1)	110.3(2)		
Pt′–Os–C(1)	104.4(2)		
Pt–Os–C(2)	101.8(2)		
Os′–Os–C(2)	97.3(2)		
Dihedral angles			
Os–Pt′–Pt–Os′	74.9	Pt–Pt′–Os–Os′	62.6
Pt–Pt′–Os′–Os	69.8	Pt–Os′–Os–Pt′	82.9

with 80.1° in the iron complex, and 70.5° for a regular tetrahedron. The presence of two platinum atoms evidently allows this 58-electron complex to exist with a butterfly geometry for the four metal atoms so that there is no direct Pt–Pt bond.[12] The osmium–osmium distance in (1) [2.781(1) Å] compares closely with the corresponding bond [2.773(1) Å] in $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$, which also adopts a butterfly structure.[11] The Pt–P distance in the latter molecule is essentially the same as that in (1). The co-ordination of one PPh_3 group to each platinum is as expected from the ^{31}P n.m.r. spectrum discussed earlier, and from the synthesis of the compound from $[Pt(C_2H_4)_2(PPh_3)]$. Evidently in the original low yield synthesis of (1) from $[Pt(C_2H_4)(PPh_3)_2]$, a PPh_3 ligand is displaced from platinum by CO so that $Pt(CO)(PPh_3)$ groups are present in the final product. This type of behaviour has been observed recently in the synthesis of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$ from $[Os_3(\mu\text{-}H)_2(CO)_{10}]$ and $[Pt(C_2H_4)(PPh_3)_2]$,[11] and in the preparation of $[Rh_2Pt(\mu\text{-}CO)_2(CO)(PPh_3)(\eta\text{-}C_5Me_5)_2]$ from $[Rh_2(\mu\text{-}CO)_2(\eta\text{-}C_5Me_5)_2]$ and $[Pt(C_2H_4)(PPh_3)_2]$.[13] The preparation of compounds (1)—(3) using the species $[Pt(C_2H_4)_2(PR_3)]$ provides a further example of the ability of these reagents to remove CO from a co-ordinatively saturated metal carbonyl complex to afford mixed-metal complexes in good yield.

EXPERIMENTAL

Nuclear magnetic resonance spectra were recorded on JEOL PFT and PS 100 spectrometers, with ^{31}P shifts relative to H_3PO_4 (external) taken as positive to low frequency (high field). Spectra of compounds (1) and (3) were measured in [$^2H_1$]chloroform, that of (2) in [$^2H_6$]benzene. Infrared spectra were measured in cyclohexane and obtained with a Perkin-Elmer 257 spectrophotometer. Syntheses were carried out under dry oxygen-free nitrogen in Schlenk tubes. Light petroleum refers to that fraction of b.p. 40—60 °C. The complexes $[OsH_2(CO)_4]$ [14] and $[Pt(C_2H_4)_2(PR_3)]$ [6] were made by methods described previously.

Synthesis of the Diosmiumdiplatinum Complexes.—(*a*) To a stirred suspension of $[Pt(C_2H_4)_2(PPh_3)]$ (0.26 g, 0.5 mmol) in light petroleum (40 cm^3) was added $[OsH_2(CO)_4]$ (0.15 g, 0.5 mmol) in hexane (5 cm^3). The solution quickly turned orange and a precipitate formed. Volatile material was removed *in vacuo* and the residue dissolved in toluene (5 cm^3) and chromatographed on alumina. Elution with toluene gave a bright yellow band which afforded yellow *crystals* of $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$, (1) (0.2 g, 52%) (Found: C, 34.8; H, 2.2. $C_{44}H_{32}O_8Os_2P_2Pt_2$ requires C, 34.8; H, 2.1%), from diethyl ether, m.p. 185—189 °C (decomp.), $\nu_{max.}$ (CO) at 2 059s, 2 031vs, 2 011w, 1 981s, 1 963w, and 1 943m cm^{-1}. N.m.r.: ^1H, τ 2.68—2.78 (m, 30 H, Ph) and 17.72 [d of d, 2 H, Os(μ-H)Pt, *J*(PH) 20 and 2, *J*(PtH) 520 Hz]; ^{31}P (^1H-decoupled), δ −33.8 p.p.m. [s, PPt, *J*(PP) 0, *J*(PtP) 2 741 and 58, *J*(PtPt) 1 744 Hz].

(*b*) In a similar manner, $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ (0.55 g, 1 mmol) and $[OsH_2(CO)_4]$ (0.3 g, 1 mmol) afforded yellow *crystals* of $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8\{P(C_6H_{11})_3\}_2]$, (2) (0.52 g, 65%) (Found: C, 40.0; H, 4.8. $C_{44}H_{68}O_8Os_2P_2Pt_2$ requires C, 33.9; H, 4.4%), m.p. 255—260 °C (decomp.), $\nu_{max.}$ (CO) at 2 063w (sh), 2 053m, 2 023vs, 2 011 (sh), 1 989w, 1 977s, 1 955w, 1 943m, and 1 935m cm^{-1}. N.m.r.: ^1H, τ 8.32—8.83 (m br, 66 H, C_6H_{11}) and 18.29 [d, 2 H, Os(μ-H)Pt, *J*(PH) 18, *J*(PtH) 515 Hz]; ^{31}P (^1H-decoupled), δ −53.3 p.p.m. [s, PPt, *J*(PP) 0, *J*(PtP) 2 678 and 49, *J*(PtPt) 1 542 Hz].

(*c*) In an analogous manner, $[Pt(C_2H_4)_2(PMe_3)]$ (0.33 g, 1 mmol) and $[OsH_2(CO)_4]$ (0.3 g, 1 mmol) gave orange *crystals* of $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PMe_3)_2]$, (3) (0.22 g, 40%) (Found: C, 14.7; H, 1.6. $C_{14}H_{20}O_8Os_2P_2Pt_2$ requires C, 14.6; H, 1.7%), m.p. 164—168 °C (decomp.) $\nu_{max.}$ (CO) 2 057m, 2 027vs, 2 019 (sh), 1 993w, 1 983m, 1 961w, 1 947w (sh), and 1 939m cm^{-1}. N.m.r.: ^1H (−50 °C), τ 8.34 [d, 18 H, Me, *J*(PH) 10, *J*(PtH) 30] and 18.37 [d, 2 H, Os(μ-H)Pt, *J*(PH) 20, *J*(PtH) 533 Hz]; ^{31}P (^1H-decoupled), δ −1.4 p.p.m. [s, PPt, *J*(PP) 0, *J*(PtP) 2 562 and 71 Hz].

Crystal-structure Determination of $[Os_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$.—Crystals of (1) grow as yellow rhombs from toluene. Diffracted intensities were collected from a crystal of dimensions 0.15 × 0.10 × 0.17 mm at 200 K, according to methods described earlier.[15,16] Of the total 4 912 independent intensities recorded to $2\theta = 60°$, 4 192 had $I > 2.0\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics, and these were used in the solution and refinement of the structure. All computations were carried out with the '*X*-RAY' system of programs [17] on the CDC 7600 computer at the University of London Computing Centre.

Crystal data. $C_{44}H_{32}O_8Os_2P_2Pt_2$, $M = 1\,521$, Monoclinic, $a = 15.488(4)$, $b = 12.949(3)$, $c = 21.364(5)$ Å, $\beta = 93.71(2)°$, $U = 4\,276(4)$ Å^3, $D_m = 2.35$, $Z = 4$, $D_c = 2.37$ g cm^{-3}, $F(000) = 2\,792$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 132.7 cm^{-1}, space group *C*2/*c* (no. 15).

Structure solution and refinement. The metal atom locations were deduced from a Patterson synthesis, and the distribution of platinum and osmium atoms among the four sites was determined by least-squares refinement of thermal parameters. Successive electron-density difference syntheses revealed all other non-hydrogen atoms. The structure was refined by blocked-matrix least squares, with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms for the phosphine ligands were incorporated at calculated positions and were not refined. The suspected locations of the bridging hydride ligands (see main text) coincided with peaks of *ca.* 1.2 e Å^{-3} on the final electron-density difference maps, although there were peaks of somewhat similar height elsewhere. Refinement converged at R 0.031 (R' 0.028), and a satisfactory weighting analysis was obtained by use of $w = 1/\sigma^2(F)$. The original intensity data were corrected for Lorentz, polarisation, and X-ray absorption effects. Atomic scattering factors were from refs. 18, 19, and 20 with corrections for anomalous dispersion for Pt, Os, and P. Positional parameters are in Table 1, interatomic distances and bond angles in Table 2. Observed and calculated structure factors, hydrogen atom co-ordinates, and all thermal parameters are in Supplementary Publication No. SUP 23040 (19 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

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