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Covalently linked anthracene-containing supramolecular complexes of triosmium carbonyl clusters: synthesis, crystal structures and solvatochromic behaviour

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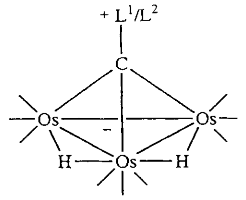
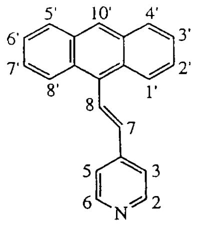
Three novel anthracene-containing supramolecules $[Os_3(\mu-H)_2(CO)_9(\mu_3-CNC_5H_4CHCHC_{14}H_9)]$ **1**, $[Os_3(\mu-H)_2(CO)_9(\mu_3-CNC_5H_4CH_2CH_2C_{14}H_9)]$ **2** and $[Os_3(\mu-H)(CO)_{10}(\mu-NC_5H_3CHCHC_{14}H_9)]$ **3** ($C_{14}H_{10}$ = anthracene) have been synthesised and the crystal structures of **2** and **3** determined; UV/VIS spectroscopic studies indicated a significant metal–anthracene interaction in the ground state *via* the conjugated ligand group in **1**.

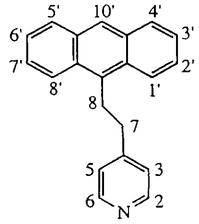
Supramolecular systems incorporating electronically coupled photo- and/or redox-active sites have attracted great interest as molecular assemblies for intramolecular energy- or electron-transfer processes.[1] Recently, we have reported a series of covalently linked metallosupramolecular cluster complexes bearing redox-active ferrocenyl chromophores which show significant electronic communication between the ferrocenyl moiety and the metal cluster core.[2] However, related systems possessing photoactive substituents are, to our knowledge, unknown. We therefore sought to design a new supramolecular cluster system featuring these characteristics. In this respect, anthracene-containing molecules serve as good candidates as anthracene has long been recognised for its intriguing photophysical properties and is a representative chromophore in organic energy-transfer processes.[3] It has also proved to be an important luminescence probe in fundamental studies of energy transfer in organised media.[4] Herein is described a convenient entry into a new class of supramolecules consisting of triosmium cluster moieties covalently appended to an anthracene subunit. We have chosen the anthracene derivatives 4-[2-(9-anthryl)vinyl]pyridine (L^1) and 4-[2-(9-anthryl)ethyl]-pyridine (L^2) as the auxiliary ligands on the basis of the well documented reactions of substituted pyridines with triosmium cluster complexes.[5]

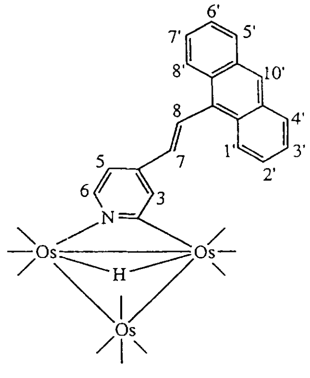


1 L^1 =



2 L^1 =





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Results and Discussion

The two anthracene-substituted pyridyl ligands L^1 and L^2 were prepared by the literature methods.[6] Treatment of $[Os_3(\mu-H)_3(CO)_9(\mu_3-CCl)]$ with 1 equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) in the presence of a 10-fold excess of L^1 or L^2 in CH_2Cl_2 for 15 min affords the complexes **1** and **2** respectively in high yields (> 55%).[2,7] Complex **3** was prepared by addition of 1 equivalent of the ligand L^1 to the precursor complex $[Os_3(CO)_{10}(NCMe)_2]$ in refluxing CH_2Cl_2 for 2 h.[5] The compounds **1**–**3** were isolated as air-stable solids (deep red **1**, orange **2**, yellow **3**) upon TLC purification. They all gave satisfactory elemental analyses and have been characterised by IR, ^1H NMR and FAB mass spectroscopies, see Table 1. The solid-state structures of **2** and **3** have been established by X-ray crystallography.

Single crystals of both compounds **2** and **3** suitable for X-ray analysis were grown by slow evaporation of their respective solutions in cyclohexane–$CHCl_3$ at room temperature. Fig. 1 shows a perspective view of **2** and some selected bond parameters are presented in Table 2. The structure consists of a dihydrido-bridged triosmium alkylidyne metal core with the ligand L^2 directly co-ordinated to the apical carbon atom. Within the osmium triangle, the two hydride-bridged Os–Os edges (average length 2.885 Å) are significantly longer than the Os(1)–Os(3) bond [2.7781(9) Å]. The metal-alkylidyne carbon bond lengths (average 2.10 Å) are essentially equivalent and are typical of those found in other alkylidyne clusters.[7] Each

Table 1 Spectroscopic data for complexes **1–3**

Compound	IR, $\tilde{\nu}(\mathrm{CO})^a/\mathrm{cm}^{-1}$	^{1}H NMR, $\delta(J/\mathrm{Hz})^b$	Mass spectrum, m/z^c
1	2089m, 2045vs, 2023vs, 1981s, 1949m, 1933m	9.52 (d, 2 H, J = 6.8, $\mathrm{H}^{2,6}$), 8.51 (d, 1 H, J = 16.4 H^{7}), 8.48 (s, 1 H, $\mathrm{H}^{10'}$), 8.19 (d, 2 H, J = 8.3, $\mathrm{H}^{1',8'}$), 8.00 (m, 2 H, $\mathrm{H}^{4',5'}$), 7.55 (d, 2 H, J = 6.8, $\mathrm{H}^{3,5}$), 7.47 (m, 4 H, $\mathrm{H}^{2',3',6',7'}$), 6.96 (d, 1 H, J = 16.4, H^{8}), −18.97 (s, 2 H, OsH)	1119 (1119)
2	2089m, 2053vs, 2022vs, 1981s, 1949m, 1933m	9.28 (d, 2 H, J = 6.8, $\mathrm{H}^{2,6}$), 8.36 (s, 1 H, $\mathrm{H}^{10'}$), 8.05 (m, 2 H, $\mathrm{H}^{1',8'}$), 7.96 (m, 2 H, $\mathrm{H}^{4',5'}$), 7.41 (m, 4 H, $\mathrm{H}^{2',3',6',7'}$), 7.06 (d, 2 H, J = 6.8, $\mathrm{H}^{3,5}$), 3.98 (t, 2 H, J = 8.1, H^{8}), 3.11 (t, 2 H, J = 8.1, H^{7}), −19.13 (s, 2 H, OsH)	1121 (1121)
3	2104m, 2063vs, 2053vs, 2022vs, 2010vs, 2003s, 1991s, 1976w	8.49 (s, 1 H, $\mathrm{H}^{10'}$), 8.27–8.19 [m, 4 H, $\mathrm{H}^{1'8',6,7}$), 8.06 (m, 2 H, $\mathrm{H}^{4',5'}$), 7.54–7.50 (m, 5 H, $\mathrm{H}^{2',3',6',7',3}$), 7.05 (dd, 1 H, J = 5.9, 2.0, H^{5}), 6.78 (d, 1 H, J = 16.5, H^{8}), −14.75 (s, 1 H, OsH)	1133 (1133)

[a] In CH_2Cl_2 for complexes **1**, **2**, in hexane for **3**. [b] In C_6D_6. [c] Simulated values given in parentheses.

Table 2 Selected bond distances (Å) and angles (°) for compound **2**

Os(1)–Os(2)	2.8805(7)	Os(3)–C(10)	2.07(1)
Os(1)–Os(3)	2.7781(9)	N–C(10)	1.47(1)
Os(2)–Os(3)	2.8890(8)	C(13)–C(16)	1.51(2)
Os(1)–C(10)	2.08(1)	C(16)–C(17)	1.54(2)
Os(2)–C(10)	2.13(1)	C(17)–C(18)	1.52(2)
Os(2)–Os(1)–Os(3)	61.37(2)	Os(2)–C(10)–N	120.9(7)
Os(1)–Os(2)–Os(3)	57.57(2)	Os(3)–C(10)–N	132.6(7)
Os(1)–Os(3)–Os(2)	61.06(2)	C(13)–C(16)–C(17)	113.0(10)
Os(1)–C(10)–N	130.9(8)	C(16)–C(17)–C(18)	113.2(10)

Table 3 Selected bond distances (Å) and angles (°) for compound **3**

Os(1)–Os(2)	2.866(1)	N–C(11)	1.42(2)
Os(1)–Os(3)	2.882(2)	C(13)–C(16)	1.43(3)
Os(2)–Os(3)	2.922(1)	C(16)–C(17)	1.33(4)
Os(2)–N	2.10(2)	C(17)–C(18)	1.47(3)
Os(3)–C(11)	2.11(2)		
Os(2)–Os(1)–Os(3)	61.11(3)	Os(2)–N–C(11)	111(1)
Os(1)–Os(2)–Os(3)	59.72(3)	Os(3)–C(11)–N	110(1)
Os(1)–Os(3)–Os(2)	59.16(3)	C(13)–C(16)–C(17)	131(2)
Os(2)–Os(3)–C(11)	69.1(6)	C(16)–C(17)–C(18)	125(2)
Os(3)–Os(2)–N	69.3(5)		

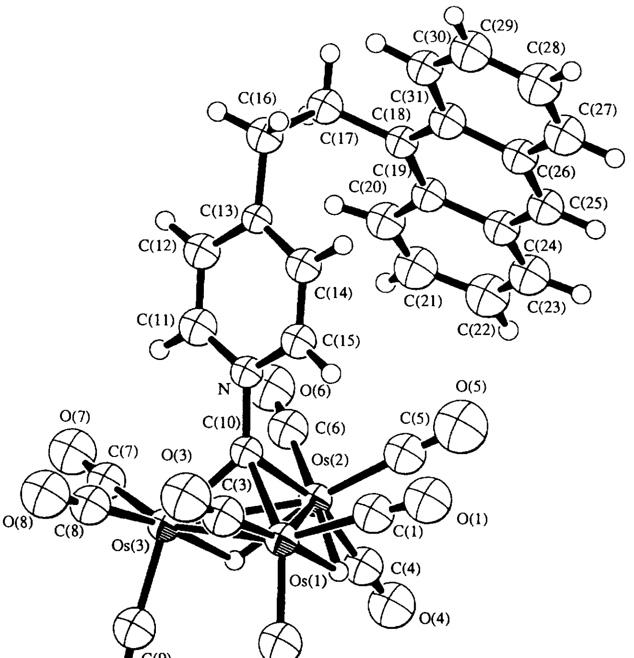

Fig. 1 Molecular structure of compound **2** showing the atomic numbering scheme

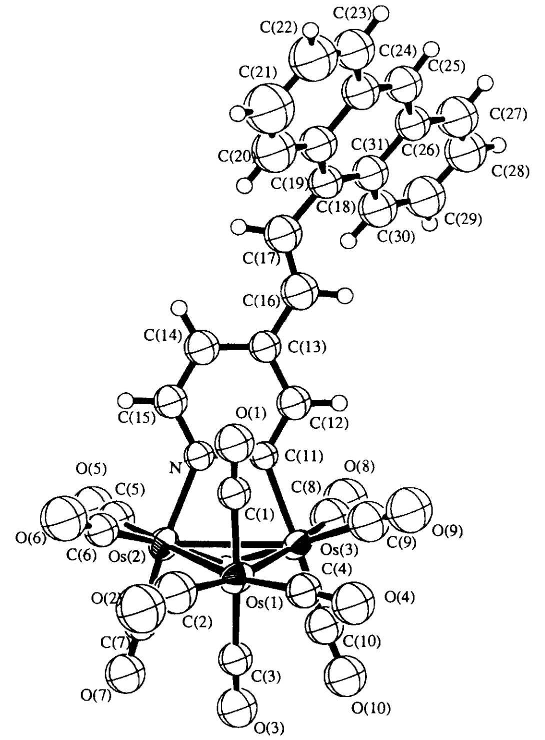

Fig. 2 Molecular structure of compound **3** showing the atomic numbering scheme

osmium atom is co-ordinated to three terminal carbonyl ligands. The bond C(16)–C(17) is a single bond [1.54(2) Å]. The anthryl group is found to bend at C(17) towards the metal core with the torsion angle of the fragment C(13)–C(16)–C(17)–C(18) being 55°. However, there is no intermolecular stacking interaction between individual anthracene units in the crystal lattice of **2**.

The molecular structure of compound **3** is depicted in Fig. 2 and some important bond parameters are given in Table 3. It reveals that the pyridyl ring of L^1 is orthometallated and bridges the edge Os(2)–Os(3) of the Os_3 triangle to afford a four-membered ring containing Os(2), Os(3), C(11) and N. The four-membered osmacycle makes dihedral angles of 79.9 and 2.7° with the metal triangle and pyridyl plane respectively. The length of the Os–Os edge that is bridged by the hydride and pyridyl ring is longer [Os(2)–Os(3) 2.922(1) Å] than the two non-bridged Os–Os bonds. There are ten carbonyl ligands terminally bound to the osmium atoms. The fragment C(16)–C(17) is nearly coplanar with the pyridyl plane with a mean deviation from the plane of 0.022 Å. The bond C(16)–C(17) is 1.33(4) Å long and slight shortenings of the

Table 4 Electronic absorption spectral data for complexes **1**–**3** and their corresponding ligands L[1] and L[2]

	λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})			
Compound	C_6H_{14}	$CHCl_3$	CH_2Cl_2	Me_2CO
L[1]			372 (sh) (9.28)	
			392 (9.93)	
L[2]			336 (6.14)	
			352 (10.26)	
			370 (10.78)	
			390 (9.80)	
1	478*	474 (10.41)	468 (11.28)	464 (10.00)
	584	558 (10.64)	544 (11.87)	506 (10.61)
2	352 (7.57)	354 (9.96)	334 (9.65)	330 (9.47)
	370 (9.20)	372 (11.77)	352 (10.40)	352 (9.85)
	390 (8.53)	392 (10.88)	372 (12.51)	370 (11.65)
	514 (5.67)	492 (6.50)	392 (11.84)	390 (11.24)
			482 (6.77)	456 (5.94)
3	404 (10.46)	402 (10.97)	402 (11.16)	396 (8.21)

* Limited solubility for accurate determination of ε values.

bonds C(13)–C(16) and C(17)–C(18) are observed [1.43(3) and 1.47(3) Å respectively] consistent with a partial conjugation effect. As in **2**, X-ray analysis suggests no molecular stacking in the solid state.

From a supramolecular point of view, the most striking structural feature of compounds **2** and **3** is that an appropriate cluster-type chromophore {*i.e.* [$Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_5)$] for **2** and [$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NC_5H_4)$] for **3**} is covalently linked to an anthracene moiety *via* a suitable organic spacer. In **2** the bridge is fully saturated and sufficiently flexible to allow a considerable conformational freedom. Co-ordination complexes of this type have been previously reported by others and their importance has been demonstrated.[8] However, to our knowledge, there is only one structurally characterised example of such an anthracene-based complex in the literature.[6]

Table 4 summarises data for the electronic absorption spectra in the range 300–700 nm for compounds **1**–**3** together with data for the corresponding anthryl ligands L[1] and L[2] in CH_2Cl_2. The UV/VIS absorption spectra of L[2] and **2** in CH_2Cl_2 display similar structured intense bands in the near UV (*ca.* 330–390 nm) which arise from anthracene-localised $\pi \longrightarrow \pi^*$ transitions of L[2].[9] Comparison of their electronic spectra reveals no significantly ground-state interaction between the anthryl moiety and the Os_3C core *via* the saturated CH_2CH_2 unit in **2**. Complex **2** also exhibits an intense low-energy absorption feature in the visible region, which is tentatively assigned to a metal-to-ligand charge-transfer (m.l.c.t.) transition. The m.l.c.t. nature of this transition has been confirmed by solvatochromic studies. The red shift in absorption energies from acetone (λ 456 nm) to hexane (λ 514 nm) in order of decreasing polarity is in accordance with the charge-transfer nature of the transition[10] and the zwitterionic formulation of the species in the ground state.[2,7] The assignment is supported by the results of Fenske–Hall molecular orbital calculations in which the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) are primarily metal- and ligand-based respectively.[7a,11] As a consequence, the ground state of the molecule is found to be stabilised to a greater extent than the excited state by polar solvents. Obviously, the absorption spectrum of **2** is essentially an overlay of those exhibited by L[2] and the cluster [$Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4Et)$].[12]

For compound **3** a strong featureless absorption band at around 400 nm was observed. An intraligand $\pi \longrightarrow \pi^*$ state is suggested as an analogous band was observed in the absorption spectrum of free L[1] under the same conditions. As shown in Table 4, no evidence of solvatochromic shift was detected for **3**. Apart from the $\pi \longrightarrow \pi^*$ transition, there seems no indication of low-energy bands attributable to either l.m.c.t. (ligand-to-metal charge transfer) or m.l.c.t. transitions.

The absorption spectrum of compound **1** is dominated by two intense low-energy absorption bands beyond 400 nm. The bands at *ca.* 460–480 and 505–585 nm in various solvents are ascribed to the metal-perturbed intraligand $\pi \longrightarrow \pi^*$ transition of L[1] and the m.l.c.t. transition respectively. Similar to **2**, complex **1** shows strong negative solvatochromic shifts for the m.l.c.t. bands and the demonstration of such a solvent dependency of electronic absorptions is again consistent with its zwitterionic formulation. However, a red shift in the intraligand $\pi \longrightarrow \pi^*$ transition energy was observed which is not very much affected by the solvents. This indicates the possibility of electronic communication between the appended anthryl substituent and the Os_3C core through the conjugated CH=CH group in **1**. It is therefore envisaged that **1** may provide an entry into a new class of donor–acceptor supramolecules for studies of intramolecular photoinduced energy- and electron-transfer reactions.

Experimental

None of the compounds reported here is particularly air-sensitive, however all reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques and were monitored by solution IR spectroscopy (CO stretching region). Dichloromethane was dried over CaH_2 and hexane was distilled from sodium–benzophenone in the presence of 2,5,8,11,14-pentaoxapentadecane (tetraglyme). The starting clusters [$Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)$],[13] [$Os_3(CO)_{10}(NCMe)_2$][14] and compounds L[1] and L[2] were prepared according to established methods.[6] Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer using 0.5 mm solution cells, ^1H NMR spectra on a JEOL GSX 270FT-NMR spectrometer [$SiMe_4$(δ 0)] and mass spectra on a Finnigan MAT 95 instrument with the fast atom bombardment technique. Routine separations of products were performed in the air by thin-layer chromatography with plates coated with Merck Kieselgel 60 GF_{254}.

Syntheses

[$Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4CHCHC_{14}H_9)$] 1. The complex [$Os_3(\mu\text{-}H)_3(CO)_9(\mu\text{-}CCl)$] (87.3 mg, 0.10 mmol) and compound L[1] (0.281 g, 1.0 mmol) were dissolved in CH_2Cl_2 (25 cm^3). Dropwise addition of a dbu–CH_2Cl_2 solution (0.10 mmol) gave an orange solution. The mixture was stirred at room temperature for 50 min and subsequently evaporated to dryness under vacuum. The residue was purified by TLC using hexane–acetone (70:30, v/v) as eluent. Complex **1** was isolated as an deep red solid (R_f = 0.35) in 60% yield (67 mg) (Found: C, 33.35; H, 1.50; N, 1.30. Calc. for $C_{31}H_{17}NO_9Os_3$: C, 33.30; H, 1.50; N, 1.25%).

[$Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4CH_2CH_2C_{14}H_9)$] 2. The cluster [$Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)$] (87.3 mg, 0.10 mmol) and compound L[2] (0.283 g, 1.0 mmol) in CH_2Cl_2 (25 cm^3) were stirred while a dbu–CH_2Cl_2 solution (0.10 mmol) was added dropwise. The mixture turned red immediately. After stirring for 30 min the volume was reduced to 3 cm^3. Purification was accomplished by TLC using hexane–CH_2Cl_2 (50:50, v/v) as eluent to afford complex **2** (R_f = 0.20) in 55% yield (61 mg) (Found: C, 33.45; H, 1.60; N, 1.15. Calc. for $C_{31}H_{19}NO_9Os_3$: C, 33.25; H, 1.70; N, 1.25%).

[$Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}CNC_5H_3CHCHC_{14}H_9)$] 3. The cluster [$Os_3(CO)_{10}(NCMe)_2$] (93.8 mg, 0.10 mmol) and compound L[1] (85.0 mg, 0.3 mmol) in CH_2Cl_2 (50 cm^3) were stirred for 2 h. Then the volume was reduced to 3 cm^3. Purification was accomplished by TLC using hexane–CH_2Cl_2 (50:50, v/v) as eluent to afford complex **3** (R_f = 0.55) in 65% yield (74 mg)

Table 5 Crystal data and data-collection parameters for compounds **2** and **3** *

Compound	**2**	**3**·$CHCl_3$
Formula	$C_{31}H_{19}NO_9Os_3$	$C_{32}H_{16}Cl_3NO_{10}Os_3$
Formula weight	1120.09	1251.44
Colour, habit	Orange block	Yellow block
Crystal dimensions/mm	0.18 × 0.24 × 0.40	0.16 × 0.38 × 0.44
Space group	$P2_1/n$ (no. 14)	$P2_1/a$ (no. 14)
a/Å	8.209(2)	18.600(3)
b/Å	14.784(1)	10.046(1)
c/Å	25.686(3)	19.881(3)
β/°	97.57(2)	105.16(2)
U/Å^3	3090.2(9)	3585.6(9)
D_c/g cm^{-3}	2.407	2.318
μ(Mo-Kα)/cm^{-1}	123.52	108.76
F(000)	2048	2296
Scan rate in ω/° min^{-1}	16.0 up to 4 scans	1.08–16.48
Scan range/°	0.58 + 0.34 tan θ	0.55 + 0.34 tan θ
Reflections collected	4780	5171
Unique reflections	4358	5083
Observed reflections [$I > 3\sigma(I)$]	3063	3419
Transmission factors	0.6948–1.0000	0.1771–1.0000
Weighting scheme g in $w = 4F_o^2/[\sigma^2(F_o^2) + gF_o^2]^2$	0.009	0.004
R	0.030	0.067
R'	0.032	0.065
Residual electron density (close to Os)/e Å^{-3}	0.96, −0.76	1.85, −2.50

* Details in common: monoclinic; $Z = 4$; data collection range 2θ 4–45 °.

(Found: C, 33.00; H, 1.30; N, 1.10. Calc. for $C_{31}H_{15}NO_{10}Os_3$: C, 32.90; H, 1.35; N, 1.25%).

Crystallography

Suitable crystals of compounds **2** and **3** for X-ray analysis were mounted on a glass fibre using epoxy resin. The crystal data and refinement are summarised in Table 5. Intensity data were collected at 298 K on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) using the ω–2θ scan method. The stability of the crystals was monitored at regular intervals using three standard reflections and no significant variation was observed. Intensity data were corrected for Lorentz and polarisation effects and semi-empirical absorption corrections (ψ-scan method) were also applied.[15] The structures were solved by a combination of direct methods (SIR 88)[16] and Fourier-difference techniques and refined on F by full-matrix least-squares analysis. The hydrogen atoms of the organic moieties were placed in their idealised positions (C–H 0.95 Å), while all metal hydrides were estimated by potential-energy calculations.[17] All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.[18]

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 its full literature citation and the reference number 186/4.

Acknowledgements

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