New Thiosulfato Complexes of Osmium *

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The reactions of the complex $[OsO_2(S_2O_3)_2]^{2-}$ with a variety of inorganic and organic ligands have been studied and the vibrational spectra and structures of the resulting compounds are discussed. They include the new complexes $[OsO_2(S_2O_3)_2L_2]^{2-}$ [L = pyridine (py), 4-*tert*-butylpyridine, ½ 1,10-phenanthroline or *N,N,N',N'*-tetramethylethylenediamine] and $[OsO_2(py)_3(S_2O_3)]$. X-Ray photoelectron data are reported for some of them. The X-ray crystal structure of one of the products, $[NBu^n{}_4][Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]$, reveals an octahedral geometry around the osmium atom with the two *trans* S-bonded thiosulfate ligands adopting a *syn* geometry with respect to each other, each forming a strong hydrogen bond to the axial aqua ligand.

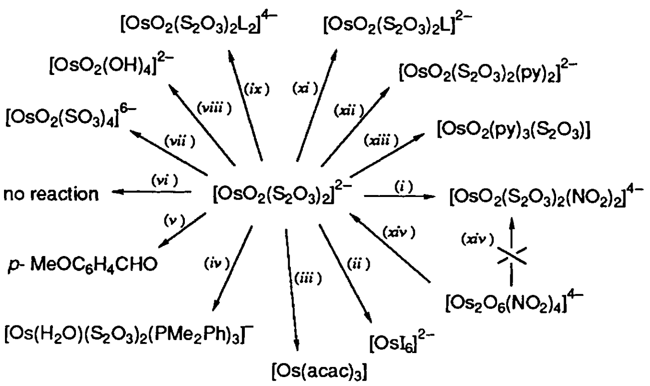
We have earlier reported the preparation and vibrational spectral characteristics of a number of Group 8–10 sulfito ($SO_3{}^{2-}$) complexes.[1] During the course of work on the properties of biologically active osmium complexes we isolated the first thiosulfato complex of osmium, $[NBu^n{}_4]_2[OsO_2(S_2O_3)_2]$ **1**, the X-ray diffraction analysis of which showed the crystal structure to be an unusual one in which the S-bound thiosulfato groups are monodentate and there is tetrahedral co-ordination about osmium.[2] Complex **1** is unusually reactive with both inorganic and organic ligands, and in this paper we report these reactions, most of which lead to new thiosulfato complexes of osmium, and describe the X-ray crystal structure of one of these products, $[NBu^n{}_4][Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]$ **2**.

Results and Discussion

(*a*) *Preparation of* $[OsO_2(S_2O_3)_2]^{2-}$.—The tetrabutylammonium and tetraphenylphosphonium salts of $[OsO_2(S_2O_3)_2]^{2-}$ were prepared by reaction of osmium tetraoxide and sodium thiosulfate in aqueous solution with the addition of excess of cation to precipitate the product. The X-ray crystal structure[2] shows the co-ordination sphere to be distorted tetrahedral [O–Os–O 127.2(2)°, Os=O 1.692(3) Å; S–Os–S 89.2(1)°, Os–S 2.218(1) Å]. Few other *cis* dioxoosmium(VI) complexes have been reported: (dihydroquinine *p*-chlorobenzoate)dioxo(2,2,5,5-tetramethylhexane-3,4-diolato)osmium(VI),[3] (dihydroquinidine *p*-chlorobenzoate)(2,5-dimethylhexane-3,4-diolato)dioxoosmium(VI),[3] $K[OsO_2(O_2CMe)_3]\cdot 2MeCO_2H$,[4] $[OsO_2(C_6H_2Me_3\text{-}2,4,6)_2]$[5] and $[OsO_2(C_6H_3Me_2\text{-}2,6)_2]$.[6] Only the last two are tetrahedral and these have similar O–Os–O parameters to those of **1**. We attempted to prepare $K_2[OsO_2(S_2O_3)_2]$ but could not isolate it in a pure state.

(*b*) *Reactions of Complex* **1**.—These are summarised in Scheme 1.

(*i*) *N-Donor ligands.* We find that complex **1** is very reactive, much more so than is *trans*-$[OsO_2(SO_3)_4]^{6-}$. At room temperature it reacts with a number of nitrogen-donor ligands; with 1,10-phenanthroline (phen), *N,N,N',N'*-tetramethylethylenediamine (tmen) and *N,N'*-diisopropylethylenediamine (dipen) it undergoes addition reactions to give complexes of the type $[NBu^n{}_4]_2[OsO_2(S_2O_3)_2L]$ for which we propose octahedral structures containing *trans* O=Os=O 'osmyl' groups[2] [see section (*d*)]. It is interesting that although **1** reacted with phen it would not react with 2,2'-bipyridyl (bipy) at all even when the ligand was present in a great excess and heat was applied. By using the tetraphenylphosphonium salt of **1** the complexes $[PPh_4]_2[OsO_2(S_2O_3)_2L'_2]$ [L' = ½*N,N,N',N'*-tetraethylenediamine (teen), pyridine, 4-*tert*-butylpyridine or ammonia] were prepared (these four amines with the tetrabutylammonium salt of **1** gave intractable oils). The amine ligands in these complexes appear to be very labile in solution: they readily dissociate from the complexes, allowing the peculiarly stable tetrahedral structure to be readopted; evidence for this may be found in the UV and vibrational spectra of the complexes. Ultraviolet measurements for $[OsO_2(S_2O_3)_2(dipen)]^{2-}$, using the peak of the latter at 411 nm, show that for equilibrium (1)



Scheme 1 (*i*) $NO_2{}^-$; (*ii*) HI; (*iii*) acac; (*iv*) PMe_2Ph; (*v*) *p*-methoxybenzyl alcohol; (*vi*) HCl, ethylene glycol, bipy; (*vii*) $SO_3{}^{2-}$; (*viii*) concentrated OH^-; (*ix*) NCO^- or SCN^-; (*xi*) phen or tmen; (*xii*) py; (*xiii*) py, heat; (*xiv*) $S_2O_3{}^{2-}$

$$[OsO_2(S_2O_3)_2(dipen)]^{2-} \underset{}{\overset{K}{\rightleftharpoons}} [OsO_2(S_2O_3)_2]^{2-} + dipen \quad (1)$$

K is 1.9 mol dm^{-3} at 25 °C which corresponds to 73% dissociation for a 1 mol dm^{-3} solution in acetone.

With excess of pyridine (py) under reflux conditions complex **1** undergoes reaction with displacement of one of the thiosulfate groups to give the neutral species $[OsO_2(py)_3(S_2O_3)]$. The anionic ligands nitrite and cyanate react with **1** similarly to the

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: eV ≈ 1.60 × 10^{-19} J.

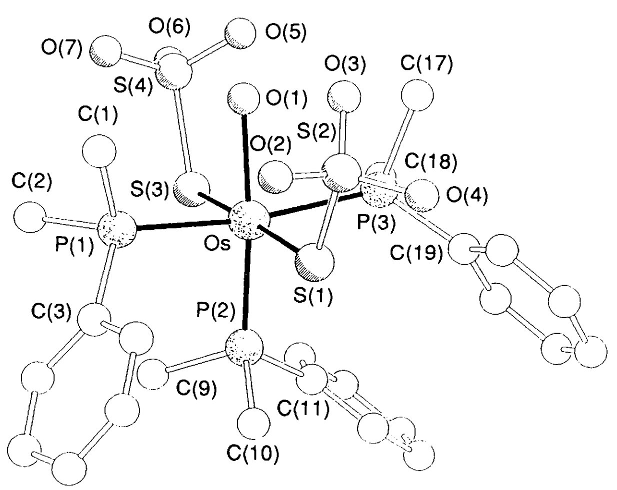

Fig. 1 Molecular structure of the $[Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]^-$ anion

Table 1 Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[NBu^n{}_4][Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]$

Os–S(1)	2.319(3)	Os–S(3)	2.328(3)
Os–O(1)	2.188(6)	Os–P(1)	2.441(2)
Os–P(2)	2.314(2)	Os–P(3)	2.449(2)
S(1)–S(2)	2.118(3)	S(2)–O(2)	1.435(9)
S(2)–O(3)	1.420(8)	S(2)–O(4)	1.438(10)
S(3)–S(4)	2.111(4)	S(4)–O(5)	1.442(9)
S(4)–O(6)	1.389(9)	S(4)–O(7)	1.411(8)
P(1)–C(1)	1.816(10)	P(1)–C(2)	1.805(10)
P(1)–C(3)	1.808(9)	P(2)–C(9)	1.814(7)
P(2)–C(10)	1.786(9)	P(2)–C(11)	1.826(9)
P(3)–C(17)	1.841(10)	P(3)–C(18)	1.789(10)
P(3)–C(19)	1.801(10)		
S(1)–Os–S(3)	175.2(1)	S(1)–Os–O(1)	92.5(2)
S(3)–Os–O(1)	91.9(2)	S(1)–Os–P(1)	89.9(1)
S(3)–Os–P(1)	92.5(1)	O(1)–Os–P(1)	83.6(2)
S(1)–Os–P(2)	89.2(1)	S(3)–Os–P(2)	86.5(1)
O(1)–Os–P(2)	175.9(2)	P(1)–Os–P(2)	92.7(1)
S(1)–Os–P(3)	87.8(1)	S(3)–Os–P(3)	90.6(1)
O(1)–Os–P(3)	86.3(2)	P(1)–Os–P(3)	169.6(1)
P(2)–Os–P(3)	97.5(1)	Os–S(1)–S(2)	116.3(1)
S(1)–S(2)–O(2)	106.3(4)	S(1)–S(2)–O(3)	108.8(4)
O(2)–S(2)–O(3)	113.3(6)	S(1)–S(2)–O(4)	105.0(4)
O(2)–S(2)–O(4)	111.2(6)	O(3)–S(2)–O(4)	111.7(6)
Os–S(3)–S(4)	111.9(1)	S(3)–S(4)–O(5)	106.7(4)
S(3)–S(4)–O(6)	105.1(4)	O(5)–S(4)–O(6)	112.4(6)
S(3)–S(4)–O(7)	107.1(4)	O(5)–S(4)–O(7)	109.0(5)
O(6)–S(4)–O(7)	116.0(6)		

amines mentioned above giving complexes of the type $[OsO_2(S_2O_3)_2L_2]^{4-}$, which may be isolated as their alkali-metal salts. The infrared spectrum of the cyanato complex suggests N-bonding of the cyanate ligand, using the criteria of Burmeister and O'Sullivan[7] [ν(CN) 2239, ν(CO) 1332, δ(NCO) 593 cm^{-1}].

We attempted similar reactions with the sulfite complex $[OsO_2(SO_3)_4]^{6-}$, but this did not react with any of the amines tried, despite there being an apparent driving force for the reaction to proceed (*i.e.* a resultant decrease in charge of a very highly negatively charged species). This lack of reactivity may arise because the latter complex is co-ordinatively saturated with sulfur-bonded ligands which are better ligands for osmium than are N-donors. Further evidence for the affinity of osmium for S-donors is given by the observation that when the complex $K_4[Os_2O_6(NO_2)_4]$ is treated with thiosulfate in a 1:4 ratio the product obtained is not $[OsO_2(S_2O_3)_2(NO_2)_2]^{4-}$ but $[OsO_2(S_2O_3)_2]^{2-}$.

(*ii*) *S-Donor ligands.* Sulfite displaces the thiosulfate ligands of complex **1** completely to give the known complex *trans*-$[OsO_2(SO_3)_4]^{6-}$; this is in agreement with recent work on platinum(II) complexes where it has been shown that SO_3^{2-} is a better ligand than $S_2O_3^{2-}$.[8] The complex was isolated as the sodium salt; neither tetrabutylammonium nor tetraphenylphosphonium salts would precipitate from the solution, presumably due to packing factors. With diethyldithiocarbamate **1** underwent reaction with displacement of the original ligands to give the known[9] compound $[OsO_2(Et_2NCS_2)_2]$. Attempts to cause complex **1** to react with further $S_2O_3^{2-}$ to obtain $[Os(S_2O_3)_3]^{n-}$ using a variety of conditions were not successful.

The thiocyanate group is ambidentate, being able to co-ordinate to the metal through the nitrogen or the sulfur atom or both. We find that thiocyanate adds to complex **1** in a similar fashion to that of cyanate, giving the complex *trans*-$[OsO_2(S_2O_3)_2(SCN)_2]^{4-}$; the position of the ν(CN) (2124 cm^{-1}), ν(CS) (690 cm^{-1}) and δ(NCS) (411 cm^{-1}) bands suggests[10] that the thiocyanate is S-bonded.

(*iii*) *O-Donor ligands.* Reaction of complex **1** at room temperature with both 3,5-di-*tert*-butylcatechol and 3,5-di-*tert*-butyl-*o*-benzoquinone gave the same product, tris(3,5-di-*tert*-butylcatecholato)osmium, the preparation and properties of which have previously been reported.[11] On heating **1** with pentane-2,4-dione (Hacac) in acetone the known[12] $[Os(acac)_3]$ was formed. No reaction occurred with the diols ethylene glycol or cyclohexane-1,2-diol even under reflux conditions. Dissolution of **1** in a concentrated solution of OH^- gave the purple osmate ion, *trans*-$[OsO_2(OH)_4]^{2-}$.

Salts of complex **1** appeared to be totally unreactive towards added sulfate, the starting materials being isolated unchanged from the reaction solution. An alternative approach was to add hydrogen peroxide to **1** in an attempt to oxidise the co-ordinated thiosulfate groups to sulfate. The transformation was achieved but the resultant sulfate was not bound to the osmium and crystallised out of solution as $[NBu^n{}_4]_2[SO_4]$.

(*iv*) *P-Donor ligands.* We find that complex **1** reacts with an excess of dimethylphenylphosphine in an open vessel to give a deep blue solution from which can be isolated an emerald-green compound. This compound, after recrystallisation from dichloromethane and toluene, yielded crystals suitable for X-ray analysis. It is paramagnetic having a solid-state magnetic moment of 1.66 μ_B, close to the spin-only value of one unpaired electron, and has been shown by a single-crystal X-ray crystallographic study to be $[NBu^n{}_4][Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]$ **2**. Analogous products could not be obtained with $PMePh_2$ and PPh_3; this may be due to the greater bulk of these phosphine ligands.

(*v*) *Other reactions.* No reaction occurred between complex **1** and hydrochloric acid but the more reducing hydroiodic acid gave $[OsI_6]^{2-}$.

Complex **1** also acts as a very mild oxidant for alcohols. Over 3 h at room temperature a solution of **1** in dichloromethane, under a nitrogen atmosphere, oxidises stoichiometrically *p*-methoxybenzyl alcohol to the aldehyde with a 26% yield. This reaction will also proceed catalytically with the use of *N*-methylmorpholine *N*-oxide as co-oxidant, giving an 81% yield of product with a turnover (moles of product per moles of complex) of 30 under similar reaction conditions.

(*c*) *Crystal Structure of* $[NBu^n{}_4][Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]$ **2**.—The structure of the complex is shown in Fig. 1 together with the atom labelling. Selected bond lengths and angles are given in Table 1 and fractional atomic coordinates for the non-hydrogen atoms in Table 2. The complex has a distorted-octahedral geometry with a *trans* disposition of S-bonded thiosulfato ligands, a *mer* arrangement of phosphine ligands and the sixth site occupied by a co-ordinated water molecule. The S–S bonds of the thiosulfato groups have a *syn* relationship and the S(1), S(2), S(3), S(4) and Os–O(1) atoms are coplanar to within 0.087 Å. The deviations from octahedral geometry are all less than 5° with the exception of O(1)–Os–P(1)

Table 2 Atomic coordinates (× 10^4)

Atom	x	y	z
Os	−822(1)	3810(1)	1276(1)
S(1)	779(2)	4454(2)	1050(1)
S(2)	1071(2)	5909(2)	1263(1)
S(3)	−2415(2)	3073(2)	1448(1)
S(4)	−3458(2)	4038(2)	1795(1)
O(1)	−1292(5)	5156(4)	1640(2)
O(2)	1693(7)	5857(6)	1696(3)
O(3)	102(6)	6389(5)	1333(4)
O(4)	1651(8)	6326(6)	867(3)
O(5)	−3324(7)	4973(6)	1566(3)
O(6)	−4442(6)	3648(7)	1713(4)
O(7)	−3145(7)	4106(6)	2286(3)
P(1)	−108(2)	3396(2)	2072(1)
P(2)	−326(2)	2335(2)	944(1)
P(3)	−1551(2)	4528(2)	535(1)
C(1)	89(8)	4465(7)	2448(4)
C(2)	−920(8)	2661(7)	2463(3)
C(3)	1160(7)	2822(6)	2093(3)
C(4)	2076(7)	3328(7)	1959(3)
C(5)	3021(7)	2893(8)	1952(4)
C(6)	3129(9)	1921(9)	2054(4)
C(7)	2231(8)	1378(7)	2207(4)
C(8)	1297(7)	1844(8)	2227(4)
C(9)	−664(7)	1279(8)	1307(4)
C(10)	1042(7)	2142(6)	867(3)
C(11)	−846(7)	1939(6)	358(3)
C(12)	−240(7)	1930(7)	−59(3)
C(13)	−605(8)	1569(8)	−502(4)
C(14)	−1628(9)	1199(8)	−510(4)
C(15)	−2230(8)	1218(7)	−107(3)
C(16)	−1841(8)	1602(7)	324(4)
C(17)	−1875(9)	5825(7)	603(4)
C(18)	−2796(8)	4067(7)	352(4)
C(19)	−789(8)	4563(7)	−15(3)
C(20)	98(8)	5207(8)	−54(4)
C(21)	719(10)	5194(10)	−456(4)
C(22)	535(11)	4575(10)	−829(5)
C(23)	−352(11)	3950(9)	−819(4)
C(24)	−962(9)	3967(8)	−410(4)
N	4628(3)	7213(3)	1501(1)
C(25)	5772(3)	7171(4)	1662(2)
C(26)	6456(3)	7898(6)	1380(3)
C(27)	7580(3)	7871(7)	1594(3)
C(28)	8327(5)	8453(8)	1265(4)
C(29)	4151(4)	8219(3)	1639(2)
C(30)	2983(4)	8227(4)	1491(4)
C(31)	2699(4)	9219(6)	1265(6)
C(32)	1500(4)	9308(7)	1213(6)
C(33)	4004(4)	6399(3)	1764(2)
C(34)	4030(8)	6585(6)	2319(2)
C(35)	3450(9)	5741(7)	2582(3)
C(36)	4263(9)	4995(7)	2766(3)
C(37)	4523(4)	7081(3)	944(1)
C(38)	5103(9)	6180(5)	763(1)
C(39)	4788(10)	5960(3)	228(2)
C(40)	4928(12)	6883(6)	−84(3)

83.6(2), P(2)–Os–P(3) 97.5(1) and P(1)–Os–P(3) 169.6(1)°. We attribute these distortions to steric crowding of the osmium centre by bulky phosphine groups. The Os–O (H_2O) distance of 2.188(6) Å is slightly longer than that found in $[PPh_4][Os(NS)Cl_4(H_2O)]$ [2.165(4) Å].[13] The S_2O_3 groups are oriented so as to permit the formation of two strong O–H ··· O hydrogen bonds (2.60 and 2.63 Å) between O(1) and O(3) and O(5) respectively; this does not produce any significant perturbation in the S–O bond lengths. The angle subtended at O(1) by O(3) and O(5) is 136°. The Os–S distances are 2.319(3) and 2.328(3) Å to S(1) and S(3) respectively, shorter than found for other sulfur ligands bound to osmium.[14–16] The two *trans* Os–P distances in **2** [Os–P(1) 2.441(2) and Os–P(3) 2.449(2) Å] are slightly longer than those found in the comparable complex *mer*-$[Os(PMe_2Ph)_3Cl_3]$[17] and are noticeably longer than that involving the phosphine *trans* to the aqua ligand, Os–P(2) 2.314(2) Å. The S(1)–S(2) and S(3)–S(4) distances of 2.118(3) and 2.111(4) Å respectively are comparable with those found in other complexes of monodentate S-bonded ligands[18,19] but significantly shorter than the S–S distance [2.152(1) Å] in **1**.[2]

(*d*) *Raman and Infrared Spectra.*—The very strong Raman band of complex **1** (polarised in acetone solution) at 931 cm^{-1} we assign to the symmetric stretch $\nu_{sym}(OsO_2)$ of the *cis*-OsO_2 unit, while the weaker, depolarised Raman band at 915 cm^{-1}, strong in the infrared, is likely to arise from the asymmetric mode $\nu_{asym}(OsO_2)$. Comparable values were found for the infrared spectra of $[OsO_2(C_6H_2Me_3\text{-}2,4,6)_2]$[5] and $[OsO_2(C_6H_3Me_2\text{-}2,6)_2]$,[6] and in these laboratories we have recently identified IR bands at 866 and 886 cm^{-1} for $\nu_{sym}(RuO_2)$ and $\nu_{asym}(RuO_2)$ respectively of the *cis*-$Ru^{VI}O_2$ moiety in $[PPh_4][RuO_2(O_2CMe)Cl_2]$.[20] The essential similarity of spectral profiles for the Raman and infrared spectra of solid **1** and its solution in CH_2Cl_2 suggests that its quasi-tetrahedral geometry is retained in solution, a fact also supported by the observation for a $C^2H_2Cl_2$ solution of **1** of ^{17}O shifts at δ 825.9 and 241.0 (relative to $H_2{}^{17}O$) in a 1:3 ratio,[2] as expected from the structure of **1** in the solid state.

The Raman and infrared spectra of complex **1** (Table 3) also shows bands typical[21] of monodentate S-bonded thiosulfate ligands. Although a number of infrared studies have been reported on S-bonded monodentate thiosulfato complexes *e.g.* $[Zn(tu)_3]S_2O_3\cdot H_2O$ (tu = thiourea),[25] $Na_3[Au(S_2O_3)_2]\cdot 2H_2O$,[21] and $[\{Co(NH_3)_5(S_2O_3)\}_2]\cdot S_2O_3$,[26] only $[Pd(en)_2][Pd(en)(S_2O_3)_2]$ (en = ethane-1,2-diamine)[27] and $[M^{II}(NH_3)_3(S_2O_3)]$ (M^{II} = Zn or Cd[28]) have been subjected to Raman study. The thiosulfate ion (C_{3v} symmetry) has vibrational modes $3A_1 + 3E$ (A_1 polarised, E depolarised), which are both Raman and IR active; all the bands have been assigned for the free ion.[23,29] For complex **1** most of these bands are easily discerned (bands due to the cation are not reported in Table 3). The strongest thiosulfate band in the Raman spectrum is that at 409 cm^{-1}, polarised in dichloromethane solution and clearly arising from the S–S stretch (found at 448 cm^{-1} for aqueous $S_2O_3{}^{2-}$);[23] the low frequency of ν(S–S) in **1** is consistent with the particularly long S–S bond distance. The strong, polarised band at 1017 cm^{-1} we assign to $\nu_{sym}(SO_3)$ (ν_1) (996 cm^{-1} for $S_2O_3{}^{2-}$, ref. 23) and the strong IR bands at 1223 and 1232 cm^{-1} to the asymmetric SO_3 stretch (ν_4) (1126 cm^{-1} for $S_2O_3{}^{2-}$, ref. 23). The small magnitude of the splitting of $\nu_{asym}(SO_3)$, which is not observed in the Raman spectrum, is likely to be due to a site splitting effect.[30] The increase in frequency of the S–O stretches relative to their free-ion values is characteristic of co-ordinated, monodentate S-bound thiosulfate.[21]

Vibrational data for those reaction products of complex **1** where thiosulfate ligands are retained are also given in Table 3. The octahedral co-ordination of the dioxo complexes with a *trans* arrangement of oxo-ligands is indicated not only by the analyses, but also by the Raman and infrared spectra. The bands at 931 and 915 cm^{-1} assigned to the *cis*-OsO_2 unit in **1** disappear and are replaced by a strong Raman band near 880 cm^{-1} not observed in the infrared, assigned to $\nu_{sym}(OsO_2)$ (polarised in solution), and an IR band near 840 cm^{-1}, not observed in the Raman, assigned to $\nu_{asym}(OsO_2)$ in each case. Such frequencies are observed for other *trans* O=Os–O 'osmyl' complexes.[31] The IR spectrum of the complex $[NBu^n{}_4][Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]$ however shows no such metal–oxo stretches but

Table 3 Vibrational data (cm^{-1}) for thiosulfato complexes

Complex		$\nu_{asym}(SO)_3$ (ν_4, E)	$\nu_{sym}(SO_3)$ (ν_1, A_1)	$\delta_{sym}(SO_3)$ (ν_2, A_1)	$\delta_{asym}(SO_3)$ (ν_5, E)	ν(SS) (ν_3, A)	$\rho(SO_3)$ (ν_6, E)	ν_{asym}-(OsO_2)	ν_{sym}-(OsO_2)
$Na_2S_2O_3$(s)	IR[21]	1160 (sh), 1130s	1002s	680 (sh)	555m, 535m		338w		
$Na_2S_2O_3 \cdot 5H_2O$	Raman[22]	1172, 1115	1018	673, 635	550, 545	434	348, 323		
$Na_2S_2O_3$(aq)	Raman[23,24]	1126(4)dp	999(6)p	671(3)p	538(2)dp	448(10)p	339(4)dp		
$[NBu^n_4]_2[OsO_2(S_2O_3)_2]$		1232s, 1223s	1011s	594s	532m, 519w	412vw	—	915s	933m
	IR[a]	1236s	1016s	601s	533m, 525w	—	—	913m	933w
	Raman	1225(1)	1017(3)	610(1)	527, 522(2)	409(4)	350(3)	915(2)	932(10)
	Raman[a]	1227(1)	1013(5)p	611(1)	526(4)	417(6)	359(3)	912(1)	931(10)p
$[PPh_4]_2[OsO_2(S_2O_3)_2]$		1239s, 1226s	1012s	600s	*b*	408vw	—	908s	930w
	Raman	1235(1)	1010(4)	605(2)	*b*	414(4)	359(3)	907(2)	930(10)
$[NBu^n_4]_2[OsO_2(S_2O_3)_2(phen)]$		1216s, 1192s	1009vs	616s	535m, 526m	426w	—	839s	883w
	IR[a]	1216s, 1202 (sh)	1010s	621s	525w	—	—	842vs	—
$[NBu^n_4]_2[OsO_2(S_2O_3)_2(tmen)]$		1222m, 1210s	1012s	628s, 611s	528m	406w	—	844s	877w
	IR[a]	1204m	1019s	616s	527m	—	—	852m	884w
	Raman	1210(2)	1009(4)	—	520(1)	410(4)	367(3)	—	876(10)
$[NBu^n_4]_2[OsO_2(S_2O_3)_2(dipen)]$		1206s, 1183s, 1168s	1008s	631m, 621s	537m, 533m	420w	—	844s	885w
	IR[a]	1206s	1008s	621s	535m	—	—	846s	—
$[PPh_4]_2[OsO_2(S_2O_3)_2(py)_2]$		1216s, 1209s, 1184m	1010s	619s, 609s	*b*	407w	—	838m	—
	IR[a]	1218s, 1190s	1014s	606s, 601s	*b*	—	—	850m	—
	Raman	1210(1)	1007(3)	598(1)	*b*	417(4)	353(10)	—	876(3)
$[PPh_4]_2[OsO_2(S_2O_3)_2(4Bu^t\text{-}py)_2]$		1227m, 1212s, 1184m	1012s	617s, 612s	*b*	409w	—	836s	876w
	IR[a]	1227s	1014s	607s, 601s	*b*	—	—	—	—
$[PPh_4]_2[OsO_2(S_2O_3)_2(teen)]$		1220s, 1201s, 1186s	1015s	629s, 613s	*b*	418w	—	846s	882w
	IR[a]	1208m, 1184s	1017s	618s	*b*	—	—	850m	—
$[OsO_2(py)_3(S_2O_3)]$		1226m, 1185s	1011s	614s	537m, 527m	429w	—	843s	886w
$K_4[OsO_2(S_2O_3)_2(NO_2)_2]$		1234s, 1224s, 1169s	1020s	637s	542m, 533m	428w, 415w	332vw	864s	905w
$K_4[OsO_2(S_2O_3)_2(NCO)_2]$		1187s	1016s	646s	546m, 537m	454vw, 415w	—	841m	—
$K_4[OsO_2(S_2O_3)_2(NCS)_2]$		1187s	1021s	638s	537m	431w	—	858m	—
$[NBu^n_4][Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]$		1227, 1162s, 1151s	1004s	632s, 611s	528m, 519m	424w, 400w	—	—	—

All data are for the solid state IR unless otherwise stated. [a] Solution data in dichloromethane. [b] Obscured by cation band.

does contain large broad bands at 3430 and 1630 cm^{-1}, attributable to modes of the co-ordinated aqua ligand. Vibrational bands due to co-ordinated thiosulfate for these complexes have been assigned where possible and are given in Table 3; from the position of these it appears that in all cases the $S_2O_3^{2-}$ ligand binds through one sulfur atom as in **1**. For those compounds with chelating co-ligands there is no ambiguity about the geometry of the complex since the thiosulfate ligands are necessarily mutually *cis*, but where monodentate ligands are used the question of whether the thiosulfate groups are *cis* or *trans* to each other occurs. Although vibrational modes of thiosulfate have been used to give information about the mode of bonding and geometry of its complexes,[21,30] many anomalies occur and we find it is more diagnostically useful to consider the vibrational modes of the co-ligands in our complexes, which are (with the exception of pyridine) simpler, when attempting to determine the geometries of the complexes.

For the complex $Na_4[OsO_2(S_2O_3)_2(NO_2)_2]$ bands assignable to vibrations of the NO_2 group are $\nu_{asym}(NO_2)$ 1391, $\nu_{sym}(NO_2)$ 1338, 1328 and $\delta(NO_2)$ 831, 826 cm^{-1}. Such values are consistent with nitro ($-NO_2$) rather than nitrito ($-ONO$) co-ordination.[32] The splitting of bands in the 830 and 1330 cm^{-1} regions is suggestive of the two nitro-groups being *cis* to each other;[33] similar splitting is found for $K_4[Os_2O_6(NO_2)_4]$.[34] For $K_4[OsO_2(S_2O_3)_2(NCO)_2]$ the simplicity of its vibrational spectra together with the absence of coincident bands in its IR and Raman spectra suggest that it is a *trans* complex.[35]

(*e*) *X-Ray Photoelectron Spectra*.—We report here XPS $4f_{\frac{7}{2}}$ binding energies for some of the complexes described in the paper since it is known that such data are indicative of the oxidation state of the osmium.[36,37] The values may be compared with values for the standard compounds $K_2[Os^{VI}O_2(OH)_4]$ (54.5), $K_2[Os^{IV}Cl_6]$ (53.0) and $[Os^{III}Cl_2(acac)(PPh_3)_2]$ (51.9 eV).[2]

Complex **1** was found[2] to have a $4f_{\frac{7}{2}}$ energy of 54.1 eV, which is consistent with the osmium being in the hexavalent oxidation state. For the addition products $[NBu^n_4]_2[OsO_2(S_2O_3)_2L]$ (L = tmen or dipen) and $[PPh_4]_2[OsO_2(S_2O_3)_2L'_2]$ [L′ = py or 4-*tert*-butylpyridine (4Bu^t-py)] the corresponding energies are 54.1, 53.8, 54.1 and 54.4 eV respectively, which show that they too are likely to contain osmium(VI). Complex **2** is formally of osmium(III) and its $4f_{\frac{7}{2}}$ value of 51.4 eV is in agreement with this. Each spectrum also contained a signal at 163 and and another at 168 eV attributable to S(2p). The values were measured relative to a C 1s binding energy of 285 eV.

(*f*) *Redox Properties*.—The electrochemical properties of complexes **1** and **2** were investigated using cyclic voltammetric techniques. For complex **1** we found a reversible one-electron reduction at -1.19 V (*vs*. ferrocene–ferrocenium 0.0 V) with $\Delta E = 85$ mV [presumably arising from reduction to an osmium(V) dioxo species] and an irreversible oxidation at $+0.92$ V. Similar electrochemical behaviour was found for the complex $[OsO_2(C_6H_2Me_3\text{-}2,4,6)_2]$.[38] We were not able to record the cyclic voltammograms of compounds of the type $[OsO_2(S_2O_3)_2L]^{2-}$ because of their dissociation in solution. For **2** in dichloromethane the voltammogram revealed a pair of cathodic and anodic peaks which correspond to an Os^{III}–Os^{II} reduction and an Os^{III}–Os^{IV} oxidation respectively. The reduction couple was observed at -1.04 V and the oxidation at 0.12 V (Fig. 2). For both couples at scan speeds from 20 to 200 mV s^{-1} the peak separation was close to that anticipated for a Nernstian one-electron process (59 mV).[39]

(*g*) *ESR Spectra*.—Complex **2** is ESR active and the solution

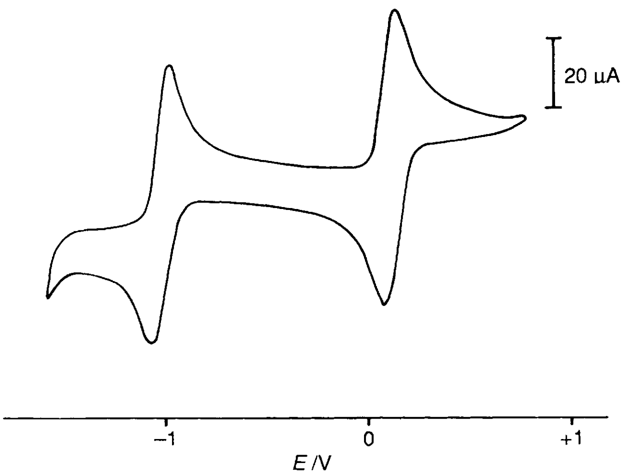

Fig. 2 Cyclic voltammogram of $[NBu^n_4][Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]$ in dichloromethane with $[NBu^n_4][PF_6]$ as supporting electrolyte. The potentials are relative to the ferrocene–ferrocenium couple (0.00 V)

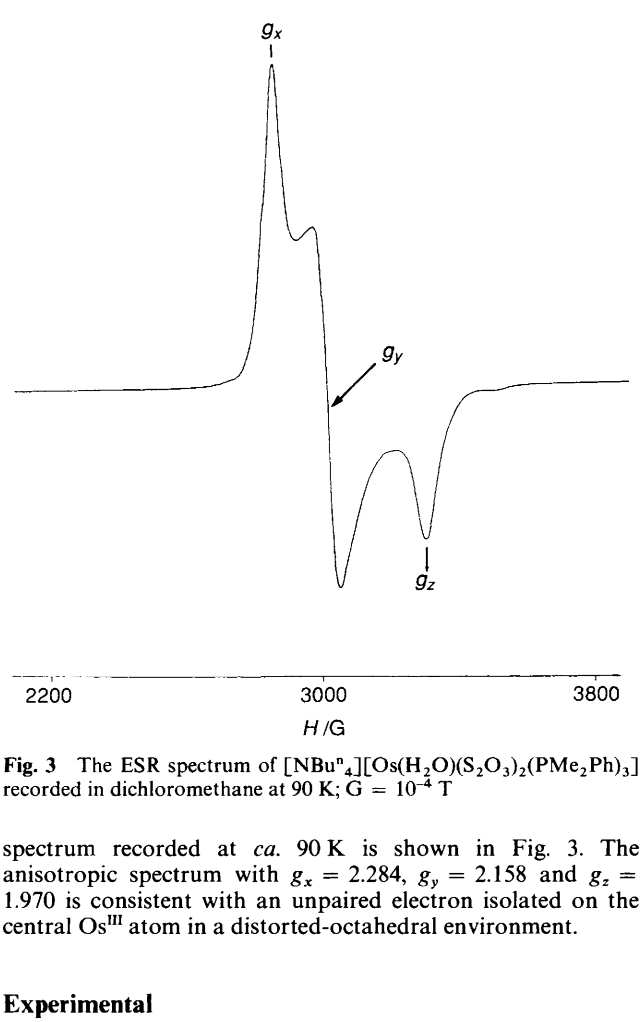

Fig. 3 The ESR spectrum of $[NBu^n_4][Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3]$ recorded in dichloromethane at 90 K; G = 10^{-4} T

spectrum recorded at *ca.* 90 K is shown in Fig. 3. The anisotropic spectrum with $g_x = 2.284$, $g_y = 2.158$ and $g_z = 1.970$ is consistent with an unpaired electron isolated on the central Os^{III} atom in a distorted-octahedral environment.

Experimental

Preparation of Complexes.—$[NBu^n_4]_2[OsO_2(S_2O_3)_2]$ **1**. To a chilled stirred solution of OsO_4 (1 g, 3.9 mmol) in water (75 cm^3) was added $Na_2S_2O_3\cdot5H_2O$ (3.9 g, 15 mmol). The solution immediately became dark red and $[NBu^n_4][HSO_4]$ (2.8 g, 8.2 mmol) was added. The solution was refrigerated and the complex precipitated as a green powder. This was recrystallised from dichloromethane and toluene (2.7 g, 80%) (Found: C, 41.0; H, 7.8; N, 3.0; S, 13.7. Calc. for $C_{32}H_{72}N_2O_8OsS_4$: C, 41.3; H, 7.8; N, 3.0; S, 13.8%). The salt $[PPh_4]_2[OsO_2(S_2O_3)_2]$ was prepared similarly but with the addition of PPh_4Cl to precipitate the product (Found: C, 51.4; H, 3.5; P, 5.7; S, 11.3. Calc. for $C_{48}H_{40}O_8OsP_2S_4$: C, 51.3; H, 3.6; P, 5.5; S, 11.4%).

With N-donor ligands. $[NBu^n_4]_2[OsO_2(S_2O_3)_2(phen)]$. To a solution of complex **1** (0.1 g, 0.11 mmol) in acetone (5 cm^3) was added 1,10-phenanthroline until the solution turned from green to orange; a large excess (*ca.* 1 g) was required to do this. The honey-yellow complex precipitated from the chilled solution. It was washed with diethyl ether and stored in a freezer as it was somewhat unstable at room temperature (0.08 g, 65%) (Found: C, 47.3; H, 7.2; N, 5.1; S, 11.4. Calc. for $C_{44}H_{80}N_4O_8OsS_4$: C, 47.5; H, 7.3; N, 5.0; S, 11.5%).

$[NBu^n_4]_2[OsO_2(S_2O_3)_2(tmen)]$. To complex **1** (0.10 g, 0.11 mmol) dissolved in acetone (5 cm^3) was added *N,N,N′,N′*-tetramethylethylenediamine (1 drop). The red solution was chilled and the product isolated as deep red crystals (0.10 g, 90%) (Found: C, 44.0; H, 8.5; N, 5.5; S, 11.9. Calc. for $C_{38}H_{88}N_4O_8OsS_4$: C, 43.6; H, 8.5; N, 5.4; S, 12.2%). The salt $[NBu^n_4]_2[OsO_2(S_2O_3)_2(dipen)]$ was prepared similarly (0.07 g, 60%) (Found: C, 44.7; H, 8.6; N, 5.0; S, 11.8. Calc. for $C_{40}H_{92}N_4O_8OsS_4$: C, 44.7; H, 8.6; N, 5.2; S, 11.9%).

$[PPh_4]_2[OsO_2(S_2O_3)_2(teen)]$. To a dichloromethane solution of $[PPh_4]_2[OsO_2(S_2O_3)_2]$ (0.10 g, 0.10 mmol) was added *N,N,N′,N′*-tetraethylethylenediamine (0.5 cm^3). Addition of a small volume of diethyl ether and subsequent chilling of the solution yielded the red crystalline complex (0.08 g, 60%) (Found: C, 53.0; H, 4.6; N, 2.1; P, 4.6; S, 10.4. Calc. for $C_{40}H_{64}N_2O_8OsP_2S_4$: C, 53.7; H, 5.0; N, 2.2; P, 4.8; S, 9.9%). The complexes $[PPh_4]_2[OsO_2(S_2O_3)_2(py)_2]$ (0.12 g, 90%) (Found: C, 54.2; H, 3.9; N, 2.5; P, 4.6; S, 9.7. Calc. for $C_{58}H_{50}N_2O_8OsP_2S_4$: C, 54.3; H, 3.9; N, 2.2; P, 4.8; S, 10.0%) and $[PPh_4]_2[OsO_2(S_2O_3)_2(4Bu^t\text{-}py)_2]$ (0.129 g, 85%) (Found: C, 57.0; H, 4.8; N, 2.2; P, 4.5; S, 8.7. Calc. for $C_{66}H_{66}N_2O_8OsP_2S_4$: C, 56.8; H, 4.8; N, 2.0; P, 4;4 S, 9.2%) were prepared similarly and dried under vacuum.

$[OsO_2(py)_3(S_2O_3)]$. To a solution of complex **1** (0.3 g, 0.34 mmol) in dichloromethane (20 cm^3) was added pyridine (3 cm^3). The solution was refluxed for 4 h during which time it changed from red to brown. Subsequent reduction of volume and chilling afforded a brown complex which was filtered off, washed several times with diethyl ether and dried under vacuum (0.07 g, 35%) (Found: C, 31.7; H, 3.0; N, 7.0; S, 10.7. Calc. for $C_{15}H_{15}N_3O_5OsS_2$: C, 31.5; H, 2.7; N, 7.4; S, 11.2%).

$K_4[OsO_2(S_2O_3)_2(NO_2)_2]$. Complex **1** (0.30 g, 0.34 mmol) was dissolved in acetone (20 cm^3) and the solution stirred while KNO_2 (0.17 g, 2 mmol) in water (2 cm^3) was added. The solution immediately became orange and after some time a red oil was deposited. The yellow solution was decanted from the oil which was triturated with ethanol giving an orange compound which was washed with diethyl ether (0.09 g, 40%) (Found: K, 22.0; N, 4.1; S, 18.0. Calc. for $K_4N_2O_{12}OsS_4$: K, 22.5; N, 4.0; S, 18.5%). The salts $K_4[OsO_2(S_2O_3)_2(NCO)_2]$ (Found: C, 3.7; K, 22.5; N, 4.3; S, 18.4. Calc. for $C_2K_4N_2O_{10}OsS_4$: C, 3.5; K, 22.8; N, 4.1; S, 18.7%) and $K_4[OsO_2(S_2O_3)_2(SCN)_2]$ (Found: C, 3.4; K, 21.5; N, 4.1; S, 26.4. Calc. for $C_2K_4N_2O_8OsS_6$: C, 3.3; K, 21.8; N, 3.9; S, 26.8%) were prepared analogously from **1** and potassium cyanate and potassium thiocyanate respectively.

With S-, O- and P-donor ligands. To a solution of complex **1** (0.2 g, 0.22 mmol) in acetone (10 cm^3) was added Na_2SO_3 (0.22 g, 0.88 mmol) in the minimum quantity of water. Upon mixing of the two solutions a colour change to orange was observed and a red oil deposited. This was triturated with ethanol to give red-brown powdery $Na_6[OsO_2(SO_3)_4]$ (0.08 g, 55%).

$[OsO_2(Et_2NCS_2)_2]$. To a solution of complex **1** (0.14 g, 0.15 mmol) in acetone (10 cm^3) was added sodium diethyldithiocarbamate (0.10 g, 0.45 mmol) in water (3 cm^3) and the resultant solution stirred. The complex was isolated upon cooling and recrystallised from dichloromethane–hexane. Yield 50%.

$[Os(acac)_3]$. To a solution of complex **1** (0.665 g, 0.7 mmol) in acetone (60 cm^3) was added acetylacetone (12 cm^3). The solution was refluxed and went gradually from green to deep red-brown. The acetone was removed under vacuum and to the oily residue were added equal volumes of water and dichloromethane. The brown dichloromethane layer was separated from the reddish aqueous layer, and the product precipitated by the addition of hexane. It was recrystallised from ethanol (0.07 g, 20%).

$[\mathrm{NBu^n_4}][\mathrm{Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3}]$ **2**. To complex **1** (0.15 g, 0.175 mmol) in acetone (10 cm^3) in an open vessel was added dimethylphenylphosphine (0.15 g, 1.05 mmol). The solution went red then blue then green. The solvent was allowed slowly to evaporate to half its original volume, when diethyl ether was added and the emerald-green complex precipitated. It was recrystallised from dichloromethane and toluene (0.15 g, 80%) (Found: C, 44.2; H, 6.7; N, 1.3; P, 8.3; S, 11.4. Calc. for $\mathrm{C_{40}H_{71}NO_7OsP_3S_4}$: C, 44.1; H, 6.6; N, 1.3; P, 8.5; S, 11.8%).

Miscellaneous reactions.—The salt $\mathrm{K_2[OsO_2(S_2O_3)_2]}$ (0.24 g, 0.46 mmol) was dissolved in water and hydroiodic acid (5 cm^3) added, giving a solution which gradually became deep red. An excess of KI in water was added, from which $\mathrm{K_2[OsI_6]}$ was isolated (0.14 g, 30%).

Stoichiometric oxidation of p-*methoxybenzyl alcohol.* This was carried out in degassed solution, under a nitrogen atmosphere. Complex **1** (0.45 g, 0.5 mmol) and *p*-methoxybenzyl alcohol (0.07 g, 0.51 mmol) were dissolved in dichloromethane (15 cm^3) and left to stir for 3 h at room temperature, after which time the solution was evaporated to dryness and the residue extracted with diethyl ether. The ether extracts were evaporated to dryness, dissolved in the minimum of ethanol and the quantity of aldehyde product determined by formation of its 2,4-dinitrophenylhydrazone derivative.

Catalytic oxidation of p-*methoxybenzyl alcohol.* A similar procedure to that used in the stoichiometric oxidations was employed, except that a three-fold excess of *N*-methylmorpholine *N*-oxide (with respect to the alcohol substrate) was added and a catalytic amount of complex **1** was used. After the 3 h reaction the solution was washed with a saturated solution of copper(II) sulphate in order to remove *N*-methylmorpholine *N*-oxide and its reduced products.

Crystal Structure Determination of $[\mathrm{NBu^n_4}][\mathrm{Os(H_2O)(S_2O_3)_2(PMe_2Ph)_3}]$ **2**.—*Crystal data.* $\mathrm{C_{40}H_{71}NO_7OsP_3S_4}$, M = 1087.4, orthorhombic, space group $P2_12_12_1$, a = 12.817(3), b = 13.750(4), c = 27.502(7) Å, U = 4847 Å^3, Z = 4, D_c = 1.49 g cm^{-3}, Cu radiation, λ = 1.541 78 Å, μ(Cu-Kα) = 79 cm^{-1}, F(000) = 2228.

Data collection and processing. Data were measured on a Nicolet R3m diffractometer with Cu-Kα radiation (graphite monochromator) using ω scans. A crystal of dimensions 0.08 × 0.17 × 0.28 mm was used. 3385 Independent reflections ($2\theta \leqslant 116°$) were measured, of which 3264 had $|F_o| > 3\sigma(|F_o|)$ and were considered observed. The data were corrected for Lorentz and polarisation factors; a numerical absorption correction (face-indexed crystal) was applied (maximum and minimum transmission factors 0.550 and 0.262).

Structure analysis and refinement. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. The $\mathrm{NBu^n_4}^+$ ion was disordered and was refined subject to C–C distance constraints. The hydrogen atoms of the aqua ligand could not be located. The positions of the remaining hydrogen atoms were idealised, C–H 0.96 Å, assigned isotropic thermal parameters, $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$, and allowed to ride on their parent carbon atoms. The methyl groups were refined as rigid bodies. The chirality of the structure was determined by an R-factor test. Refinement was by block-cascade full-matrix least squares to R = 0.036, R' = 0.039 [$w^{-1} = \sigma^2(F) + 0.000\,99F^2$]. The maximum and minimum residual electron densities in the final ΔF map were 0.76 and −0.56 e Å^{-3} respectively. The mean and maximum shift/error in the final refinement were 0.056 and 0.307 respectively. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.[40]

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

Physical Measurements.—Infrared spectra were measured on a Perkin-Elmer 1720 Fourier-transform spectrometer with samples as KBr discs, Raman spectra on a Spex Ramalog 5 instrument with a Datamate acquisition unit, as spinning discs on a KBr matrix or as solutions in sealed capillary tubes using the red 6471 Å line of a Coherent Radiation Innova-90 krypton-ion laser. The X-ray photoelectron spectroscopic (XPS) measurements were on powdered samples mounted on sample stubs using chlorine-free double-sided adhesive tape and analysed using Mg-Kα radiation at 15 kV and 10 mA using 6 mm slits on a Kratos XSAM 800 instrument. Cyclic voltammograms were recorded using an OE-PP2 instrument with platinum working, tungsten auxiliary and silver pseudo-reference electrodes. The ESR spectra were recorded on a Varian E12 X-band spectrometer (9.5 GHz), at low temperature with flowing cooled $\mathrm{N_2}$ gas. Microanalyses were by the Microanalytical Departments of Imperial College and the University of Strathclyde.

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