Osmium(III) and Osmium(IV) Complexes of Bi- and Polydentate Thioethers

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Osmium(III) complexes of the dithioethers (L–L) $PhS(CH_2)_2SPh$, cis-$PhSCHCHSPh$, $MeS(CH_2)_2SMe$, cis-$MeSCHCHSMe$ *and* o-$C_6H_4(SMe)_2$ *of type* $Os(L-L)_{1.5}X_3$ *(X = Cl, Br) have been prepared from* Na_2OsX_6 *and excess L–L in 2-ethoxyethanol. The trithioether* $S(CH_2CH_2CH_2SMe)_2$ *(*L^3*) produces both* Os^{IV} $[OsL^3X_4]$ *and* Os^{III} mer-$[OsL^3X_3]$ *complexes. New* $[OsL^nCl_4]$ *(*$L^n = CH_3C(CH_2SMe)_3$, $\overline{S(CH_2)_2S(CH_2)_3S(CH_2)_2S(CH_2)_3}$*),* mer-$[Ru(S(CH_2CH_2CH_2SMe)_2)Cl_3]$ *and* fac-$[Ru(\overline{S(CH_2)_2S(CH_2)_3S(CH_2)_2S(CH_2)_3})X_3]$ *(X = Cl, Br) are described. The complexes were characterised by IR, electronic and EPR spectra and by magnetic measurements.*

Introduction

Some time ago [1] we reported the synthesis of a series of osmium(IV) dithioether complexes $[Os(S-S)X_4]$ (S–S = $RSCH_2CH_2SR$, $RSCH=CHSR$, o-$C_6H_4(SR)_2$, R = Me, Ph, X = Cl, S–S = $MeSCH_2CH_2SMe$, $MeSCH=CHSMe$, X = Br) by reaction of the ligand with the appropriate sodium haloosmate(IV) Na_2OsX_6. In the present paper we report the preparation of osmium(III) complexes of dithioethers, and Os(III) and Os(IV) polythioethers. Only one Os(III) complex of a thioether ligand $[Os(Et_2S)_3Cl_3]$ has been described [2], but a considerable number of ruthenium(III) adducts of types $Ru(S-S)_{1.5}X_3$, $Ru(S-S)X_3$, $[Ru(S-S)X_4]^-$, $[Ru(SR_2)_3X_3]$ are known [1, 3, 4], and recently complexes of macrocyclic tetrathioethers have been described [5–8]. Osmium(III) phosphine compounds are well established [9] and there has been much recent interest in mono-, di- and polyamine derivatives [10–13].

Results and Discussion

Osmium(IV)

The reaction of Na_2OsCl_6 with $S(CH_2CH_2CH_2SMe)_2$ in refluxing 2-ethoxyethanol gave dark green $[Os(S(CH_2CH_2CH_2SMe)_2)Cl_4]$ (40%), and from the filtrate the yellow-brown Os(III) complex (below) could be isolated. The isomeric trithioether $CH_3C(CH_2SMe)_3$ gave a low yield of $[Os(CH_3C(CH_2SMe)_3)Cl_4]$ in a similar reaction and sodium hexabromoosmate(IV) produced poor yields of the bromo analogues. In contrast the cyclic tetrathioether, 1,4,8,11-tetrathiacyclotetradecane (TTP) $\overline{S(CH_2)_2S(CH_2)_3S(CH_2)_2S(CH_2)_3}$ gave a high yield (94%) of the green $[Os(TTP)Cl_4]$ (Table I). The three chlorocomplexes are poorly soluble in most organic solvents, non-electrolytes in 10^{-3} *M* CH_3NO_2, and have magnetic moments *ca.* 1.3–1.4 BM consistent with low spin d^4 Os(IV) [14]. The far IR and electronic spectra (Table II) of these complexes are very similar to the dithioether complexes $[Os(S-S)Cl_4]$ [1] and coupled with the non-electrolyte nature leads to their formulation as six-coordinate with S_2Cl_4 donor sets, the polythioethers binding as bidentates. The bromocomplexes are clearly analogous. The linear tetrathioether $MeS(CH_2)_2S(CH_2)_2S(CH_2)_2SMe$ (S^4) when reacted with Na_2OsCl_6 in $EtOC_2H_4OH$ gave grey-green $Os_2(S^4)Cl_8$ irrespective of the S^4:Os ratio used. This complex is insoluble in common solvents and has a low magnetic moment 1.57 BM (*ca.* 1.1 BM/Os). The structure is uncertain; generally this ligand binds in a tetradentate polymetallic manner *e.g.* $Pt_2(S^4)Cl_4$ [15] and $Rh_4(S^4)_3Cl_{12}$ [16] where it does not compete with halides for coordination sites on the neutral metal. A tetradentate bimetallic manner is likely in $Os_2(S^4)Cl_8$.

Ruthenium(III)

The brown $[Ru(S(CH_2CH_2CH_2SMe)_2)Cl_3]$ was readily prepared by refluxing $RuCl_3 \cdot 3H_2O$ with the ligand in ethanol, and from the presence of three ν(RuCl) in the far IR spectrum (Table II) is identified as the *mer* isomer. Repeated attempts to isolate a complex with $CH_3C(CH_2SMe)_3$ gave only intractable oils, although $[Ru(CH_3C(CH_2SEt)_3)Cl_3]$ is known [4]. Poon [5] prepared $Ru(TTP)Cl_2 \cdot 2H_2O$ from $RuCl_3 \cdot 3H_2O$ and TTP in refluxing $EtOC_2H_4OH$ for 2 days, and showed it to be the *cis* isomer with *endo-cis* TTP bound as a tetradentate [7].

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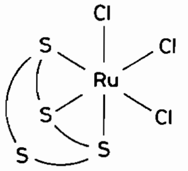
TABLE I. Analytical Data.

	Colour	C%[a]	H%	X%[b]	μ_{eff}[c,d]
$[Os(CH_3C(CH_2SMe)_3)Cl_4]$	grey-green	18.0(17.7)	3.3(3.3)	25.9(26.1)	1.36[e]
$[Os(S(CH_2CH_2CH_2SMe)_2)Cl_4]$	dark-green	17.5(17.7)	3.1(3.3)	26.9(26.2)	1.32[e]
$[Os(TTP)Cl_4]$	dark-green	20.2(20.0)	3.4(3.4)	22.2(23.6)	1.39[e]
$[Os(CH_3C(CH_2SMe)_3)Br_4]$	brown-green	12.9(13.3)	2.4(2.5)	–	–
$[Os(S(CH_2CH_2CH_2SMe)_2)Br_4]$	dark-green	13.7(13.3)	2.4(2.5)	–	–
$Os_2[-CH_2S(CH_2)_2SMe]_2Cl_8$	grey-green	10.9(10.6)	2.0(2.0)	30.4(31.2)	1.04[e]
$[Ru(S(CH_2CH_2CH_2SMe)_2)Cl_3]$	brown	22.9(23.0)	4.5(4.3)	25.1(25.5)	1.62[e]
$[Ru(TTP)Cl_3]$	brown	24.6(25.2)	3.9(4.2)	21.2(22.4)	1.71[e]
$[Ru(TTP)Br_3]$	brown-purple	20.0(19.7)	3.2(3.3)	–	1.60[e]
$Ru_2[-CH_2S(CH_2)_2SMe]_2Cl_6$	brown	14.8(14.6)	2.8(2.7)	31.4(32.4)	1.47[e]
$[Os(S(CH_2CH_2CH_2SMe)_2)Cl_3]$	yellow-brown	19.0(18.9)	3.4(3.6)	22.8(21.0)	1.92
$[Os(S(CH_2CH_2CH_2SMe)_2)Br_3]$	brown	14.9(15.0)	2.8(2.8)	42.3(42.8)	2.21
$Os(MeSCH_2CH_2SMe)_{1.5}Cl_3$	brown	14.8(15.2)	3.3(3.2)	21.0(22.2)	1.71
$Os(MeSCHCHSMe)_{1.5}Cl_3$	brown	15.0(15.0)	2.8(2.5)	21.2(22.0)	1.67
$Os[o\text{-}C_6H_4(SMe)_2]_{1.5}Cl_3$	brown	25.6(26.0)	2.6(2.7)	19.2(19.3)	1.74
$Os(PhSCH_2CH_2SPh)_{1.5}Cl_3$	brown	38.2(38.1)	2.6(2.7)	15.7(16.1)	1.78
$Os(PhSCHCHSPh)_{1.5}Cl_3$	brown	37.4(37.9)	3.1(3.2)	15.4(16.1)	1.65
$Os(MeSCH_2CH_2SMe)_{1.5}Br_3$	greenish-brown	11.8(11.8)	2.2(2.5)	38.7(39.1)	f
$Os(MeSCHCHSMe)_{1.5}Br_3$	greenish-brown	11.5(11.75)	2.1(2.0)	–	f
$Os[o\text{-}C_6H_4(SMe)_2]_{1.5}Br_3$	brown	21.6(21.0)	2.2(2.2)	34.3(34.9)	f
$Os(PhSCH_2CH_2SPh)_{1.5}Br_3$	brown	31.6(31.4)	2.4(2.6)	29.9(30.0)	f
$Os(PhSCHCHSPh)_{1.5}Br_3$	brown	31.9(31.6)	2.2(2.25)	29.8(30.0)	f

[a] Calculated value in parenthesis. [b] X = halide. [c] BM ±0.05 BM. [d] All non-electrolytes in 10^{-3} *M* CH_3NO_2 except for the S^4 complexes which are insoluble. [e] Gouy method, others Evans' NMR method in dimethylsulphoxide. [f] Insufficiently soluble.

We find that in ethanol with much shorter reaction time *ca.* 2 hours, the product is brown $[Ru(TTP)Cl_3]$. This is a non-electrolyte and is formulated as the *fac* isomer with tridentate TTP (I). The $[Ru(TTP)Cl_2]\cdot 2H_2O$ is converted to *cis*-$[Ru(TTP)Cl_2]ClO_4(S_4Cl_2)$ by conc $HClO_4$ [5, 7], but $[Ru(TTP)Cl_3]$ does not react with $LiClO_4$ in ethanol. $[Ru(TTP)Cl_3]$ is converted to purple $[Ru(TTP)Br_3]$ by refluxing overnight with LiBr in acetone, but $[Ru(S(CH_2CH_2CH_2SMe)_2)Cl_3]$ fails to exchange cleanly with LiBr. The tetradentate (S^4) gave $Ru_2(S^4)Cl_6$, which like the Os(IV) complex, has a low magnetic moment 2.1 BM (1.47 BM/Ru). Rice [3] reported $[Ru(S–S)Cl_3]_n$ (S–S = $PhS(CH_2)_2SPh$, $MeS(CH_2)_2SMe$, n = probably 2) with $\mu \approx 1.3$ BM, and suggested a halide-bridged dimer structure, and a similar structure may be present in $Ru_2(S^4)Cl_6$. The mononuclear Ru(III) complexes gave EPR spectra from the powdered solids at –196 °C, consistent with a low-spin d^5 configuration [17, 18] (Table III).



(I)

Osmium(III)

Our initial attempts to prepare Os(III) complexes were based upon reduction of the $[Os(S–S)Cl_4]$, sometimes with added dithioether, with zinc/HCl, $NaBH_4$/EtOH, $CrCl_2$/THF, Zn amalgam, or Na_2HPO_2. Although reaction seemed to occur in several cases, attempts to isolate the osmium complexes were generally unsuccessful. In fact, the yellow-brown $[Os(S(CH_2CH_2CH_2SMe)_2)Cl_3]$ was isolated in high yield (~55%) from the filtrate from the reaction of the trithioether with Na_2OsCl_6 (after removal of the much less soluble Os(IV) complex). The corresponding reaction using Na_2OsBr_6 gave brown-orange $[Os(S(CH_2CH_2CH_2SMe)_2)Br_3]$ as major product (66%) with only small amounts of the Os(IV) complex (~6%). Although relatively poor yields of Os(IV) complexes of $CH_3C(CH_2SMe)_3$ were obtained, we did not isolate Os(III) analogues (*cf.* the Ru(III) reaction), work up of the filtrates giving only oils. The $[Os(S(CH_2CH_2CH_2SMe)_2)X_3]$ are readily soluble in organic solvents, and the far IR spectra (Table 2) show they are *mer* isomers (theory $C_{2v} = 2A_1 + B_1$)

TABLE II. Spectroscopic Data.

	$\nu(MX)$ cm^{-1} [a]	UV–VIS 10^3 cm^{-1} (ϵ_{mol} dm^3 cm^{-1} mol^{-1})
$[Os(CH_3C(CH_2SMe)_3)Cl_4]$	290(br)	[b] 16.9, 21.0, 24.8, 30.0
$[Os(S(CH_2CH_2CH_2SMe)_2)Cl_4]$	315, 300(sh)	[c] 18.0(837), 23.25(7300), 29.1(9030)
$[Os(TTP)Cl_4]$	305(sh), 290	[b] 16.7, 21.4, 23.3, 26.7
$[Os(CH_3C(CH_2SMe)_3)Br_4]$	243(m)	[b] 16.8, 18.5sh, 20.8, 24.7
$[Os(S(CH_2CH_2CH_2SMe)_2)Br_4]$	245(s)	[b] 16.2sh, 19.6, 22.6, 28.4
$Os_2[-CH_2S(CH_2)_2SMe]_2Cl_8$	325(sh), 310(br)	[b] 14.6(w), 16.6, 18.2, 19.6, 22.8, 26.9
$[Ru(S(CH_2CH_2CH_2SMe)_2)Cl_3]$	332(br), 314, 294(sh)	[c] 19.6(991)sh, 22.4(1280), 25.0(1410)
$[Ru(TTP)Cl_3]$	320	[b] 19.4, 22.6, 24.0sh, 26.0
$[Ru(TTP)Br_3]$	246(m)	[b] 16.7(sh), 19.5, 20.7, 22.2, 26.6
$Ru_2[-CH_2S(CH_2)_2SMe]_2Cl_6$	316(br), 288(w)	[b] 19.8, 22.4, 25.5
$[Os(S(CH_2CH_2CH_2SMe)_2)Cl_3]$	310, 298(sh), 284	[d] 19.3(39)sh, 23.0(220)sh, 26.2(955)sh, 29.2(2450)
$[Os(o\text{-}C_6H_4(SMe)_2)_{1.5}Cl_3]$	300(sh), 290	[d] 21.2(2020)sh, 23.25(2380), 25.8sh
$Os(MeSCH_2CH_2SMe)_{1.5}Cl_3$	301(sh), 290	[d] *ca.* 19.0sh, 22.5sh, 27.5, *ca.* 30.0
$Os(MeSCHCHSMe)_{1.5}Cl_3$	300(sh), 287	[d] 22.6(822), 26.4(3740)sh, *ca.* 31.0(6000)
$Os(PhSCH_2CH_2SPh)_{1.5}Cl_3$	300(sh), 291	[d] 21.8(2990)sh, 23.25(3550), 26.7(4650), *ca.* 29.0(7000)
$Os(PhSCHCHSPh)_{1.5}Cl_3$	306(sh), 274	[d] 19.8(2570)sh, 23.6(9314)sh, 29.7(12840)
$[Os(S(CH_2CH_2CH_2SMe)_2)Br_3]$	223(sh), 207	[d] 20.1(1208)sh, 22.7(6870), 25.9(1730)sh
$Os[o\text{-}C_6H_4(SMe)_2]_{1.5}Br_3$	186	[d] 21.8(1795)sh, 24.75(3045), 29.9(4840)
$Os(MeSCH_2CH_2SMe)_{1.5}Br_3$	191(sh)	[d] 19.8sh, 21.0, 25.4sh, *ca.* 30.0
$Os(MeSCHCHSMe)_{1.5}Br_3$	186	[d] 21.55, 24.75, 29.4sh
$Os(PhSCH_2CH_2SPh)_{1.5}Br_3$	195(sh)	[d] 20.8(2830), 25.0(5340), 29.4(9080)
$Os(PhSCHCHSPh)_{1.5}Br_3$	192	[d] 20.6(3040), 25.0(6540), 29.4(8280)

[a] Nujol mulls 400–170 cm^{-1}. [b] Diffuse reflectance. [c] Dmso solution. [d] CH_2Cl_2 solution.

TABLE III. EPR[†] data for Os(III) and Ru(III) Complexes.

Complex	g-values, linewidths* and comments
$Ru_2[-CH_2S(CH_2)_2SMe]_2Cl_6$	g = 2.035(2500) – broad and asymmetric
$[Ru(TTP)Cl_3]$	g = 1.957(1750)
$[Ru(TTP)Br_3]$	g = 1.993(1750)
$[Ru(S(CH_2CH_2CH_2SMe)_2)Cl_3]$	g = 1.931 (1625)
$[Os(S(CH_2CH_2CH_2SMe)_2)Cl_3]$ $[Os(S(CH_2CH_2CH_2SMe)_2)Br_3]$	EPR spectra poorly resolved under experimental conditions
$Os(PhSCHCHSPh)_{1.5}Cl_3$	g = 1.923(225); g = 1.731(broad)
$Os(PhSCHCHSPh)_{1.5}Br_3$	g = 1.973(300); g = 1.785
$Os(MeSCHCHSMe)_{1.5}Cl_3$	g = 2.136 (hfc observed, 4 lines, A_{iso} = 70G), g = 2.024(200G)
$Os(MeSCHCHSMe)_{1.5}Br_3$	g = 2.361; g = 2.123(210)
$Os(MeSCH_2CH_2SMe)_{1.5}Cl_3$	g = 2.050(300); g = 1.798(broad)
$Os(MeSCH_2CH_2SMe)_{1.5}Br_3$	g = 2.033(425); g = 1.784(broad)
$Os[o\text{-}C_6H_4(SMe)_2]_{1.5}Cl_3$	g = 1.861 (hfc observed, 10 lines, A_{iso} = 80G, 3 × Cl's) linewidth 375G, g = 1.645
$Os[o\text{-}C_6H_4(SMe)_2]_{1.5}Br_3$	g = 2.361; g = 2.096(420)
$Os(PhSCH_2CH_2SPh)_{1.5}Cl_3$	g = 1.930(350)
$Os(PhSCH_2CH_2SPh)_{1.5}Br_3$	g = 2.36(600); g = 1.95

[†] All spectra recorded on powders at –196 °C. *Linewidths (in parenthesis, units G) are derivative peak-to-peak.

[17, 19]. The room temperature magnetic moments 1.92 BM (Cl), 2.21 BM (Br) are in excellent agreement with the values expected for t_{2g}^5 Os(III) 1.6–2.2 BM [14], and with those of $[Os(PR_3)_3X_3]$ [9]. Both complexes gave very broad absorptions in the EPR spectra at −196 °C.

Based upon these results, a route to Os(III) complexes of dithioethers was developed, using prolonged reflux of OsX_6^{2-} with excess ligand in $2\text{-}EtOC_2H_4OH$. In the case of Na_2OsBr_6 after 3–6 hours reflux, concentration of the filtered solution, and precipitation with diethyl ether gave brown $Os(S{-}S)_{1.5}Br_3$ in good yield. The reduction of Na_2OsCl_6 or $[Os(S{-}S)Cl_4]$ by dithioethers was much less easy and required 3–5 days reflux. The phenyl substituted ligands gave moderate yields of brownish $Os(S{-}S)_{1.5}Cl_3$ under these conditions, but with $MeS(CH_2)_2SMe$, and MeSCHCHSMe, the major products were black insoluble materials which were removed by filtration of the hot mixture, and poor yields of the Os(III) compounds obtained from the filtrates. The ease of reduction Br ≫ Cl and with $PhS(CH_2)_2SPh > MeS(CH_2)_2SMe$ parallel Chatt's results in the Ru(III)–Ru(II) systems [4], although the osmium reactions take considerably longer. Tertiary phosphines reduce Na_2OsCl_6 to $[Os(PR_3)_3Cl_3]$ in a few hours [9], reflecting the much stronger reducing power of phosphine ligands.

Once isolated the $Os(S{-}S)_{1.5}X_3$ proved to be poorly soluble in solvents suitable for M.Wt measurements, but were non-electrolytes in nitromethane, and the chlorides had μ_{eff} 1.65–1.78 BM/Os by the Evans method [20] in dimethyl sulphoxide. The bromides were not sufficiently soluble to measure μ_{eff} in solution. In the solid state Gouy measurements indicated lower moments for both series. Like the $Ru(S{-}S)_{1.5}Cl_3$ [4], these $Os(S{-}S)_{1.5}X_3$ must be at least binuclear, and it is probable that they have a dithioether bridge $[X_3(S{-}S)Os(S{-}S)Os(S{-}S)X_3]$. The poor solubility has so far prevented the preparation of single crystals for an X-ray study to confirm this. From the positions and number of ν(OsX) stretches in the far IR spectra (Table II) a *fac* arrangement of halides [17, 19] is proposed.

The $Os(S{-}S)_{1.5}X_3$ are indefinitely stable in air, and chemically unreactive. For example $[Os(PR_3)_3Cl_3]$ are converted to $[Os(PR_3)_2Cl_4]$ by refluxing CCl_4 [9], but $Os(PhSCH_2CH_2SPh)_{1.5}Cl_3$ was recovered unchanged from CCl_4 after 72 hours reflux. The grey-green $[Os(PhSCH_2CH_2SPh)Cl_4]$ [1] was however produced by prolonged treatment (~3 days) with Cl_2 in refluxing CCl_4.

The electronic spectrum of $[Os(S(CH_2CH_2CH_2SMe)_2Cl_3]$ (Fig. 1) contains a main absorption at 29200 cm^{-1} with several shoulders at lower energy, and the bromide has a similar spectral profile with the major peak at 23250 cm^{-1} (Table II). These spectra are believed to be mainly charge transfer in origin, taking χ_{opt} [Os(III)] = 2.0 [21, 22] and the usual optical electronegativities for Cl^- (3.0), Br^- (2.8), SR_2 (2.9), leads to predictions of $Os^{III} \leftarrow Cl$, $Os^{III} \leftarrow Br$, $Os^{III} \leftarrow SR_2$, of 30000, 24000, 27000, ±2000 cm^{-1} respectively, in good agreement with the observed spectra. The $Os(S{-}S)_{1.5}X_3$ gave generally similar but less clearly defined spectra, the bands appearing as shoulders on a rising absorption >20000 cm^{-1}.

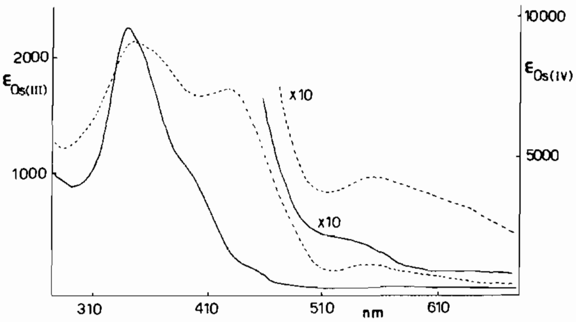


Fig. 1. Electronic spectra of $[Os(S(CH_2CH_2CH_2SMe)_2Cl_4]$ (– – –) and $[Os(S(CH_2CH_2CH_2SMe)_2)Cl_3]$ (——).

Attempts to prepare Os(III) complexes with SMe_2 and SPh_2 under a variety of conditions failed. Os(IV) analogues are also unknown [1].

Experimental

Physical measurements were made as described previously [1]. Dithioethers were made as described elsewhere [23] and TTP by Busch's method [24].

Bis(3-methylthiopropyl)sulphide $S(CH_2CH_2CH_2SMe)_2$

3-chloropropylmethylsulphide [25] (15.0 g, 0.12 mol) in ethanol (300 cm^3) was refluxed with sodium sulphide $Na_2S{\cdot}9H_2O$, (14.5 g, 0.06 mol) under nitrogen for 6 hours. The mixture was hydrolysed with water, extracted with diethyl ether (3 × 300 cm^3), and the extracts dried with Na_2SO_4. Distillation of the ether, and fractionation of the residue *in vacuo* gave a yellowish oil, b.p. 100–102 °C/1 torr. 8.3 g, 66%. ^{1}H NMR (δ) = 2.0(q) [2H] CH_2CH_2S, 2.1(s) [3H] CH_3S, 2.6(t) [4H] CH_2S.

1,1,1-tris(methylthiomethyl)ethane $CH_3C(CH_2SMe)_3$

$CH_3C(CH_2OH)_3$ was converted to $CH_3C(CH_2Br_3)$ in a similar manner to that described [26]. (50% yield).

Dry tetrahydrofuran (200 cm^3) was added to $LiAlH_4$ (11 g, 0.3 mol) under nitrogen, and dimethyldisulphide (14.0 g, 0.15 mol) added dropwise. The grey solution was treated dropwise with $CH_3C(CH_2Br)_3$ (26.0 g, 0.08 mol) and heated to reflux. The cooled mixture was hydrolysed with ethanol (10 cm^3) and dilute hydrochloric acid (1:5 v/v 200 cm^3), extracted with diethyl ether (2 × 200 cm^3), and the extracts dried (Na_2SO_4). The solvent was distilled off, and the residue fractionated *in vacuo* to give a colourless liquid 5.5 g, 33%. b.p. 78 °C/4 torr. ^1H NMR 2.5(m) [2H] CH_2, 2.1(s) [3H] CH_3S, 1.15(s) [1H] CH_3C.

Tetrachloro[bis(3-methylthiopropyl)sulphide]-osmium(IV)

The ligand (0.46 g, 2 mmol) and Na_2OsCl_6 (0.9 g, 2 mmol) were refluxed together in 2-ethoxyethanol (20 cm^3) for 3 hours under nitrogen. The solution was filtered hot, the green solid washed with 2-ethoxyethanol, and diethyl ether, and dried *in vacuo*, 0.43 g, 40%†.

The filtrate was concentrated *in vacuo* to *ca.* 5 cm^3, and treated dropwise with diethyl ether to give a yellow-brown powder, trichloro[bis(3-methylthiopropyl)sulphide]osmium(III). 0.56 g (55%).

A similar route gave $[Os(S(CH_2CH_2CH_2SMe)_2)Br_4]$ (8%), $[Os(S(CH_2CH_2CH_2SMe)_2)Br_3]$ (66%), from Na_2OsBr_6.

$[Os(CH_3C(CH_2SMe)_3)Cl_4]$ (25%); $[Os(CH_3C(CH_2SMe)_3)Br_4]$ (8%); $[Os(TTP)Cl_4]$ (90%), $Os_2(S^4)Cl_8$ (94%) were the only isolated products from similar reactions involving the appropriate ligand.

[Os(S–S)$_{1.5}$Br$_3$]$_2$. General Method

A mixture of Na_2OsBr_6 (0.72 g, 1 mmol) and the dithioether (2 mmol) in 2-ethoxyethanol (30 cm^3) was refluxed for 3 hours, cooled and filtered. The filtrate was concentrated to *ca.* 5 cm^3, diethyl ether added dropwise, and the brown products filtered off, well washed with diethyl ether and dried. Yields 40–80%.

[Os(S–S)$_{1.5}$Cl$_3$]$_2$. General Method

A suspension of $[Os(S-S)Cl_4]$ [1] (1 mmol) in $EtOC_2H_4OH$ (20 cm^3) was refluxed with an excess of S–S (*ca.* 5 mmol) for 3–5 days. The mixture was filtered hot to remove appreciable amounts of black solid, and the products isolated from the filtrate, as for the bromo complexes. Yields vary with the ligand from *ca.* 20% for $MeS(CH_2)_2SMe$, to *ca.* 50% for *o*-$C_6H_4(SMe)_2$ or $PhS(CH_2)_2SPh$.

[Ru(TTP)Cl$_3$]

Ruthenium trichloride, $RuCl_3 \cdot 3H_2O$ (0.26 g, 1 mmol) was refluxed with TTP (0.27 g, 1 mmol) in ethanol (20 cm^3) for 2 hours, cooled, and the brown solid filtered from the solution and dried *in vacuo* (91%).

$[Ru(S(CH_2CH_2CH_2SMe)_2)Cl_3]$, (71%), $Ru_2(S^4)Cl_6$ (95%) were made similarly and $[Ru(TTP)Br_3]$ was obtained in essentially quantitative yield by refluxing $[Ru(TTP)Cl_3]$ with LiBr (10 fold excess) in acetone overnight.

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† Yields based upon Os.