Co-ordination Chemistry of Higher Oxidation States. Part 1. Thioether Complexes of Osmium(IV), Iridium(IV), and Platinum(IV)

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Osmium(IV) dithioether complexes [$OsLCl_4$] [L = $RS(CH_2)_2SR$, RSCH=CHSR, or o-$C_6H_4(SR)_2$; R = Me or Ph] have been prepared from the ligands and sodium hexachloro-osmate(IV); [$OsL'Br_4$] (L' = $MeS(CH_2)_2SMe$ or MeSCH=CHSMe) are formed from $K_2[OsBr_6]$. Iridium(III) anions, $[NMe_4][IrLCl_4]$, *cis*- and *trans*-$[Ir(SMe_2)_2Cl_4]^-$, $[Ir(SPh_2)_2Cl_4]^-$, and $[Ir(SPh_2)Cl_5]^{2-}$, are oxidized by chlorine to the corresponding iridium(IV) complexes. Halogen oxidation of [$PtLX_4$] produces [$PtLX_4$] (X = Cl or Br) and two unstable complexes [$PtL''I_4$] [L'' = $MeS(CH_2)_nSMe$, n = 2 or 3]. Attempts to prepare thioether complexes of Ru^{IV}, Rh^{IV}, Pd^{IV}, Co^{III}, and Ni^{III} have been unsuccessful. The isolated complexes have been characterized by i.r. and electronic spectroscopy, and where appropriate magnetic measurements and ^1H n.m.r. spectroscopy. Variable-temperature ^1H n.m.r. spectra show that inversion at sulphur co-ordinated to Pt^{IV} is more difficult than in the platinum(II) analogues. Thermal decomposition of [$PtLX_4$] (X = Cl, Br, or I) involves both dehalogenation and dealkylation.

THE ability of tertiary phosphine and arsine ligands to stabilize higher oxidation states of the Group 8 metals is well known.[1] Charged sulphur-donor ligands, dithiocarbamates, and 1,1-dithiolenes are similarly effective,[2,3] but neutral sulphur donors have been little studied. Thioether complexes are known for metals in their normal oxidation states, *e.g.* cobalt(II),[4] nickel(II),[4,5] ruthenium(III),[6,7] rhodium(III),[8-10] palladium(II),[11,12] and platinum(II).[11,12] Iridium(III) complexes are isolated with difficulty [9] and only one osmium complex has been reported.[13] The only complexes of metals in their higher oxidation states are *cis*- and *trans*-$[Pt(SMe_2)_2X_4]$ (X = Cl or Br),[14] *trans*-$[Pt(SMe_2)_2I_4]$,[15] $[Pt(SMe_2)X_5]^-$,[14] and *trans*-$[Ir(SEt_2)_2Cl_4]$.[16,17] Here we report some systematic attempts to prepare higher oxidation state complexes with mono- and di-thioethers.

RESULTS

Osmium.—The reaction of osmium tetraoxide or potassium tetrahydroxodioxo-osmate(VI), $K_2[OsO_2(OH)_4]$, in concentrated hydrochloric acid with 2,5-dithiahexane, $MeSCH_2CH_2SMe$, in alcohol gave poor yields of the green complex $[Os(MeSCH_2CH_2SMe)Cl_4]$, but attempts to extend this to other thioethers were not very successful. A more general route is from sodium hexachloro-osmate(IV) and the thioether in refluxing 2-ethoxyethanol. The reactions required 2—3 h at reflux and gave *ca.* 30—65% yields of [$OsLCl_4$] [L = $MeSCH_2CH_2SMe$, *cis*-MeSCH=CHSMe, o-$C_6H_4(SMe)_2$, $PhSCH_2CH_2SPh$, PhSCH=CHSPh, or o-$C_6H_4(SPh)_2$]. More prolonged refluxing gave carbonyl complexes (*cf.* ref. 7). 2,6-Dithiaheptane, $MeS(CH_2)_3SMe$, gave very poor yields of a yellow-green carbonyl complex which has not been completely characterized, and no reaction seemed to occur with 1,3-di(phenylthio)propane, diphenyl sulphide, or dimethyl sulphide. Osmium tetraoxide, aqueous HBr, and various dithioethers yielded only brown oils. However, $K_2[OsBr_6]$ reacted with the ligands in 2-ethoxyethanol to form grey-green [$OsLBr_4$] [L = $MeS(CH_2)_2SMe$ or MeSCH=CHSMe]. Attempts to prepare iodo-complexes from $K_2[OsI_6]$ gave intractable green oils. Thioethers are only weak reducing agents and, in contrast to the corresponding phosphine reactions,[18] reduction to lower oxidation states of osmium was not a problem.

The osmium(IV) complexes (Table 1) are slightly soluble in most organic solvents, and easily soluble in dimethyl sulphoxide (dmso), in which they are non-electrolytes. The magnetic moments ($\mu_{eff.}$ 1.3—1.4 B.M.) † are much lower than the 'spin-only' value for a low-spin d^4 ion (2.8 B.M.), but are comparable with those reported for $[Os(PR_3)_2X_4]$ [18] or $[OsX_6]^{2-}$.[19] In contrast to the $[Os(PR_3)_2Cl_4]$ complexes which exhibit sharp ^1H n.m.r. spectra,[20] we did not observe n.m.r. spectra for [$OsLCl_4$], presumably due to unfavourable relaxation times. The far-i.r. spectra of [$OsLCl_4$] contains three or four partially resolved bands assignable as ν(Os–Cl) (Table 1), consistent with a *cis*-octahedral structure for which theory predicts four i.r.-active bands ($2A_1 + B_1 + B_2$). The bromo-complexes give several medium-intensity absorptions in the range 180—250 cm^{-1} but assignment of ν(Os–Br) is not possible with any certainty The electronic spectra of the complexes [$OsLCl_4$] consist of several broad absorptions with rather ill defined maxima which are assigned as ligand→Os(t_{2g}) charge-transfer transitions. The spectra are broadly similar to those of $[Os(PR_3)_2Cl_4]$,[21] but the lowest-frequency transition (σ) is at higher energy for the thioethers. This is expected on the basis of Jørgensen's optical electronegativity concept,[22] $\sigma(cm^{-1}) = 30 \times 10^3[\chi_{opt.}(SR_2) - \chi_{opt.}M]$; adopting Chatt's [7] value of 2.9 for $\chi_{opt.}(SR_2)$ and estimating $\chi_{opt.}Os^{IV}$ as 2.3,[21] this predicts $\sigma = 18 \times 10^3$ cm^{-1}. The value is necessarily approximate since $\chi_{opt.}Os^{IV}$ was not corrected for spin-pairing or spin-orbit effects. The spectra of the bromo-complexes were similar.

Iridium.—Chatt *et al.*[9] were able to prepare only a few iridium(III) thioether complexes, dithioethers in particular giving oils. We too obtained oils from a variety of solvents, but treatment of the oil from the reaction of $IrCl_3 \cdot 3H_2O$ + $2MeS(CH_2)_2SMe$ with Cl_2–CCl_4 produced a pink solid $[\{Ir(MeSCH_2CH_2SMe)Cl_3\}_n]$. This is insoluble in all common solvents and is probably polymeric (*cf.* the Rh complex [8]). Further treatment with chlorine for 1 month produced only superficial conversion into a red product. In marked contrast to the difficulties encountered in attempts to prepare neutral complexes, anionic $[IrLCl_4]^-$ species are easily obtained as tetramethylammonium salts by combin-

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† Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

TABLE 1

Analytical, physical, and spectroscopic data

Complex	Colour	Analyses (%) [a] C	H	N	ν(M–X)/cm^{-1}	10^{-3} $E_{max.}(\epsilon)$/[b] cm^{-1}	$\mu_{eff.}$/ B.M.[c]	Λ/[d] ohm^{-1} cm^2 mol^{-1}
[Pt(MeSCH$_2$CH$_2$SMe)Cl$_4$]	Deep yellow	10.0 (9.8)	2.1 (2.0)		358, 340, 324, 298	28.80 (sh), 31.70 (sh)	diam	5.5
[Pt(MeSCH$_2$CH$_2$CH$_2$SMe)Cl$_4$]	Deep yellow	12.5 (12.7)	2.5 (2.5)		358, 338, 311, 305	*ca.* 27.0 (sh), 34.00 (15 460)		
[Pt(*cis*-MeSCH=CHSMe)Cl$_4$]	Yellow	10.5 (10.5)	1.9 (2.0)		357, 337, 322, 297	*ca.* 29.0 (sh), 34.90 (5 958)		
[Pt{*o*-C$_6$H$_4$(SMe)$_2$}Cl$_4$]	Yellow	18.6 (18.8)	2.2 (2.0)		355, 349, 312, 294	*ca.* 27.0 (sh), 31.50 (8 500)		
[Pt(PhSCH$_2$CH$_2$SPh)Cl$_4$]	Deep yellow	29.0 (28.8)	2.5 (2.4)		356, 336, 328, 292	30.25 (sh), 31.00 (26 400)		6.3
[Pt(PhSCH$_2$CH$_2$CH$_2$SPh)Cl$_4$]·CH$_2$Cl$_2$	Deep yellow	27.9 (28.1)	2.4 (2.6)		356, 336, 318, 289	31.50 (14 500)		
[Pt(*cis*-PhSCH=CHSPh)Cl$_4$]	Deep yellow	29.8 (29.8)	2.4 (2.1)		356, 342, 320, 292	30.70 (sh), 33.50 (6 260)		
[Pt{*o*-C$_6$H$_4$(SPh)$_2$}Cl$_4$]	Deep yellow	33.9 (34.2)	2.6 (2.2)		355, 348, 323, 285	29.10 (7 738), 34.70 (7 588)		
[Pt(MeSCH$_2$CH$_2$SMe)Br$_4$]	Orange	7.5 (7.2	1.4 (1.5)		263, 246, 224, 214	29.66 (19 240)		5.6
[Pt(MeSCH$_2$CH$_2$CH$_2$SMe)Br$_4$]	Orange	9.1 (9.3)	1.9 (1.8)		263, 249, 226, 208	28.00 (sh), 34.05 (11 050)		
[Pt(*cis*-MeSCH=CHSMe)Br$_4$]	Orange	8.1 (7.6)	1.1 (1.2)		265, 250, 226, 218	28.60 (8 900), 32.80 (9 250)		
[Pt{*o*-C$_6$H$_4$(SMe)$_2$}Br$_4$]	Orange	13.6 (14.0)	1.4 (1.4)		265, 251, 240, 223	27.00 (sh), 33.80 (sh)		
[Pt(PhSCH$_2$CH$_2$SPh)Br$_4$]	Orange	22.2 (22.1)	1.8 (1.8)		262, 246, 230, 218	28.87 (18 160), 34.60 (33 000)		
[Pt(PhSCH$_2$CH$_2$CH$_2$SPh)Br$_4$]·CH$_2$Cl$_2$	Orange	21.7 (22.3)	1.9 (2.0)		265, 248, 220, 216 (sh)	28.00 (19 000)		
[Pt(*cis*-PhSCH=CHSPh)Br$_4$]	Orange	21.7 (22.1)	1.8 (1.6)		265, 244, 235, 216	28.30 (16 530)		
[Pt{*o*-C$_6$H$_4$(SPh)$_2$}Br$_4$]	Orange	26.7 (26.7)	1.7 (1.7)		265, 244, 230, 217 (sh)	27.56 (9 000), 34.50 (8 010)		
[Pt(MeSCH$_2$CH$_2$SMe)I$_4$]	Black	6.1 (5.9)	1.1 (1.2)		215, 200w, 168, 163 (sh)	24.0br, 27.0, 33.0 [dr]		
[Pt(MeSCH$_2$CH$_2$CH$_2$SMe)I$_4$]	Black	7.4 (7.2)	1.5 (1.4)		218, 188, 168, 157	23.7br, 27.0, 32.0 [dr]		
[Ir(MeSCH$_2$CH$_2$SMe)Cl$_4$]	Red-purple	10.5 (10.5)	2.0 (2.0)		336 (sh), 326, 316, 303	17.40 (447) (sh), 19.60 (4 673), 22.3 (4 940)	1.72	
[Ir(MeSCH$_2$CH$_2$CH$_2$SMe)Cl$_4$]	Dark red	13.1 (12.8)	2.2 (2.5)		335 (sh), 325, 315 (sh), 303	16.90 (343), 19.65 (3.290), 22.4 (3 991), 34.4 (sh) (1 296)	1.70	
[Ir(*cis*-MeSCH=CHSMe)Cl$_4$]	Red-brown	10.2 (10.6)	1.6 (1.8)		333, 323, 315 (sh), 305	17.00 (325), 19.60 (3 074), 22.3 (3 124), 33.1 (946)	1.71	0.5
[Ir{*o*-C$_6$H$_4$(SMe)$_2$}Cl$_4$]	Dark red-brown	19.2 (19.0)	1.8 (2.0)		331, 324, 316, 308 (sh)	16.90 (575), 19.70 (2 465), 22.4 (2 605), 31.4 (1 225), 33.0 (1 495)	1.75	
[Ir(PhSCH$_2$CH$_2$SPh)Cl$_4$]	Dark red-brown	29.4 (29.1)	2.3 (2.4)		336 (sh), 329, 318, 305	17.00 (300), 19.90 (2 950), 22.4 (3 500), 33.0 (1 075)	1.70	1.2
[Ir(PhSCH$_2$CH$_2$CH$_2$SPh)Cl$_4$]	Dark red-brown	30.5 (30.3)	2.8 (2.7)		333, 328, 318, 306	17.00 (163), 19.80 (2 150), 22.5 (2 166), 33.0 (sh) (1 615)	1.77	
[Ir(*cis*-PhSCH=CHSPh)Cl$_4$]	Red-brown	30.0 (29.5)	1.9 (2.1)		333, 324, 314, 306 (sh)	17.00 (300), 19.80 (3 420), 22.5 (3 675), 33.2 (sh) (945)	1.69	
[Ir{*o*-C$_6$H$_4$(SPh)$_2$}Cl$_4$]	Red-brown	34.3 (34.4)	2.3 (2.2)		335, 327, 318, 310 (sh)	17.00 (345), 19.70 (3 330), 22.4 (3 340), 33.20 (991)	1.69	
cis-[Ir(SMe$_2$)$_2$Cl$_4$]	Purple	10.7 (10.45)	2.4 (2.6)		334 (sh), 326, 308	16.00 (sh), 19.30 (2 104), 20.60 (2 060), 23.6 (608), 29.0 (sh)	1.78 [e]	
trans-[Ir(SMe$_2$)$_2$Cl$_4$] [f]	Purple	11.5 (10.45)	2.8 (2.6)	0.8 (0.0)	330br	16.50 (sh), 19.30, 20.70, 23.2		
[NMe$_4$][Ir(MeSCH$_2$CH$_2$SMe)Cl$_4$]	Fawn	18.4 (18.1)	4.3 (4.2)	2.8 (2.8)	325, 318, 306, 290 (sh)	26.00 (180), 32.5 (sh)	diam	33
[NMe$_4$][Ir(PhSCH$_2$CH$_2$CH$_2$SPh)Cl$_4$]	Greenish fawn	33.3 (34.1)	3.9 (4.0)	2.3 (2.1)	320, 313, 296, 284 (sh)			
[NMe$_4$]*cis*-[Ir(SMe$_2$)$_2$Cl$_4$]	Pale orange	17.9 (18.0)	4.5 (4.5)	2.3 (2.4)	315br, 286 [Raman 316, 299, 288 (sh)]		diam	103 [g]
[NMe$_4$]*trans*-[Ir(SMe$_2$)$_2$Cl$_4$]	Khaki	17.6 (18.0)	4.2 (4.5)	2.3 (2.4)	315, 293			Insoluble
[NMe$_4$]*cis*-[Ir(SPh$_2$)$_2$Cl$_4$]	Fawn	43.1 (43.1)	4.8 (4.1)	1.6 (1.7)	325, 310, 290 (sh)			
[NEt$_4$][Ir(MeSCH$_2$CH$_2$SMe)Br$_4$]	Fawn	13.6 (13.6)	3.0 (3.1)	2.0 (2.1)	224, 212, 205 (sh), 194			34
[NMe$_4$]$_2$[Ir(SPh$_2$)Cl$_5$]	Fawn	34.3 (34.1)	4.5 (4.8)	3.7 (4.0)	318, 308, 294			170 [g]
[{Ir(MeSCH$_2$CH$_2$SMe)Cl$_3$}$_n$]	Pink	10.9 (11.4)	2.2 (2.4)			insoluble		
[NMe$_4$][Ru(MeSCH$_2$CH$_2$SMe)Cl$_4$]	Dark brown	22.8 (21.8)	4.8 (5.0)	3.3 (3.2)	340 (sh), 320, 316	16.85 (925), 20.00 (sh), 23.35 (5 300)	1.78	39
[AsPh$_4$][Ru(MeSCH$_2$CH$_2$SMe)Cl$_4$]·Me$_2$CO	Dark red	46.5 (46.2)	4.2 (4.4)		340 (sh), 320, 318, 290 (sh)	16.40 (934), 20.10 (sh), 23.50 (5 587) (CH$_2$Cl$_2$)	1.80	28.5
[NEt$_4$][Rh(MeSCH$_2$CH$_2$SMe)Cl$_4$]	Orange	28.7 (29.0)	5.9 (6.0)	2.8 (2.8)	342, 316, 285	21.75 (sh), 24.7 (692)	diam	31
[Au(MeSCH$_2$CH$_2$SMe)Cl$_2$][AuCl$_4$]	Yellow	6.4 (6.6)	1.2 (1.4)		350, 330, 285	29.75 (2 032) (MeCN)	diam	45.5
[Au(MeSCH$_2$CH$_2$CH$_2$SMe)Cl$_2$][AuCl$_4$]	Yellow	8.1 (8.1)	1.4 (1.6)		354, 330, 287	28.50 (—) (MeCN)		decomp.
[Au(MeSCH=CHSMe)Cl$_2$][AuCl$_4$]	Yellow	6.5 (6.3)	1.1 (1.1)		356, 325, 281	26.40 (sh) (335), 30.8 (2 830) (MeCN)		decomp.
[Au(MeSCH$_2$SMe)Br$_2$]Br	Red	8.9 (8.6)	1.0 (1.0)		228, 186	25.35 (2 760), 32.90 (1 426) (MeCN)		40.2
[Au(MeSCH$_2$CH$_2$SMe)I$_2$]I	Black	7.0 (6.9)	1.3 (1.4)		138, 118 (?)	19.5 (—), 28.0 (sh), 32.40 (sh) (MeCN)		decomp.
[Au(PhSCH$_2$CH$_2$SPh)Cl$_2$]	Yellow	31.8 (30.6)	2.3 (2.5)			30.50 (sh) (—) (MeCN)		decomp.
[Os(MeSCH$_2$CH$_2$SMe)Cl$_4$]	Green	10.9 (10.6)	2.4 (2.2)		333 (sh), 318, 299	16.20 (240), 24.70 (1 930), 27.20 (2 915)	1.36	0.6
[Os{*o*-C$_6$H$_4$(SMe)$_2$}Cl$_4$]	Green	18.8 (19.1)	1.8 (2.0)		330 (sh), 316, 296 (sh)	16.50 (296), 24.50 (sh), 26.90 (1 320), 28.80 (1 700)	1.31	
[Os(MeSCH=CHSMe)Cl$_4$]	Grey-green	10.9 (10.6)	1.9 (1.8)		328 (sh), 320, 314 (sh), 302	17.70 (876), 24.00 (sh), 26.50 (sh), 28.75 (3 400)	1.32	
[Os(PhSCH$_2$CH$_2$SPh)Cl$_4$]	Grey-green	30.1 (29.2)	2.4 (2.4)		326 (sh), 314, 298	17.80 (630), 23.00 (sh), 26.20 (sh), 28.90 (3 280)	1.32	0.4
[Os(PhSCH=CHSPh)Cl$_4$]	Grey-green	29.6 (29.2)	2.4 (2.1)		324, 313, 301, 295 (sh)	17.00 (700), 25.60 (sh), 28.90 (5 275)	1.35	
[Os{*o*-C$_6$H$_4$(SPh)$_2$}Cl$_4$]	Green	34.0 (34.5)	1.9 (2.2)		326 (sh), 315, 304	17.20 (735), 24.50 (sh), 27.70 (9 425)	1.37	
[Os(MeSCH$_2$CH$_2$SMe)Br$_4$]	Green	7.8 (7.6)	1.3 (1.5)			17.00 (221), 21.50 (1 127), 24.95 (5 950), 28.60 (8 630)	1.40	
[Os(MeSCH=CHSMe)Br$_4$]	Grey-green	7.5 (7.6)	1.6 (1.3)			17.70 (103), 22.5 (sh), 27.50 (sh),	1.36	

[a] Calculated values are given in parentheses. [b] Electronic solution spectra except [dr] = diffuse reflectance. Solutions in dmso unless otherwise specified. Absorption coefficients (ϵ/dm^3 mol^{-1} cm^{-1}) are given in parentheses. [c] $\pm$0.05 B.M. by the Gouy method; diam = diamagnetic. [d] In 10^{-3} mol dm^{-3} dmso. [e] By Evans n.m.r. method [f] Contaminated with [NMe$_4$]Cl. [g] In Me$_2$CO; 1 : 1 electrolytes in dmso have Λ = 25—40 ohm^{-1} cm^2 mol^{-1}; in acetone Λ 100—140 for 1 : 1, 160—200 ohm^{-1} cm^2 mol^{-1} for 1 : 2 electrolytes (W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81).

ation of IrCl$_3$·3H$_2$O, [NMe$_4$]Cl, and the dithioether in ethanol. These are buff or fawn solids, readily soluble in polar solvents, in which they are 1 : 1 electrolytes. Spectroscopic data on [NMe$_4$][Ir(MeSCH$_2$CH$_2$SMe)Cl$_4$], a typical example, are given in Tables 1 and 3. The complexes can also be prepared from Na$_2$[IrCl$_6$], but in this case 2-methoxyethanol or *NN*-dimethylformamide (dmf) is required in place of ethanol.

The [NMe$_4$][IrLCl$_4$] compounds are converted into deep red-brown or purple iridium(IV) complexes by Cl$_2$–CCl$_4$ at room temperature. The iridium(IV) complexes are slightly soluble in dmso and insoluble in or reduced by other solvents, which prevented recrystallization to remove the [NMe$_4$]Cl produced as a by-product. However, the latter was removed by washing with nitromethane, leaving analytically pure [IrLCl$_4$] [L = MeS(CH$_2$)$_n$SMe or PhS-

TABLE 2

Proton n.m.r. spectral data on platinum(IV) complexes [a]

Complex	δ/p.p.m.[b]	^3J(Pt–H)/Hz [c]	Coalescence temperature/ °C	Δ shift [d]
$[Pt(MeSCH_2CH_2SMe)Cl_4]$	2 61 (2.62)	36.0	>150 (120)	0.52
$[Pt(MeSCH_2CH_2CH_2SMe)Cl_4]$	2.49 (2.62)	33.3	96 (30)	0.44
$[Pt(MeSCH{=}CHSMe)Cl_4]$	2.78 (2.82)	32.4	90 (35)	0.50
$[Pt\{o\text{-}C_6H_4(SMe)_2\}Cl_4]$	2.89 (3.03)	32.4	*e*	0.44
$[Pt(MeSCH_2CH_2SMe)Br_4]$	2.63 (2.66)	36.0	120 (92)	0.54
$[Pt(MeSCH_2CH_2CH_2SMe)Br_4]$	2.61 (2.70)	36.0	85 (<20)	0.56
$[Pt(MeSCH{=}CHSMe)Br_4]$	2.91 (2.89)	32.4	50 (<20)	0.63
$[Pt\{o\text{-}C_6H_4(SMe)_2\}Br_4]$	*f*			
$[Pt(MeSCH_2CH_2SMe)I_4]$	2.75 (2.68) [f]	45.0		
$[Pt(MeSCH_2CH_2CH_2SMe)I_4]$	2.75 (2.75) [f]	45.0		

[a] In $(CD_3)_2SO$ relative to $SiMe_4$. [b] Average of DL and *meso* resonances; values in parentheses are those of platinum(II) analogues from ref. 12. [c] Platinum(II) analogues have ^3J(Pt–H) 44—48 Hz. [d] Shift of CH_3 resonance relative to free ligand. [e] Reduction occurs on warming. [f] Reduction occurs in dmso even at room temperature.

$(CH_2)_nSPh$, $n = 2$ or 3; RSCH=CHSR or o-$C_6H_4(SR)_2$, R = Me or Ph], Table 1. The solids are indefinitely stable, but dmso solutions decompose in a few hours. The magnetic moments are *ca.* 1.7 B.M., consistent with d^5 ($t_{2g}{}^5,e_g{}^0$) iridium(IV), and the far-i.r. spectra show the four ν(Ir–Cl) vibrations expected for a *cis*-octahedral complex. A comparison with the corresponding $[IrLCl_4]^-$ spectra shows that oxidation results in a shift of ν(Ir–Cl) to higher frequency by 10—15 cm^{-1}. The electronic spectra of the complexes $[IrLCl_4]$ either in dmso solution or in Nujol mulls consist of two intense absorptions at *ca.* 19 700 and 22 500 cm^{-1}, and a weaker absorption at 17 000 cm^{-1} assigned as (S, Cl)$\rightarrow$Ir (t_{2g}) charge-transfer bands, whilst broader absorptions at 30 000—35 000 cm^{-1} are probably (S, Cl)$\rightarrow$Ir (e_g) charge-transfer bands.[17] Attempts to oxidise $[NMe_4][Ir(MeSCH_2CH_2SMe)Br_4]$ to Ir^{IV} were unsuccessful, and $[Ir(MeSCH_2CH_2SMe)Cl_4]$ in dmso was reduced by KBr or KI to iridium(III). Reaction of $[NMe_4]Cl$ and $IrCl_3{\cdot}3H_2O$ with dimethyl sulphide formed $[NMe_4][Ir(SMe_2)_2Cl_4]$, which was separated by extraction with acetone into soluble pale orange and insoluble fawn products. The ^1H n.m.r. spectrum of the orange form in $(CD_3)_2CO$ had $\delta(SMe_2) = 2.25$, whilst a freshly prepared $(CD_3)_2SO$ solution [*] of the fawn form had $\delta(SMe_2) = 2.52$, indicating these are *cis* and *trans* isomers respectively.[10] Vibrational spectra were less helpful in identifying the isomers. The orange *cis* form had a very broad absorption at 315 cm^{-1} and a second band at 286 cm^{-1}, whilst the Raman spectrum had bands at 316, 299, and 288 (sh) cm^{-1}, compared with the four i.r.- and Raman-active bands predicted ($2A_1 + B_1 + B_2$). The i.r. spectrum of '*trans*'-$[NMe_4][Ir(SMe_2)_2Cl_4]$ has two bands of similar intensity at 315 and 293 cm^{-1} which may be the E_u mode split by solid-state effects,[22] although it is possible that the band at 315 cm^{-1} is the E_u and that at 293 cm^{-1} is either the A_{2u} (Ir–S) or the C_2S deformation. The compound decomposed in the laser beam and a Raman spectrum was not obtained. We note that the spectra of the $[Ir(SMe_2)_2Cl_4]^-$ isomers are similar to those of the corresponding *cis*- and *trans*-$[Ir(py)_2Cl_4]^-$ complexes (py = pyridine).[23] The *cis* and *trans* isomers of $[Rh(SMe_2)_2Cl_4]^-$ have recently been identified (but not apparently separated [10]), and *trans*-$[Ir(SEt_2)_2Cl_4]^-$ has been separated from the polymerization isomer $[Ir(SEt_2)_4Cl_2]$-$[Ir(SEt_2)_2Cl_4]$.[16] The reaction of $[NMe_4]Cl$ and $IrCl_3{\cdot}3H_2O$ with diphenyl sulphide produced a fawn complex $[NMe_4][Ir(SPh_2)_2Cl_4]$, which was probably the *cis* isomer (Table 1), although a small proportion of the *trans* isomer would not have been detected from the far-i.r. spectrum. An attempt to prepare $[NMe_4]_2[Ir(SMe_2)Cl_5]$ produced a complicated mixture, but $[NMe_4]_2[Ir(SPh_2)Cl_5]$ was readily isolated from the constituents mixed in the correct ratio. Chlorine oxidation of *cis*-$[NMe_4][Ir(SMe_2)_2Cl_4]$ and recrystallization from CH_2Cl_2 produced purple $[Ir(SMe_2)_2Cl_4]$, which has a similar far-i.r. spectrum to $[Ir(MeSCH_2CH_2SMe)Cl_4]$ and is thus the expected *cis* isomer. It is similar to $[IrLCl_4]$ but more soluble in organic solvents, and more easily decomposed. Oxidation of *trans*-$[NMe_4][Ir(SMe_2)_2Cl_4]$ occurred much more rapidly than for the *cis* isomer, and also produced a purple complex, but this could not be obtained pure; some decomposition occurred on recrystallization even from cold CH_2Cl_2. The far-i.r. spectrum of the crude product contained a single band at 330 cm^{-1}, confirming it contains *trans*-$[Ir(SMe_2)_2Cl_4]$. The electronic spectra of *cis*- and *trans*-$[Ir(SMe_2)_2Cl_4]$ are very similar, which is not unexpected, since charge-transfer spectra are generally insensitive to stereochemistry. The diphenyl sulphide complexes $[NMe_4][Ir(SPh_2)_2Cl_4]$ and $[NMe_4]_2[Ir(SPh_2)Cl_5]$ also underwent oxidation on treatment with chlorine, forming purple solutions with electronic spectra characteristic of Ir^{IV}, but the products were too unstable to be isolated in the pure state.

TABLE 3

Proton n.m.r. data for other complexes [a]

	δ		
	$NR_4{}^+$	Me–S	Others
$[NMe_4][Ir(MeSCH_2CH_2SMe)Cl_4]$	3.1 (s)	2.29	3.4 (m) CH_2
$[NEt_4][Rh(MeSCH_2CH_2SMe)Cl_4]$	1.2 (t), 3.3 (q)	2.15 (d)	3.1 (m) CH_2
$[NMe_4]$[*cis*-$Ir(SMe_2)Cl_4]$	3.1 (s)	2.25	
$[NMe_4]$[*trans*-$Ir(SMe_2)_2Cl_4]$ [b]	3.1 (s)	2.52	
$[NMe_4]$[*cis*-$Ir(SPh_2)_2Cl_4]$ [c]	3.0 (s)		7.4 Ph–S
$[NEt_4][Ir(MeSCH_2CH_2SMe)Br_4]$	1.2 (t), 3.3 (q)	2.36	3.1 (m) CH_2
$[NMe_4]_2[Ir(SPh_2)Cl_5]$ [c]	2.85 (s)		7.35 (Ph–S)

[a] In $(CD_3)_2SO$ unless otherwise stated. [b] Freshly prepared solution in $(CD_3)_2SO$. [c] In $(CD_3)_2CO$.

Platinum.—Unidentate thioether complexes have been thoroughly studied [14,15] and the present study was confined to dithioethers. Oxidation of $[PtLX_2]$ [12] [L = $RS(CH_2)_nSR$, R = Me or Ph, $n = 2$ or 3; *cis*-RSCH=CHSR or o-$C_6H_4(SR)_2$, X = Cl or Br] with the appropriate halogen in CCl_4–CH_2Cl_2 gave high yields of $[PtLX_4]$. These complexes are insoluble in $CHCl_3$, Me_2CO, or MeCN, and slightly soluble in dmf and dmso. In Nujol mulls or dmso

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[*] The solution decomposes rapidly, the $\delta(SMe_2) = 2.52$ being replaced by a signal at 2.2 which we assign to a mono(dimethyl sulphide) complex, and finally by a single peak at 2.0 corresponding to the free ligand.

solution the electronic spectra consist of broad intense absorptions at 27 000—35 000 cm^{-1} assignable as (S, Cl)→ Pt (e_g) transitions, which completely obscured the expected '*d–d*' bands. The far-i.r. spectra (Table 1) are consistent with *cis*-octahedral complexes. The ^1H n.m.r. spectra in $(CD_3)_2SO$ of the complexes of the methyl-substituted dithioethers showed the two closely spaced resonances expected for *meso* and DL forms of the co-ordinated ligand.[12] The shifts in δ(Me–S) on co-ordination are similar to those for the platinum(II) analogues (Table 2), but ^3J(PtH) is significantly smaller for the platinum(IV) complexes. Poor solubility and the reduction of several complexes by dmso on heating complicated attempts to record the variable temperature n.m.r. spectra, but approximate coalescence temperatures were obtained. These reveal that inversion at sulphur co-ordinated to Pt^{IV} is more difficult than at Pt^{II}, and is again markedly dependent upon the *trans* X group and the ligand backbone.

Spectrophotometric studies on mixtures of $[PtLI_2]$ and I_2 in CH_2Cl_2 suggested a new species, possibly $[PtLI_4]$, was present in equilibrium with the starting materials. However, attempts to isolate platinum(IV) complexes produced brownish black solids which lost iodine on washing with CCl_4, leaving $[PtLI_2]$. Only in the cases of $MeSCH_2CH_2SMe$ and $MeSCH_2CH_2CH_2SMe$ were black $[PtLI_4]$ complexes obtained which did not lose iodine. Their far-i.r. and solid reflectance spectra (Table 1) are in keeping with the platinum(IV) formulation. They dissolve only in dmso and the solutions have identical electronic spectra to free iodine, and the ^1H n.m.r. spectra, ^3J(PtH) *ca.* 46 Hz, suggest platinum(II) complexes. The dissociation of $[Pt(PtMe_3)_2I_4]$ into $[Pt(PMe_3)_2I_2] + I_2$ has been noted previously,[14] and in the present case because dmso and iodine form a charge-transfer complex (evident from the shifts in the u.v. spectrum of iodine), the equilibrium is shifted in favour of Pt^{II}.

TABLE 4

Thermogravimetric data on the platinum(IV) complexes

Complex	Wt. loss/% [a]	Calc.wt.loss $(-X_2)$/%	Calc.wt.loss$(-X_2, -2RX)$/%
$[Pt\{o\text{-}C_6H_4(SPh)_2\}Cl_4]$	11.9	11.25	
$[Pt\{o\text{-}C_6H_4(SPh)_2\}Br_4]$	20.6	19.8	
$[Pt(MeSCH_2CH_2CH_2SMe)Cl_4]$	35.8	15.0	36.4 $(-Cl_2, -2MeCl)$ 38.9 $[-Cl_2, -Cl(CH_2)_3Cl]$
$[Pt\{MeSCH_2CH_2CH_2SMe)Br_4]$	50.5	24.6	53.7 $(-Br_2, -2MeBr)$ 55.6 $[-Br_2, -Br(CH_2)_3Br]$
$[Pt(PhSCH_2CH_2CH_2SPh)Cl_4]$	29.4	11.9	30.8 $[-Cl_2, -Cl(CH_2)_3Cl]$
$[Pt\{o\text{-}C_6H_4(SMe)_2\}Cl_4]$	35.4	14.0	34.0 $(-Cl_2, -2MeCl)$
$[Pt(MeSCH_2CH_2CH_2SMe)I_4]$	15.5 [b]	30.2	

[a] Estimated error ±2%. [b] Weight loss before melting (see text) corresponding to −I (15.1%).

The complex $[Pt(MeSCH_2CH_2SMe)_2][ClO_4]_2$ [12] was insoluble in, and apparently unaffected by, Cl_2–CCl_4, but a solution in nitromethane became deep yellow on treatment with chlorine, and $[Pt(MeSCH_2CH_2SMe)Cl_4]$ precipitated from the solution on standing.

Chatt [24] demonstrated that thermal decomposition of $[Pt(PR_3)_2Cl_4]$ gave principally $[Pt(PR_3)_2Cl_2]$. We examined the decomposition of $[PtLX_4]$ by t.g.a.; typical results are given in Table 4. The results for complexes of o-$C_6H_4(SPh)_2$ are in good agreement with loss of X_2 to form $[PtLX_2]$, but for the other ligands the reactions are more complicated. There is a slow loss of halogen over a wide temperature range, but then the complexes melt with decomposition and the total weight loss corresponds to loss of halogen (X_2) and dealkylation, which occur together. The weight losses (Table 4) demonstrate that alkyl but not aryl groups are lost in this way, but the results are not sufficiently accurate to determine whether for $MeS(CH_2)_3SMe$ the terminal Me groups, or the $(CH_2)_3$ backbone, or a combination of both are lost. Indeed violent foaming seems to accompany the decomposition, making accurate measurements difficult. In the cases of $[PtLI_4]$ this foaming was so violent that reproducible results were not obtained for dealkylation, but before melting the weight loss indicated formation of an approximate $PtLI_3$ composition, perhaps related to the Wollfram [25] red salts.

Ruthenium, Rhodium, and Palladium.—The $[PdLCl_2]$ complexes [12] were not oxidized by Cl_2–CCl_4, concentrated nitric acid, cerium(IV), or potassium persulphate. Irradiation of a suspension of $[Pd(MeSCH_2CH_2SMe)Cl_2]$ in CCl_4–$CHCl_3$ saturated with Cl_2 at −25 °C was similarly unsuccessful. The rhodium(III) complexes $[\{Rh(MeSCH_2CH_2SMe)Cl_3\}_n]$ and $[Rh(MeSCH_2CH_2SMe)_2Cl_2][BF_4]$ [8,9] were also unaffected by Cl_2–CCl_4 or cerium(IV). By analogy with the iridium complexes, oxidation of a rhodium anion might have been more successful, and $[NEt_4][Rh(MeSCH_2CH_2SMe)Cl_4]$ was readily obtained from $[NEt_4]Cl$, $RhCl_3{\cdot}3H_2O$, and 2,5-dithiahexane in aqueous ethanol. However, this complex was not oxidized by chlorine, and cyclic voltammetry (below) also gave no evidence of reversible oxidation to Rh^{IV}.

Ruthenium(III) complexes [6,7] including $[Ru(MeSCH_2CH_2SMe)Cl_3]$ and $[Ru(MeSCH_2CH_2SMe)_{1\cdot5}Cl_3]$ were not oxidized by Cl_2–CCl_4 or cerium(IV). The ruthenium(III) anion $[Ru(MeSCH_2CH_2SMe)Cl_4]^-$ was obtained as $AsPh_4^+$ and NMe_4^+ salts from $RuCl_3{\cdot}3H_2O$, 2,5-dithiahexane, and $[AsPh_4][HCl_2]$ in acetone or $[NMe_4]Cl$ in absolute alcohol. The properties of this anion (Table 1) are similar to those of $[Ru(PR_3)_2Cl_4]^-$.[26] It did not undergo either chemical or electrochemical oxidation to Ru^{IV}; indeed, whilst it was unaffected by chlorine in dry solvents, an excess of chlorine in wet CCl_4 removed the dithioether and $[NMe_4]_2[RuCl_5(OH_2)]$ was produced.

3d *Metals.*—The only iron(III) thioether complexes known are the very moisture-sensitive $[FeL'X_2][FeX_4]$ (L′ = tetrathioether, for example $MeS(CH_2)_2S(CH_2)_2S(CH_2)_2SMe$, X = Cl or Br).[27] In our hands mono- and di-thioethers produced only intractable oils even under rigorously anhydrous conditions. Both $[Co(MeSCH_2CH_2SMe)_2Cl_2]^4$ and $[Cu(MeSCH_2CH_2SMe)Cl_2]$ [28] were decomposed by Cl_2–CCl_4. The complex $[Ni(MeSCH_2CH_2SMe)_2Cl_2]$ [29] was not attacked by dry Cl_2–CCl_4 at 0 °C, but decomposed on warming or in the presence of moisture.

Gold.—Gold(III) complexes $[AuLX_2]^+$ were examined, as we hoped to compare their ^1H n.m.r. spectra with those of the isoelectronic $[PtLX_2]$.[12] Schmidbauer's method [30] was used to prepare [Au(MeSCH$_2$CH$_2$SMe)X$_2$]Y (X = Cl, Br, or I; Y = AuCl$_4$ or X) and [AuLX$_2$][AuCl$_4$] [L = MeSCH=CHSMe or MeS(CH$_2$)$_3$SMe] were obtained similarly. The 2,6-dithiaheptane complex decomposed unless refrigerated producing a red oil with the pungent odour of chlorosulphane, but the others are stable in the solid state. Chlorine oxidation of phenyldithioether complexes [ClAu(PhSCH$_2$CH$_2$SPh)AuCl] and [ClAu(PhSCH=CHSPh)AuCl] proceeded readily, but generally yellow oils were produced; only one solid, [Au(PhSCH$_2$CH$_2$SPh)Cl$_3$], was isolated. Physical data on these complexes are given in Table 1. The complexes dissolved only in (CD$_3$)$_2$SO of the common n.m.r. solvents, but decomposition was rapid even at room temperature and reliable spectral data were not obtained.

Electrochemistry.—Cyclic voltammetry is being increasingly used to study unusual oxidation states,[1] and is particularly suitable when the redox reaction occurs without changes in co-ordination number and stereochemistry at the metal centre. For this reason we examined the oxidation of [M(MeSCH$_2$CH$_2$SMe)Cl$_4$]$^-$ as the NEt$_4$$^+$ salt for M = Rh, and as the more soluble AsPh$_4$$^+$ salts for M = Ru and Ir, in CH$_2$Cl$_2$ and MeCN solutions. There was no evidence for oxidation to M^{IV}, either reversible or irreversible, in the cases of M = Rh and Ru.* For [Ir(MeSCH$_2$CH$_2$SMe)Cl$_4$]$^-$ a reversible one-electron oxidation occurred to form the iridium(IV) complex at $E^\ominus$ = 1.4 V *versus* a standard saturated calomel electrode. Thus the electrochemical data support the results of chemical oxidation. Indication of a reversible one-electron reduction of [Os(MeSCH$_2$CH$_2$SMe)Cl$_4$] to [Os(MeSCH$_2$CH$_2$SMe)Cl$_4$]$^-$ was also obtained.

DISCUSSION

The results described show that thioether complexes of the quadrivalent 5*d* metals can be isolated and are reasonably stable. In contrast no complexes of the 4*d* metal(IV) ions or, with the exception of iron(III), of the 3*d* metal(III) ions have been characterized. Many factors contribute to the stability of a particular oxidation state,[32] and their relative importance varies from metal to metal, but some general points concerning the differences between thioethers and other neutral ligands can be made. Compared to amines, phosphines, and arsines, thioethers are weaker σ donors (π-acceptor ability will be unimportant in high oxidation states). The electronegative sulphur will be less efficient at transferring electron density to the metal centre to partially offset the high formal charge. Sulphur is also lower in the spectrochemical and nephelauxetic series than P or As and thus the low-spin states in these metal ions will be less stabilized on ligand-field grounds by thioethers. This is probably a major factor in the failure to obtain palladium(IV) complexes with SR$_2$. (Diphosphine and diarsine complexes are easily obtained but not particularly stable.[33]) The $t_{2g}{}^6$ configuration in Pd^{IV} will be particularly stabilized by ligands which produce large Δ values. For Pt^{IV} the increase in Δ (5*d* > 4*d*) makes the effect less noticeable; even ligands relatively low in the spectrochemical series can still stabilize Pt^{IV}.

It is apparent that the metal prefers to co-ordinate terminal halide ligands to neutralize the formal charge, hence [PtL$_2$][ClO$_4$]$_2$ oxidizes to [PtLCl$_4$] rather than [PtL$_2$Cl$_2$]$^{2+}$, and [IrLCl$_4$]$^-$ oxidizes readily whilst [Ir(SR$_2$)$_3$Cl$_3$] and [{Ir(MeSCH$_2$CH$_2$SMe)Cl$_3$}$_n$] do not. When the starting material is kinetically inert to ligand substitution, oxidation is often only viable if the starting material has the same stereochemistry as the product, hence the use of [IrLCl$_4$]$^-$ to prepare [IrLCl$_4$]. The stabilizing effect of the halide ions is as expected in the order Cl$^-$ > Br$^-$ > I$^-$, and dithioether complexes seem slightly more stable than monothioether analogues (*cf.* Ir^{IV}), which may merely reflect the greater ease with which unidentate ligands dissociate (the free ligands are reducing agents although much less so than PR$_3$). Finally, as noted before,[25] the effect of changing terminal groups or backbone in the dithioethers has only a small effect on the stability of the complexes.

EXPERIMENTAL

Dithioethers were prepared as previously described,[12] and SMe$_2$ and SPh$_2$ were commercial samples (Aldrich) used as supplied.

Physical Measurements.—Carbon, H, and N analyses were measured on an F & M Analyser. Infrared spectra were recorded for Nujol mulls on Perkin-Elmer 580 and 577 and Beckman IR II spectrometers, Raman spectra on a Cary 81, and electronic spectra on a Unicam SP 700. Proton n.m.r. spectra were obtained on Perkin-Elmer R12 and R32 spectrometers. Magnetic measurements were made by the Gouy method. Conductivities were obtained on a Cambridge Instruments conductivity bridge between Pt electrodes. Thermogravimetric measurements were made on a Stanton-Redcroft TG/750/770 with a STA/780 thermal analyser. Electrochemical measurements were carried out with a type DT 2 101 Hi-Tek potentiostat and a Hi-Tek PPR1 waveform generator. Solutions of tetrabutylammonium tetrafluoroborate (0.2 mol dm^{-3}) were used as base electrolyte.

Tetrachloro(2,5-*dithiahexane*)*platinum*(IV), [Pt(MeSCH$_2$CH$_2$SMe)Cl$_4$].—Finely powdered [Pt(MeSCH$_2$CH$_2$SMe)Cl$_2$] [12] (0.2 g, 0.5 mmol) was suspended in dichloromethane (20 cm^3) and a small excess of chlorine in carbon tetrachloride added. The mixture was stirred vigorously at room temperature for 3 h, the yellow crystalline product filtered off, rinsed with dichloromethane and diethyl ether, and dried *in vacuo*, yield 0.22 g (95%). The other platinum(IV) chloro-complexes were prepared similarly, as were [PtLBr$_4$] using the corresponding [PtLBr$_2$] complex [12] and Br$_2$–CCl$_4$, yields *ca.* 90%.

[Pt(MeSCH$_2$CH$_2$SMe)I$_4$].—The [Pt(MeSCH$_2$CH$_2$SMe)I$_2$] complex (0.5 mmol) was suspended in CCl$_4$ (20 cm^3) and iodine (0.38 g, 1.5 mmol), dissolved in the minimum amount of CCl$_4$, added. The solution was concentrated *in vacuo* to *ca.* 15 cm^3 and cooled to 0 °C for 6 h. The greenish black product was filtered off, suspended in CCl$_4$ (10 cm^3), and stirred for 5 min. This procedure was repeated until the washings were colourless. The residue was dried *in vacuo* (0.37 g, 89%). A similar method yielded [Pt(MeSCH$_2$CH$_2$CH$_2$SMe)I$_4$], but application to other [PtLI$_2$] complexes generally resulted in recovery of the starting material.

Tetraethylammonium *Tetrachloro*(2,5-*dithiahexane*)-*rhodate*(III), [NEt$_4$][Rh(MeSCH$_2$CH$_2$SMe)Cl$_4$].—Rhodium

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* A preliminary report on the irreversible oxidation of [Ru(SMe$_2$)$_3$Cl$_3$] to a ruthenium(IV) complex of transient stability has been published.[31]

trichloride hydrate (0.26 g, 1 mmol) in ethanol (10 cm^3), $[NEt_4]Cl\cdot H_2O$ (0.55 g, 3 mmol) in ethanol–water (1 : 1) (20 cm^3), and $MeSCH_2CH_2SMe$ (0.12 g, 1 mmol) were mixed, 1 cm^3 of concentrated hydrochloric acid added, and the mixture refluxed for 8 h. Concentration to small volume yielded an orange oil which was dissolved in ethanol (10 cm^3), filtered, and treated dropwise with diethyl ether. The yellow product was rinsed with ether and dried *in vacuo* (0.25 g, 50%).

Tetramethylammonium Tetrachloro(2,5-*dithiahexane*)-*iridate*(III), $[NMe_4][Ir(MeSCH_2CH_2SMe)Cl_4]$.—Iridium trichloride hydrate (0.35 g, 1 mmol) was dissolved in a mixture of concentrated hydrochloric acid (5 cm^3), water (20 cm^3), and $[NMe_4]Cl\cdot H_2O$ (0.13 g, 1 mmol) and $MeSCH_2CH_2SMe$ (0.12 g, 1 mmol) in ethanol (10 cm^3) added; the mixture was refluxed for 8 h. The product was evaporated to dryness, the residue dissolved in hot ethanol and concentrated to *ca.* 10 cm^3. On cooling a fawn powder separated, which was rinsed with diethyl ether and dried *in vacuo* (0.26 g, 49%). Tetramethylammonium tetrachloro(2,6-dithiaheptane)iridate(III) was made similarly using sodium hexachloroiridate(IV) (yield 45%). The phenyl-substituted dithioether anions $[NMe_4][IrLCl_4]$ were made similarly using 2-methoxyethanol [$L = PhS(CH_2)_nSPh$ or PhSCH=CHSPh), or *NN*-dimethylformamide as solvent [$L = o$-$C_6H_4(SPh)_2$], yields 45—55%.

Trichloro(2,5-*dithiahexane*)*iridium*(III), $[\{Ir(MeSCH_2CH_2SMe)Cl_3\}_n]$.—Reaction of $IrCl_3\cdot 3H_2O$ with several dithioethers produced only oils, as previously noted.[9] The buff oil from the reaction of $IrCl_3\cdot 3H_2O$ and $MeSCH_2CH_2SMe$ (1 : 2 mol ratio) in ethanol was dried *in vacuo*, and treated with Cl_2–CCl_4 (10 cm^3) with vigorous shaking. A pink solid was deposited which was filtered off, rinsed with CCl_4, and vacuum dried (yield *ca.* 25%).

Tetrachloro(2,5-*dithiahexane*)*iridium*(IV), $[Ir(MeSCH_2CH_2SMe)Cl_4]$.—Finely powdered $[NMe_4][Ir(MeSCH_2CH_2SMe)Cl_4]$ (0.55 g, 1 mmol) was suspended in CCl_4 (20 cm^3), excess of Cl_2–CCl_4 added (*ca.* 2 mmol Cl_2), and the mixture stirred for 24 h, during which time the solid slowly turned dark red. It was filtered off, rinsed with CCl_4, and dried *in vacuo*. The product was powdered, stirred with dry nitromethane (10 cm^3) overnight, filtered off, and dried. The Cl_2–CCl_4 oxidation was repeated and the solid finally filtered off, rinsed with CCl_4, and dried briefly *in vacuo*, yield 0.2 g (44%). The other iridium(IV) complexes were prepared similarly, yields 30—65%.

Tetraethylammonium Tetrabromo(2,5-*dithiahexane*)-*iridate*(III), $[NEt_4][Ir(MeSCH_2CH_2SMe)Br_4]$.—An aqueous solution of iridium trichloride (1 mmol) was boiled with sodium hydroxide (0.2 g). The black precipitate ($Ir_2O_3\cdot nH_2O$) was filtered off, rinsed with water, and dissolved in a mixture of hydrobromic acid (48%, 10 cm^3) and water (10 cm^3); the solution was filtered into a mixture of $[NEt_4]Br\cdot H_2O$ (0.19 g, 1 mmol) and $MeSCH_2CH_2SMe$ (0.12 g, 1 mmol) in ethanol (10 cm^3). The mixture was refluxed for 4 h, and then evaporated to *ca.* 5 cm^3. On standing a cream solid separated which was recrystallized from ethanol (0.15 g, 20%).

cis *and* trans *Isomers of Tetramethylammonium Tetrachlorobis*(*dimethyl sulphide*)*iridate*(III), $[NMe_4][Ir(SMe_2)_2Cl_4]$.—Iridium trichloride hydrate (0.71 g, 2 mmol) was dissolved in a mixture of concentrated hydrochloric acid (2 cm^3) and water (20 cm^3); $[NMe_4]Cl\cdot H_2O$ (0.25 g, 2 mmol) and dimethyl sulphide (0.25 g, 4 mmol) in ethanol (15 cm^3) were added, and the mixture refluxed for 2.5 h. The red solution was evaporated to dryness and the residue treated with four aliquots (50 cm^3) of hot acetone which were then filtered and combined. The acetone-insoluble khaki solid, the *trans* isomer, that remained was dried *in vacuo* (0.07 g, 7%). The acetone solution was concentrated to *ca.* 5 cm^3 and cooled to give an orange solid, the *cis* isomer, which was filtered off and dried *in vacuo* (0.63 g, 59%).

cis-*Tetrachlorobis*(*dimethyl sulphide*)*iridium*(IV), *cis*-$[Ir(SMe_2)_2Cl_4]$.—Finely powdered *cis*-$[NMe_4][Ir(SMe_2)_2Cl_4]$ (0.53 g, 1 mmol) was suspended in CCl_4 (20 cm^3), excess of Cl_2–CCl_4 added, and the mixture stirred for 24 h, during which time the solid slowly turned mauve. This was filtered off and washed with a small volume of Cl_2–CCl_4. The solid was treated with four aliquots (25 cm^3) of warm CH_2Cl_2 with Cl_2–CCl_4 (1 cm^3) present in each. These were combined and the mauve solution taken to dryness to give a mauve solid which was briefly dried *in vacuo* (0.21 g, 46%).

Tetramethylammonium Tetrachlorobis(*diphenyl sulphide*)-*iridate*(III), $[NMe_4][Ir(SPh_2)_2Cl_4]$.—Iridium trichloride hydrate (0.71 g, 2 mol) was dissolved in a mixture of concentrated hydrochloric acid (2 cm^3) and water (20 cm^3); $[NMe_4]Cl\cdot H_2O$ (0.25 g, 2 mmol) and diphenyl sulphide (0.75 g, 4 mmol) in ethanol (15 cm^3) were added, and the mixture refluxed for 2 h. The solution was transferred to the freezer and a brown solid separated. This was filtered off, washed with a cold water–ethanol mixture, and dried *in vacuo* (0.83 g, 53%). Tetramethylammonium pentachloro(diphenyl sulphide)iridate(III), $[NMe_4]_2[Ir(SPh_2)Cl_5]$, was prepared as above with a suitably adjusted mol ratio of reactants, yield 47%.

Tetrachloro(2,5-*dithiahexane*)*osmium*(IV), $[Os(MeSCH_2CH_2SMe)Cl_4]$.—Sodium hexachloro-osmate(IV) (0.45 g, 1 mmol) was dissolved in 2-ethoxyethanol (30 cm^3), and 2,5-dithiahexane (0.12 g, 1 mmol) added. The mixture was then refluxed for 3 h and the solution left to cool. This was treated with diethyl ether and light petroleum (b.p. 40—60 °C). The green solid that separated was washed with diethyl ether and dried *in vacuo* (0.3 g, 65%). The other osmium thioether complexes were prepared similarly by refluxing in 2-ethoxyethanol for 2—3 h.

Tetrabromo(2,5-*dithiahexane*)*osmium*(IV), $[Os(MeSCH_2CH_2SMe)Br_4]$.—Potassium hexabromo-osmate(IV) (0.75 g, 1 mmol) in 2-ethoxyethanol (30 cm^3) was refluxed for 3 h with 2,5-dithiahexane (0.12 g, 1 mmol). The reaction mixture was filtered and treated with diethyl ether. A green solid separated and this was filtered off, washed with diethyl ether, and dried *in vacuo* (0.13 g, 20%).

[cis-1,2-*Bis*(*methylthio*)*ethylene*]*tetrabromoosmium*(IV), $[Os(MeSCH=CHSMe)Br_4]$.—This was prepared by an analogous procedure, yield 18%.

Tetraphenylarsonium Tetrachloro(2,5-*dithiahexane*)-*ruthenate*(III)–*Acetone*.—Ruthenium trichloride hydrate (0.24 g, 1 mmol) and $[AsPh_4]Cl\cdot HCl$ (0.45 g, 1 mmol) were dissolved separately in hot acetone, the solutions filtered and combined. 2,5-Dithiahexane (0.12 g, 1 mmol) was added, and the mixture stirred overnight. Concentration of the solution gave a dark red crystalline solid, which was recrystallized from acetone (0.22 g, 27%). The salt $[NMe_4][Ru(MeSCH_2CH_2SMe)Cl_4]$ was prepared in an essentially similar manner in absolute ethanol, yield 30%.

Gold Complexes.—The 2,5-dithiahexane complexes were made as described by Dash and Schmidbauer,[30] and the same method was extended to prepare the other complexes, yields 60—70%. The complex $[Au(PhSCH_2CH_2SPh)Cl_3]$

was obtained as a yellow oil, which slowly solidified on being stirred overnight with n-hexane–ethanol (25 : 2 cm^3), yield 25%.

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