Rhenium Complexes with Di- and Tri-thiolate Ligands. The Synthesis and *X*-Ray Crystal Structures of Square Pyramidal $[PPh_4][ReO(SCH_2CH_2S)_2]$ and $[NMe_4][ReS(SCH_2CH_2S)_2]$ and Trigonal Prismatic $[PPh_4][Re\{(SCH_2)_3CCH_3\}_2]$ ‡

Philip J. Blower and Jonathan R. Dilworth *,†
A.F.R.C. Unit of Nitrogen Fixation, University of Sussex, Brighton, BN1 9RQ
John P. Hutchinson, Terence Nicholson, and Jon Zubieta
Chemistry Department, SUNY at Albany, Albany, NY 12222, U.S.A.

The complexes $[PPh_4][ReO(SCH_2CH_2S)_2]$ (**1**), $[NMe_4][ReS(SCH_2CH_2S)_2]$ (**3**), and $[PPh_4][Re\{(SCH_2)_3CCH_3\}_2]$ (**5**) have been synthesised by the reactions of $K_2[ReCl_6]$ or $[ReOCl_3(PPh_3)_2]$ with the respective polythiol in the presence of triethylamine in methanol solution. Complex (**1**) crystallises in space group *Pcab* with a = 15.122(3), b = 18.685(4), c = 19.648(4) Å, U = 5 542.02 Å^3, and Z = 4. Structure solution based on 2 072 independent reflections was refined to R = 0.063. Complex (**3**) crystallises in space group $P2_1/c$ with a = 9.539(3), b = 15.123(4), c = 21.815(4) Å, β = 93.58(1)°, U = 3 140.9 Å^3, and Z = 8. Structure solution based on 3 329 independent reflections was refined to R = 0.029. Complex (**5**) crystallises in space group $P2_1/n$ with a = 11.506(3), b = 17.096(4), c = 18.115(4) Å, β = 102.32(1)°, U = 3 488.9 Å^3, and Z = 4. Structure solution based on 2 380 independent reflections was refined to R = 0.0517. The $[ReS(SCH_2CH_2S)_2]^-$ and $[ReO(SCH_2CH_2S)_2]^-$ anions exhibit square pyramidal geometry with a terminal sulphido or oxo ligand in the apical position. The S^{2-} ligand is derived from decomposition of the 1,2-ethanedithiolate anion with elimination of ethylene. The $[Re\{(SCH_2)_3CCH_3\}_2]^-$ anion has a six-co-ordinate Re atom in a trigonal prismatic co-ordination sphere. The factors responsible for the adoption of the trigonal prismatic structure are discussed.

Our search for synthetic routes to metal thiolate species containing reactive ligand-binding sites has led us to consider the effect of chelation of the thiolate ligands on the stoicheiometry and chemistry of such complexes. We have examined the reactions of potassium hexachlororhenate(IV) with dithiols $HS(CH_2)_nSH$ (n = 2—4) and also with the tripod-like trithiol 1,1,1-tri(mercaptomethyl)ethane. To our knowledge, this is the first reported use of a tridentate thiolate imposing a facial geometry on a metal ion. Previous studies of rhenium with polythiolate ligands have centred on the oxo anions $[ReO(SXS)_2]^-$ (X = a variety of substituted organic backbone chains)[1] which have a square pyramidal geometry similar to that of the analogous halide complexes $[ReOX_4]^-$.[2] The chemistry described here exhibits features which may arise as a result of properties specific to thiolate and other types of sulphur ligands. In particular, we refer to the ease with which S–C bond cleavage may occur, and the sometimes strong structural influence of attractive ligand–ligand interactions within the co-ordination sphere of complexes containing sulphur ligands. The S–C bond cleavage reaction we describe proceeds with elimination of ethylene from 1,2-ethanedithiolate to yield a monomeric complex with a terminal sulphido ligand. At present, except for high-oxidation-state, usually tetrahedral species containing other strong π-donor ligands (*e.g.* $[ReO_3S]^-$ [3]), relatively few monomeric species with terminal sulphido ligands are known because of the strong tendency of sulphide to act as a bridging ligand and the instability of M=S(terminal) groups towards hydrolysis. Examples include $[MS(S_2CNR_2)_3]$ (M = Ta or Nb),[4] $[VS(OSiPh_3)_3]$,[5] [VS(acen)][acen = *NN'*-ethylenebis(acetylacetonylideneiminate)][6] and other complexes of the thiovanadyl ion VS^{2+} supported by N_4 macrocyclic ligands.[7] $[WSCl_4]$ is monomeric in the gas phase only,[8] forming a chloride-bridged polymer in the solid state.[9]

Results and Discussion

$[ReS(SCH_2CH_2S)_2]^-$.—(*i*) *Synthesis.* Reactions of finely ground potassium hexachlororhenate(IV), $K_2[ReCl_6]$, with an excess of ethanedithiol (1,2-isomer throughout) and triethylamine in refluxing methanol gives, after filtration, a brown solution from which $[A][ReS(SCH_2CH_2S)_2]$ can be obtained as a brown crystalline salt by addition of a salt of a suitable large cation $[A]^+$. In this way tetraphenylphosphonium, tetramethylammonium, and bis(triphenylphosphine)iminium salts were obtained. The same complex anion is formed in the reaction of $K_2[ReBr_6]$ or $[ReCl_4(PPh_3)_2]$ with ethanedithiol under similar conditions. In the room-temperature ^1H n.m.r. spectrum the protons of the ethanedithiolate ligands appear as a singlet, and integration indicates two ethanedithiolates per counter ion. A strong, sharp absorption at 517 cm^{-1} in the i.r. spectra of the salts, not attributable to counter ion or ethanedithiolate, is assigned to ν(Re=S).

Since there is no other source of sulphur under these conditions, it is evident that the sulphido ligand is derived from the dithiolate. If the reaction is carried out in a sealed vessel, subsequent analysis of the atmosphere in the vessel by gas chromatography shows that at least 0.26 moles of ethylene are formed per mole of rhenium {34 times the yield obtained in a control experiment with $[ReOCl_3(PPh_3)_2]$ in place of $K_2[ReCl_6]$}. This yield is therefore at least 52% of the theoretical yield assuming that both sulphurs of an ethanedithiol ultimately become sulphide ligands. The yield of $[PPh_4][ReS-$

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† *Present address:* Chemistry Department, University of Essex, Colchester CO4 3SQ.

‡ Tetraphenylphosphonium bis(1,2-ethanedithiolato)oxorhenate(V), tetramethylammonium bis(1,2-ethanedithiolato)sulphidorhenate(V), and tetraphenylphosphonium bis(2-methyl-2-sulphidomethyl-1,3-propanedithiolato)rhenate(V).

Supplementary data available (No. SUP 56493, 8 pp.): H-atom co-ordinates, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Non-S.I. unit employed: dyn = 10^{-5} N.

Table 1. Details of *X*-ray crystal structure determinations for (**1**), (**3**), and (**5**)

	(**1**)	(**3**)	(**5**)
(*i*) Crystal data[a]			
M	725.4	476.5	855.6
Space group	*Pcab*	$P2_1/n$	$P2_1/n$
a/Å	15.122(3)	9.539(3)	11.506(3)
b/Å	18.685(4)	15.123(4)	17.096(4)
c/Å	19.648(4)	21.815(4)	18.115(4)
α/°	90.0	90.0	90.0
β/°	90.0	93.58(1)	102.32(1)
γ/°	90.0	90.0	90.0
U/Å^3	5 542.02	3 140.9	3 488.9
Z	4	8	4
D_c/g cm^{-3}	1.90	2.135	1.630
F(000)	2 871	1 968	1 712
(*ii*) Measurement of intensity data[b]			
Collected reflections	4 179	4 178	3 972
Independent reflections used in solution ($\|F_o\| > 6\sigma\|F_o\|$)	2 072	3 329	2 380
(*iii*) Reduction of intensity data and summary of structure solution and refinement[c]			
Absorption coefficient (cm^{-1})	50.21	147.22	67.63
Absorption correction	Not applied	*d*	*d*
Final discrepancy factors[e] *R*	0.063	0.029	0.0517
R′	0.063	0.028	0.0517
Goodness of fit[f]	1.14	1.21	1.239

[a] From a least squares fitting of the setting angle of 25 reflections. [b] Data common to all compounds: instrument, Nicolet R3m; radiation, Mo-K_α (λ = 0.710 69 Å); scan mode, coupled θ(crystal)–2λ(counter); scan rate, 7—30° min^{-1}; scan range, $0 < 2\theta < 45°$; scan length, from [2θ($K_{\alpha1}$) − 1.0]° to [2θ($K_{\alpha2}$) + 1.0]°; background measurement, stationary crystal, stationary counter, at the beginning and end of each 2θ scan, each for the time taken for the scan; standards, 3 collected every 197. [c] All calculations were performed on a Data General Nova 3 computer with 32K of 16-bit words using local versions of the Nicolet SHELXTL interactive crystallographic software package as described in G. M. Sheldrick 'Nicolet SHELXTL Operations Manual,' Nicolet XRD Corp. Cupertio, CA, 1979. Data were corrected for background, attenuators, Lorentz, and polarization effects. Structure solution for all compounds: Re atoms located by Patterson synthesis and all other non-hydrogen atoms located by difference Fourier synthesis. Neutral atomic scattering factors were used thoughtout (D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect A*, 1968, **24**, 321). Anomalous dispersion corrections were applied to all non-hydrogen atoms ('International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3). [d] Empirical, based on a series of ψ scans. These were used by SHELXTL program XEMP to refine six parameters defining a pseudo-ellipsoid then used to calculate the correction. *R*(merge) = 0.1047 before corrections and 0.0298 after correction. [e] $R = \Sigma[|F_o| - |F_c|/\Sigma|F_o|]$, $R' = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o) + g^*(F_o)^2$; $g^* = 0.001$. [f] $[\Sigma w(|F_o| - |F_c|)^2/(\text{n.o.}-\text{n.v.})]^{\frac{1}{2}}$ where n.o. is the number of observations and n.v. is the number of variables.

$(SCH_2CH_2S)_2]$ in this reaction was 64%. These observations are consistent with the reaction proceeding according to equation (1). This accounts for the formal oxidation from Re^{IV}

$$2\,K_2[ReCl_6] + 5\,HSCH_2CH_2SH + 10\,NEt_3 \longrightarrow 2\,[NHEt_3][ReS(SCH_2CH_2S)_2] + 4\,KCl + 8\,[NHEt_3]Cl + C_2H_4 \quad (1)$$

to Re^V. The formation of ethylene as a stable by-product evidently allows the reaction to proceed to completion. Consistent with this, reaction of $K_2[ReCl_6]$ with 1,3-propanedithiol or 1,4-butanedithiol under the same conditions yields only intractable products whose i.r. spectra show no bands assignable to ν(Re=S). Attempts have been made to synthesise the $[ReS(SCH_2CH_2S)_2]^-$ anion by substitution of O for S in $[ReO(SCH_2CH_2S)_2]^-$. $[PPh_4][ReO(SCH_2CH_2S)_2]$ does not react with solid B_2S_3, but refluxing in toluene with P_4S_{10} gives a product which appears from its i.r. spectrum to be a mixture of $[PPh_4][ReO(SCH_2CH_2S)_2]$ and $[PPh_4][ReS(SCH_2CH_2S)_2]$.

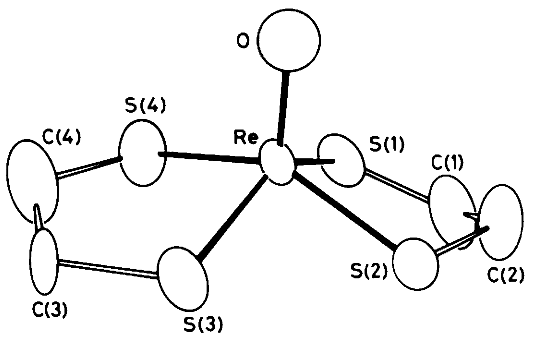

Figure 1. An ORTEP view of the structure of the anion $[ReO(SCH_2CH_2S)_2]^-$ with the atom labelling scheme

(*ii*) *Structure of* $[ReO(SCH_2CH_2S)_2]^-$. The structure of the tetraphenylphosphonium salt of $[ReO(SCH_2CH_2S)_2]^-$ has been determined by *X*-ray crystallography. The crystal data are summarised in Table 1. Atomic co-ordinates and selected bond lengths and angles are given in Tables 2 and 3 respectively. An ORTEP representation of the structure is given in Figure 1 together with the atom labelling scheme. The geometry about the rhenium is square pyramidal with an apical oxo group and the overall structure is very similar to that of the sulphido complex discussed below. The average Re–S distances and angles about the rhenium are virtually identical. The Re–O distance of 1.742(16) Å is very similar to the distance found in other monomeric rhenium oxo complexes such as $[ReO(SPh)_4]^-$.[10]

(*iii*) *Structure of* $[ReS(SCH_2CH_2S)_2]^-$. The structure of the tetramethylammonium salt of $[ReS(SCH_2CH_2S)_2]^-$ has been determined by *X*-ray crystallography. The crystal data are summarised in Table 1. The unit cell contains two similar but independent $[ReS(SCH_2CH_2S)_2]^-$ anions. The atomic co-ordinates are given in Table 4 and selected bond distances and angles are listed in Table 5. An ORTEP picture of the structure is shown in Figure 2. The anions are monomeric with a square pyramidal geometry similar to that of the complex $[ReO(SPh)_4]^-$,[10] with a sulphido ligand replacing the apical oxo ligand. The Re–S(5) distance of 2.104(2) Å is similar to other terminal sulphide bonds to metals of similar covalent radius, *e.g.* $[Mo_2S_4(SCH_2CH_2S)_2]^{2-}$ [2.085(3)—2.129(2) Å in *syn* and *anti* isomers][11] and $[WSCl_4]$ (2.08 Å).[8] It is shorter than the Re–S distances for the thiolate ligands [average 2.300(4) Å] by *ca.* 0.2 Å, consistent with some Re–S(5) multiple bonding, although this appears to be weaker than the axial π bonding in analogous oxo complexes.

(*iv*) *Physical properties.* Since the complexes $[PPh_4][ReS(SCH_2CH_2S)_2]$ and $[PPh_4][ReO(SCH_2CH_2S)_2]$ are analogous in general structure, a comparative study of their spectroscopic properties is of interest. Table 6 lists pertinent data for the two complexes. The i.r. spectra of the two are almost identical except for the presence of ν(Re=O) at 954 cm^{-1} in the oxo complex and ν(Re=S) at 517 cm^{-1} in the sulphido complex. Using an expression[12] for a single non-coupled metal–ligand vibration, values for the force constants of the Re=O and Re=S bonds of 8.0 and 4.3 mdyn Å^{-1} are obtained from the i.r. data. Thus, the Re=S bond is much weaker than the corresponding Re=O bond although it certainly has some multiple bond character as indicated by the structural data.

Table 2. Atom co-ordinates (× 10^4) of $[ReO(SCH_2CH_2S)_2]^-$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re	6 994(7)	20 534(4)	3 471(5)	C(22)	7 977(16)	4 734(11)	472(11)
P	8 891(5)	5 361(3)	1 502(3)	C(23)	7 711(20)	−235(12)	5 227(13)
S(1)	6 992(6)	3 018(4)	972(4)	C(24)	8 001(20)	95(13)	5 742(13)
S(2)	6 629(5)	2 717(3)	−570(3)	C(25)	8 708(20)	581(14)	5 566(13)
S(3)	4 936(6)	3 618(4)	−434(4)	C(26)	9 007(18)	651(12)	4 873(11)
S(4)	5 215(6)	3 784(5)	1 133(4)	C(31)	8 016(17)	5 876(11)	1 896(11)
O(1)	5 101(11)	2 176(7)	546(13)	C(32)	8 237(21)	1 315(13)	2 548(13)
C(1)	7 910(25)	2 719(15)	465(18)	C(33)	7 553(22)	1 672(12)	2 208(14)
C(2)	7 602(22)	2 344(16)	−185(16)	C(34)	6 699(20)	1 595(13)	2 391(13)
C(3)	4 174(20)	4 206(13)	45(17)	C(35)	6 501(22)	1 180(13)	2 958(13)
C(4)	4 229(28)	4 203(18)	808(18)	C(36)	7 160(19)	811(12)	3 302(11)
C(11)	9 930(17)	5 814(11)	1 643(11)	C(41)	8 939(16)	−492(11)	3 051(11)
C(12)	10 595(18)	5 520(12)	2 038(11)	C(42)	9 242(18)	−1 104(11)	3 402(11)
C(13)	11 314(23)	5 900(14)	2 201(14)	C(43)	9 322(20)	−1 746(12)	3 050(11)
C(14)	11 440(25)	6 594(16)	1 915(15)	C(44)	9 095(19)	−1 762(13)	2 383(12)
C(15)	10 797(22)	6 876(12)	1 537(13)	C(45)	8 807(19)	−1 153(13)	2 026(13)
C(16)	10 046(20)	6 530(13)	1 384(13)	C(46)	8 717(17)	−519(11)	2 389(11)
C(21)	8 634(16)	5 229(10)	639(10)				

Table 3. Selected bond lengths (Å) and bond angles (°) for $[ReO(SCH_2CH_2S)_2]^-$

Re–S(1)	2.309(8)	Re–S(4)	2.318(8)	S(1)–C(1)	1.797(38)	S(4)–C(4)	1.796(41)
Re–S(2)	2.328(7)	Re–O(1)	1.742(16)	S(2)–C(2)	1.791(33)	C(1)–C(2)	1.529(47)
Re–S(3)	2.293(8)			S(3)–C(3)	1.849(30)	C(3)–C(4)	1.502(50)
Re–S(1)–C(1)	109.8(12)	S(1)–C(1)–C(2)	111.8(25)	O(1)–Re–S(2)	109.5(8)	S(1)–Re–S(3)	138.5(3)
Re–S(2)–C(2)	103.9(11)	S(2)–C(2)–C(1)	115.1(23)	O(1)–Re–S(3)	110.0(8)	S(1)–Re–S(4)	82.9(3)
Re–S(3)–C(3)	107.3(10)	S(3)–C(3)–C(3)	118.2(23)	O(1)–Re–S(4)	104.1(8)	S(2)–Re–S(3)	83.5(3)
Re–S(4)–C(4)	108.6(12)	S(4)–C(3)–C(3)	113.6(26)	S(1)–Re–S(2)	84.9(3)	S(2)–Re–S(4)	146.4(3)
		O(1)–Re–S(1)	111.4(8)			S(3)–Re–S(4)	85.2(3)

Table 4. Atom co-ordinates for the two independent molecules of $[NMe_4][ReS(SCH_2CH_2S)_2]$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Re(1)	1.063 52(3)	0.271 23(2)	−0.019 64(1)	Re(2)	0.515 76(4)	−0.002 73(2)	0.239 67(1)
S(1)	1.192 17(24)	0.398 76(15)	−0.023 17(10)	S(6)	0.483 80(25)	0.141 90(15)	0.249 07(10)
S(2)	1.052 22(24)	0.304 04(16)	0.083 44(9)	S(7)	0.407 25(26)	0.022 96(17)	0.329 52(10)
S(3)	1.206 88(23)	0.224 38(16)	−0.094 62(10)	S(8)	0.516 22(29)	0.028 53(17)	0.135 88(10)
S(4)	1.089 68(30)	0.130 76(16)	0.017 97(11)	S(9)	0.310 13(29)	−0.076 00(18)	0.212 92(14)
S(5)	0.863 27(23)	0.290 20(18)	−0.063 74(11)	S(10)	0.684 18(28)	−0.089 36(18)	0.259 87(12)
C(1)	1.178 7(12)	0.458 4(7)	0.048 9(4)	C(5)	0.436 2(10)	0.184 2(7)	0.324 1(4)
C(2)	1.063 7(11)	0.424 3(6)	0.085 2(4)	C(6)	0.509 9(10)	0.109 7(7)	0.369 0(4)
C(3)	1.168 6(10)	0.105 9(6)	−0.098 6(4)	C(7)	0.419 1(13)	−0.061 3(8)	0.098 0(4)
C(4)	1.182 0(12)	0.064 6(6)	−0.037 1(4)	C(8)	0.284 2(14)	−0.074 4(8)	0.128 2(5)
N(1)	1.026 1(7)	0.151 3(4)	0.241 9(3)	N(2)	0.564 0(7)	0.284 2(5)	0.069 0(5)
Me(11)	0.951 8(10)	0.236 2(6)	0.252 1(5)	Me(21)	0.577 5(12)	0.371 8(7)	0.037 6(4)
Me(12)	1.174 8(8)	0.172 0(7)	0.229 8(4)	Me(22)	0.442 8(10)	0.283 6(8)	0.106 7(5)
Me(13)	1.020 2(11)	0.095 4(6)	0.297 5(4)	Me(23)	0.691 9(12)	0.267 4(9)	0.105 3(6)
Me(14)	0.957 1(9)	0.106 0(6)	0.187 8(5)	Me(24)	0.542 5(16)	0.216 6(7)	0.021 4(5)

The visible spectra of $[PPh_4][ReO(SCH_2CH_2S)_2]$ and $[PPh_4][ReS(SCH_2CH_2S)_2]$ are very similar in overall shape but the sulphido complex shows a red shift of 80—150 nm (corresponding to an energy shift of 5 200—6 000 cm^{-1}) compared to the oxo complex. A comparison of the electronic spectra of $[ReOCl_4]^-$ and $[ReO(SCH_2CH_2S)_2]^-$ suggests that the intense visible absorptions in $[ReO(SCH_2CH_2S)_2]^-$ are thiolate-to-metal charge transfer in origin. The similarity in structure of the spectra of the oxo and sulphido complexes implies that the three lowest energy peaks for the sulphido complex are also thiolate-to-metal charge transfer in character. The pronounced red shift for the sulphido complex indicates that the metal is considerably less electron rich than in the oxo complex. The intense band at 326 nm for the sulphido complex may be a charge-transfer band associated with the Re=S systems. The corresponding peak in the oxo complex may be obscured by counter-ion absorptions in the ultraviolet region.

The redox potentials, obtained from cyclic voltametric measurements in MeCN solution, show that the sulphido complex is easier to reduce, by at least 0.4 V, than the oxo complex (Table 6), inferring that the lowest unoccupied molecular orbital (l.u.m.o.) of $[ReS(SCH_2CH_2S)_2]^-$ is much lower in energy that that of $[ReO(SCH_2CH_2S)_2]^-$. The sulphido complex is also easier to oxidise, by 0.16 V, than the oxo complex, thus the highest occupied molecular orbital (h.o.m.o.) of the former is relatively high in energy. A plausible interpretation of these results is that while the l.u.m.o. of each complex is likely to be of predominantly Re(d_{xz}/d_{yz}) character, the h.o.m.o.s of the two complexes may differ in character, that of $[ReO(SCH_2CH_2S)_2]^-$ being mainly Re(d_{xy}) while that of $[ReS(SCH_2CH_2S)_2]^-$ may

Table 5. Selected bond lengths (Å) and bond angles (°) for $[ReS(SCH_2CH_2S)_2]^-$

Molecule 1		Molecule 2	
Re(1)–S(1)	2.290(2)	Re(2)–S(6)	2.306(2)
Re(1)–S(2)	2.312(2)	Re(2)–S(7)	2.287(2)
Re(1)–S(3)	2.308(2)	Re(2)–S(8)	2.313(2)
Re(1)–S(4)	2.285(2)	Re(2)–S(9)	2.296(2)
Re(1)–S(5)	2.104(2)	Re(2)–S(10)	2.098(3)
S(1)–C(1)	1.832(1)	S(6)–C(5)	1.841(9)
C(1)–C(2)	1.486(14)	C(5)–C(6)	1.525(14)
C(2)–S(2)	1.822(9)	C(6)–S(7)	1.820(10)
S(3)–C(3)	1.830(10)	S(8)–C(7)	1.813(12)
C(3)–C(4)	1.478(13)	C(7)–C(8)	1.495(18)
C(4)–S(4)	1.831(11)	C(8)–S(9)	1.850(12)
S(1)–Re(1)–S(2)	84.8(1)	S(6)–Re(2)–S(7)	84.4(1)
S(1)–Re(1)–S(3)	83.8(1)	S(6)–Re(2)–S(8)	82.8(1)
S(1)–Re(1)–S(4)	138.4(1)	S(6)–Re(2)–S(9)	135.8(1)
S(1)–Re(1)–S(5)	110.1(1)	S(6)–Re(2)–S(10)	111.7(1)
S(2)–Re(1)–S(3)	145.2(1)	S(7)–Re(2)–S(8)	145.7(1)
S(2)–Re(1)–S(4)	82.0(1)	S(7)–Re(7)–S(9)	82.9(1)
S(2)–Re(1)–S(5)	108.6(1)	S(7)–Re(2)–S(10)	107.8(1)
S(3)–Re(1)–S(4)	85.0(1)	S(8)–Re(2)–S(9)	84.5(1)
S(3)–Re(1)–S(5)	106.2(1)	S(8)–Re(2)–S(10)	106.6(1)
S(4)–Re(1)–S(5)	111.5(1)	S(9)–Re(2)–S(10)	112.5(1)
Re(1)–S(1)–C(1)	108.7(3)	Re(2)–S(6)–C(5)	109.1(3)
S(1)–C(1)–C(2)	112.5(7)	S(6)–C(5)–C(6)	112.0(7)
C(1)–C(2)–S(2)	112.4(7)	C(5)–C(6)–S(7)	109.5(6)
C(2)–S(2)–Re(1)	103.2(3)	C(6)–S(7)–Re(2)	105.5(3)
Re(1)–S(3)–C(3)	102.1(3)	Re(2)–S(8)–C(7)	105.1(4)
S(3)–C(3)–C(4)	111.4(7)	S(8)–C(7)–S(8)	109.2(8)
C(3)–C(4)–S(4)	110.3(7)	C(7)–C(8)–S(9)	112.1(8)
C(4)–S(4)–Re(1)	108.6(3)	C(8)–S(9)–Re(2)	107.9(4)

Table 6. Comparison of spectroscopic and electrochemical properties of $[ReX(SCH_2CH_2S)_2]^-$ (X = O or S)

Parameter	X=O	X = S
$\nu(Re{=}X)^a/cm^{-1}$	954	517
$\lambda_{max.}(\varepsilon)^b$	480 (sh)	640 (15)
	416 (600)	555 (598)
	362 (sh)	456 (sh)
	329 (4 400)	403 (4 400)
		326 (9 190)
$E^{red\,c}/V$	< -2	-1.79
$E^{ox\,c}/V$	$+0.73^d$	$+0.57^e$

[a] Nujol mulls. [b] MeCN solution (10^{-4} mol dm^{-3}): λ/nm, ε/dm^3 mol^{-1} cm^{-1}. [c] By cyclic voltammetry, 10^{-3} mol dm^{-3} in MeCN, 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$ as support electrolyte, scan rate 0.5 V s^{-1}, Pt electrode. [d] E_p quoted, irreversible process. [e] $E_{\frac{1}{2}}$ quoted, reversible process.

be largely associated with the sulphido ligand, since the valence atomic orbitals of sulphur are higher than those of oxygen. This suggestion is not incompatible with the electronic spectra.

In summary, the combined spectroscopic and structural properties suggest that the metal atom in $[ReS(SCH_2CH_2S)_2]^-$ is much less electron rich, and apical ligand-to-metal π-donation much weaker, than in its oxo analogue. This is consistent with the view that first-row elements show a much greater capacity for π-bonding than their second-row congeners. This interpretation is supported by extended-Hückel m.o. model calculations on vanadyl, thiovanadyl, and selenovanadyl ions which suggest that ligand–metal overlap integrals are smaller for VS and VSe than for VO bonds, largely because of the larger atomic radius of S and Se.[13] The effect of this reduced π-overlap between S and Re in decreasing the 'electron richness' of the metal relative to the oxo analogue appears to outweigh the ligand electronegativity effect which might be expected to render the metal in the oxo complex less electron rich.

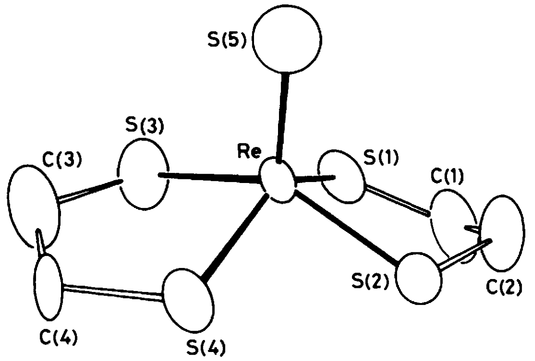

Figure 2. An ORTEP view of the structure of the anion $[ReS(SCH_2CH_2S)_2]^-$ with the atom labelling scheme

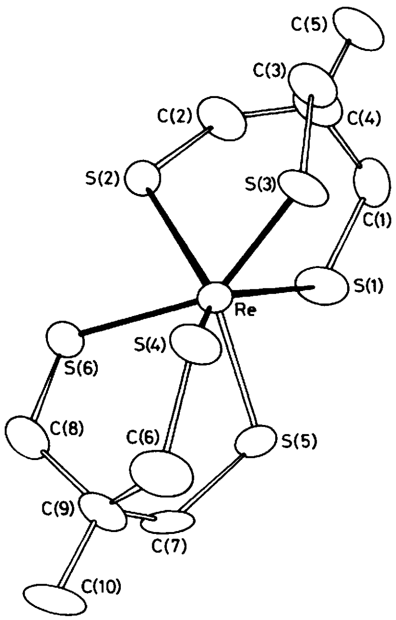

Figure 3. An ORTEP view of the structure of the $[Re\{(SCH_2)_3CCH_3\}_2]^-$ with the atom labelling scheme

$[Re\{(SCH_2)_3CCH_3\}_2]^-$.—(*i*) *Synthesis.* Reaction of $K_2[ReCl_6]$ with three equivalents of 1,1,1-tri(mercaptomethyl)ethane, $CH_3C(CH_2SH)_3$, in refluxing methanol in the presence of triethylamine gives some insoluble, uncharacterised material and, after addition of tetraphenylphosphonium bromide to the filtered solution, dark red crystalline $[PPh_4][Re\{(SCH_2)_3CCH_3\}_2]$. It is evident that the metal has formally undergone a one-electron oxidation to give the Re^V product, but the fate of the electron is unknown. One might suggest formation of H_2 from protons as the corresponding reduction process. The ^1H n.m.r. spectrum is consistent with a Re^V diamagnetic complex with two equivalent trithiolate ligands per $[PPh_4]^+$ cation. The methyl protons appear at δ 1.29 (singlet) and the methylene protons at δ 2.90 (singlet) (p.p.m. *vs.* $SiMe_4$).

(*ii*) *Structure.* A single-crystal *X*-ray structure determination has been performed on $[PPh_4][Re\{(SCH_2)_3CCH_3\}_2]$. The crystal data are presented in Table 1. An ORTEP represent-

Table 7. Atom co-ordinates (× 10^4) of $[Re\{(SCH_2)_3CCH_3\}_2]^-$

Atom	x	y	z
Re	−1 109(1)	8 877(1)	1 919(1)
S(1)	872(4)	8 715(3)	2 493(3)
S(2)	−1 584(5)	8 765(3)	3 108(2)
S(3)	−1 269(5)	7 516(3)	1 842(3)
S(4)	−2 435(4)	8 636(3)	778(3)
S(5)	−35(4)	9 675(3)	1 255(3)
S(6)	−2 263(5)	9 959(3)	2 051(3)
C(1)	1 078(10)	7 785(11)	2 995(11)
C(2)	−418(19)	8 175(12)	3 709(10)
C(3)	−893(19)	7 067(11)	2 766(9)
C(4)	88(18)	7 488(11)	3 368(11)
C(5)	596(20)	6 899(11)	3 980(11)
C(6)	−2 494(19)	9 457(10)	142(10)
C(7)	−972(18)	10 452(10)	777(11)
C(8)	−2 964(21)	10 364(12)	1 139(11)
C(9)	−2 297(18)	10 288(10)	480(9)
C(10)	−2 804(21)	10 878(12)	−102(11)
P	−2 778(4)	9 024(3)	5 907(2)
C(11)	−4 334(11)	7 795(7)	5 510(5)
C(12)	−5 051(11)	7 288(7)	5 007(5)
C(13)	−5 210(11)	7 409(7)	4 232(5)
C(14)	−4 652(11)	8 037(7)	3 960(5)
C(15)	−3 934(11)	8 544(7)	4 463(5)
C(16)	−3 775(11)	8 424(7)	5 238(5)
C(17)	−2 874(9)	10 598(7)	5 502(6)
C(18)	−2 637(9)	11 220(7)	5 059(6)
C(19)	−1 902(9)	11 110(7)	4 549(6)
C(20)	−1 402(9)	10 376(7)	4 481(6)
C(21)	−1 639(9)	9 754(7)	4 924(6)
C(22)	−2 374(9)	9 865(7)	5 434(6)
C(23)	−4 766(10)	9 462(6)	6 406(6)
C(24)	−5 364(10)	9 823(6)	6 907(6)
C(25)	−4 732(10)	10 081(6)	7 607(6)
C(26)	−3 502(10)	9 979(6)	7 807(6)
C(27)	−2 904(10)	9 618(6)	7 306(6)
C(28)	−3 536(10)	9 359(6)	6 606(6)
C(29)	−1 451(11)	7 676(8)	6 195(7)
C(30)	−442(11)	7 241(8)	6 511(7)
C(31)	551(11)	7 611(8)	6 946(7)
C(32)	535(11)	8 417(8)	7 066(7)
C(33)	−474(11)	8 852(8)	6 750(7)
C(34)	−1 467(11)	8 482(8)	6 314(7)

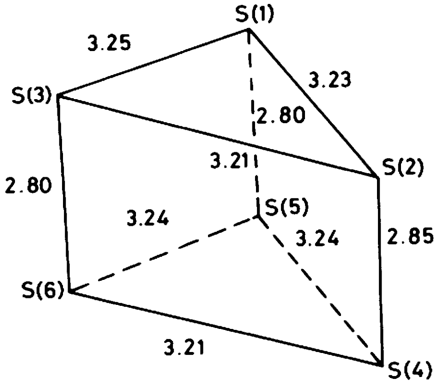

Figure 4. Polyhedral dimensions (Å) of the $[Re\{(SCH_2)_3CCH_3\}_2]^-$ anion

Table 8. Selected bond lengths (Å) and bond angles (°) for $[PPh_4]$-$[Re\{(SCH_2)_3CCH_3\}_2]$

Re–S(1)	2.312(5)	Re–S(2)	2.345(5)
Re–S(3)	2.336(4)	Re–S(4)	2.333(4)
Re–S(5)	2.340(6)	Re–S(6)	2.318(5)
S(1)–C(1)	1.821(20)	S(2)–C(2)	1.797(19)
S(3)–C(3)	1.811(11)	S(4)–C(6)	1.809(18)
S(5)–C(7)	1.812(19)	S(6)–C(8)	1.816(19)
S(1)–Re–S(2)	88.6(2)	S(1)–Re–S(3)	88.0(2)
S(2)–Re–S(3)	86.7(2)	S(1)–Re–S(4)	140.7(2)
S(2)–Re–S(4)	124.5(2)	S(3)–Re–S(4)	75.1(2)
S(1)–Re–S(5)	74.0(3)	S(2)–Re–S(5)	140.8(2)
S(3)–Re–S(5)	126.4(2)	S(4)–Re–S(5)	87.9(2)
S(1)–Re–S(6)	125.5(2)	S(2)–Re–S(6)	73.7(2)
S(3)–Re–S(6)	139.6(2)	S(4)–Re–S(6)	87.3(2)
S(5)–Re–S(6)	88.0(2)		

ation of the structure of the anion is shown in Figure 3. Table 7 gives the atomic co-ordinates and pertinent interatomic distances and angles are summarised in Table 8. The geometry of the anion is close to trigonal prismatic (t.p.) with trigonal twist of only 6° from the ideal t.p. structure. The mean Re–S distance is 2.33(5) Å, 0.03 Å longer than the mean Re–S(thiolate) distance in $[ReS(SCH_2CH_2S)_2]^-$, which is probably a reflection of the increased co-ordination number. Each tridentate ligand occupies a triangular face of the prism, which is compressed along the idealised C_3 axis so as to make inter-ligand nearest-neighbour S–S distances (average 3.23 Å), which are very much shorter than twice the van der Waals radius of sulphur (3.7 Å) (see Figure 4). One might expect inter-ligand repulsions to be minimised by formation of an octahedral structure,[14] which would impose no strain within the chelate ligands. The fact that the t.p. structure is assumed requires consideration.

Trigonal prismatic geometry is relatively uncommon, the majority of examples being complexes with sulphur ligands.[15] The exceptions to this are complexes with polydentate ligands which are rather inflexible and impose their geometry on the metal,[16] or are tris(acetylacetonate) complexes.[17] Most of the sulphur-containing species are tris('dithiolene') complexes, which have been reviewed elsewhere;[15] another related complex is $[Mo\{SC(Ph)NNH\}_3]$.[18] In the tris(dithiolene) class of compounds it is suggested that t.p. geometry is the result of attractive sulphur–sulphur interactions within the triangular faces of the prism. According to one interpretation,[19] direct interactions between 3*p* orbitals are better described as interactions between π-orbitals of the 'butadiene' type delocalised over the ligand backbones. Thus, there are low-lying vacant orbitals of the required symmetry to stabilise these otherwise unfavourable sulphur–sulphur interactions. A twist towards octahedral geometry would skew the ligands out of the orientations favourable to this overlap.

Another interpretation[20] suggests that S(3*p*)–S(3*p*) interactions, again within the triangular faces, are stabilised by interaction with the vacant metal d_{z^2} orbital. In addition, the metal d_{xy} and $d_{x^2-y^2}$ orbitals are able to mediate S–S interaction along the vertical edges of the prisms by a π interaction. As before, such interactions would be diminished by a trigonal twist towards octahedral geometry. As these complexes become more reduced, minimisation of ligand–ligand repulsion becomes more important and a change towards octahedral geometry occurs. One t.p. complex in which ligand unsaturation cannot contribute to stabilisation of t.p. geometry is $[Mo(SCH_2CH_2SCH_2CH_2S)_2]$.[21] Neither can chelate effects of the ligand alone account for the structure, since the phosphino analogue $[Mo(SCH_2CH_2PPhCH_2CH_2S)_2]$[22] has an approximately octahedral structure. However, there are sufficient distortions from the idealised t.p. geometry in $[Mo(SCH_2CH_2SCH_2CH_2S)_2]$ which make detailed analysis of the structural influences difficult.

In the new complex $[PPh_4][Re\{(SCH_2)_3CCH_3\}_2]$ the factors stabilising the t.p. structure are evidently not related to those just discussed. There is no unsaturation within the ligands;* the ligands span triangular faces rather than vertical edges; and, in contrast to the tris(dithiolene) complexes, in which the edges of square and triangular faces are of comparable length, the new complex has inter-ligand (vertical) distances shorter than intra-ligand edges by an average of 0.42 Å. There appears to be an intra-ligand sulphur–sulphur repulsion, causing the S–C–C bond angles to be opened to *ca.* 113°. This is consistent with a simple ligand-field picture in which the d_{z^2} orbital of the d^2 Re atom is occupied and can play no part in drawing the ligands in a triangular face together. On the other hand, the compression of the prism along the idealised C_3 axis suggests a definite attraction between sulphurs along the vertical edges. The same simple ligand-field picture suggests that the d_{xy} and $d_{x^2-y^2}$ orbitals are capable of facilitating this attraction through π overlap with the sulphur $3p$ orbitals. The question of whether these metal orbitals play an important role in the axial compression, or whether this is a result of attractive S–S interaction must await detailed m.o. calculations. Certainly, however, sulphur atoms are capable of such interaction to give shorter than expected 'non-bonding' S–S contacts,[23,24] and the possible significance of these in redox chemistry has been commented upon.[23] Alternatively, or perhaps additionally, there may be a contribution to the t.p. stability of $[Re\{(SCH_2)_3CCH_3\}_2]^-$ from the special constraints imposed by the tripodal structure of the ligands. Thus, when all of the S–C bonds are required to be parallel to one another (as here), t.p. geometry may actually give a stronger π overlap between metal $5d$ and sulphur $3p$ orbitals than would be possible in an octahedron, since the alignment of the sulphur $3p$ orbitals is dominated by the S–C σ-bond orientation.

It is also worth noting that t.p. geometry has only been observed hitherto in complexes with all ligands chelating {in a sense the MoS_2 lattice may be included since the S atoms are effectively linked by the lattice structure, giving a t.p. polyhedron about the metal atom of strikingly similar dimensions to that of the Mo tris(dithiolene) complexes and $[Mo(SCH_2CH_2SCH_2CH_2S)_2]$}. It is perhaps significant that monodentate thiolate ligands do not generally give structures where there are observable S···S interactions. Rather it appears that complete S–S bond formation often occurs with reduction of the metal and elimination of disulphide. The chelation of the polydentate ligands may serve at least in part to restrict the mobility of the ligating thiolate sulphurs so as to prevent weak S···S interactions from becoming full disulphide S–S bonds. A further role of the polydentate ligand may be to encourage higher coordination numbers and thereby militate against thiolate-bridge formation.

Experimental

1,2-Ethanedithiol, 1,3-propanedithiol, and 1,4-butanedithiol were used as purchased from Aldrich Chemicals Ltd. 1,1,1-Tri(mercaptomethyl)ethane,[25] $[ReOCl_3(PPh_3)_2]$,[26] and potassium hexachlororhenate(IV)[27] were prepared by literature methods. All reactions were carried out in dry, oxygen-free solvents under dinitrogen using standard Schlenk techniques. Instrumentation was as follows: Pye-Unicam SP2000 i.r. spectrophotometer, Perkin-Elmer Lambda 5 u.v.–visible spectrophotometer, JEOL FX 90Q n.m.r. spectrometer. Cyclic voltammetry was carried out in MeCN solutions containing 0.2 mol dm^{-3} $[NBu^n_4][BF_4]$ as support electrolyte, with a platinum working electrode and Ag–AgCl pseudo-reference electrodes. Ferrocene was added as an internal standard; a Chemical Electronics RBI waveform generator and TR70/2A potentiostat were used. C, H and N analyses were performed by Mrs. G. Olney, University of Sussex. Experimental details for the *X*-ray crystal structures are reported in Table 1.

Tetraphenylphosphonium Bis(1,2-*ethanedithiolato*)*oxorhenate*(V), $[PPh_4][ReO(SCH_2CH_2S)_2]$ (**1**). $[ReOCl_3(PPh_3)_2]$ (0.3 g, 0.36 mmol), 1,2-ethanedithiol (0.12 cm^3, 1.44 mmol) and trimethylamine (0.19 cm^3, 1.08 mmol) were stirred in refluxing methanol (20 cm^3) for 1.5 h. To the resulting orange-red solution was added, dropwise, after cooling to room temperature, tetraphenylphosphonium bromide (0.3 g) dissolved in methanol (10 cm^3). Stirring was continued for 10 min, giving a microcrystalline orange solid. This was collected and washed successively with isopropyl alcohol and diethyl ether, yielding 0.22 g (84%) of (**1**) (Found: C, 46.3; H, 4.3. $C_{28}H_{28}OPReS_4$ requires, C, 46.3; H, 3.9%).

Tetraphenylphosphonium Bis(1,2-*ethanedithiolato*)*sulphidorhenate*(V), $[PPh_4][ReS(SCH_2CH_2S)_2]$ (**2**).—Finely ground potassium hexachlororhenate(IV) (0.5 g, 1 mmol) was suspended in methanol (40 cm^3). 1,2-Ethanedithiol (0.53 cm^3, 6 mmol) and triethylamine (0.55 cm^3, 4 mmol) were added to the stirred suspension and the mixture was heated to reflux temperature for 4 h. The resulting brown solution was filtered, and tetraphenylphosphonium bromide (2 g) was added slowly to the filtrate with rapid stirring, causing precipitation of a brown microcrystalline solid which was collected and washed with isopropyl alcohol and then diethyl ether. Yield 0.5 g, 65%. The product was recrystallised from dichloromethane–ether (Found: C, 45.1; H, 3.8; S, 20.0. $C_{28}H_{28}PReS_5$ requires C, 45.3; H, 3.8; S, 21.6%).

Tetramethylammonium Bis(1,2-*ethanedithiolato*)*sulphidorhenate*(V), $[NMe_4][ReS(SCH_2CH_2S)_2]$ (**3**).—The procedure for (**2**) was followed to obtain the cooled, filtered reaction solution. To this was added 20 cm^3 of a saturated solution of tetramethylammonium bromide in methanol. The solution was then concentrated to 20 cm^3, affording crystals in low yield, after standing for several hours. Crystals suitable for diffraction studies were obtained in this way (Found: C, 20.3; H, 4.3; N, 3.0. $C_8H_{20}NReS_5$ requires C, 20.2; H, 4.2; N, 2.9%).

Bis(*triphenylphosphine*)*iminium Bis*(1,2-*ethanedithiolato*)-*sulphidorhenate*(V), $[N(PPh_3)_2][ReS(SCH_2CH_2S)_2]$ (**4**).—The procedure for (**3**) was followed, substituting bis(triphenylphosphine)iminium chloride in place of tetramethylammonium bromide (Found: C, 50.4; H, 4.5; N, 1.5. $C_{40}H_{38}NP_2ReS_5$ requires C, 51.0; H, 4.1; N, 1.5%).

Tetraphenylphosphonium Bis(2-*methyl*-2-*sulphidomethyl*-1,3-*propanedithiolato*)*rhenate*(V), $[PPh_4][Re\{(SCH_2)_3CCH_3\}_2]$ (**5**).—Finely ground $K_2[ReCl_6]$ (0.2 g, 1.38 mmol) was suspended in methanol (20 cm^3). To this suspension were added 1,1,1-tri(mercaptomethyl)ethane (0.2 cm^3, 1.38 mmol) and triethylamine (0.2 cm^3, 1.45 mmol). The stirred solution was heated under reflux for 1 h, cooled to room temperature and

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* This probably explains the differing electrochemistry of $[Re\{(SCH_2)_3CCH_3\}_2]^-$ and the tris(dithiolene) complexes. Whereas the latter show several one-electron reversible processes, the cyclic voltammetry of the former shows only a quasi-reversible reduction [$E_p^{red} = -1.64$ V; $E_p^{ox} = 1.46$ V *vs.* saturated calomal electrode (s.c.e.)] and an irreversible oxidation at +0.35 V *vs.* s.c.e., supporting the supposition that the redox changes in the tris(dithiolene) complexes are largely associated with the delocalisation in the ligands.

filtered. To the red-brown filtrate was added tetraphenylphosphonium bromide (0.5 g) with stirring, affording a dark red microcrystalline precipitate which was collected and washed with isopropyl alcohol and diethyl ether, yield 0.26 g (72%) (Found: C, 47.4; H, 4.9. $C_{34}H_{38}PReS_6$ requires C, 47.4; H, 4.4%). Crystals suitable for an *X*-ray structure determination were grown from dichloromethane–methanol.

Acknowledgements

We thank Hermann C. Starck of Berlin for a generous gift of rhenium metal.

References

1 A. Davison, C. Orvig, H. S. Troup, M. Sohn, B. V. De Pamphilis, and A. G. Jones, *Inorg. Chem.*, 1980, **19**, 1988.

2 D. A. Edwards and R. T. Ward, *J. Chem. Soc. A*, 1970, 1617.

3 A. Muller and B. Krebs, *Z. Anorg. Allg. Chem.*, 1966, **342**, 193.

4 P. R. Heckley and D. G. Holah, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 865; P. R. Heckley, D. G. Holah, and D. Brown, *Can. J. Chem.*, 1971, **49**, 1151.

5 M. M. Chamberlain, G. A. Jabs, and B. B. Wayland, *J. Org. Chem.*, 1962, **27**, 3321.

6 K. P. Callahan, P. J. Durand, and P. H. Reiger, *J. Chem. Soc., Chem. Commun.*, 1980, 75; K. P. Callahan and P. J. Durand, *Inorg. Chem.*, 1980, **19**, 3211; M. Sato, K. M. Miller, J. H. Enemark, C. E. Strouse, and K. P. Callahan, *Inorg. Chem.*, 1981, **20**, 3571.

7 J-L. Poncet, R. Guilard, P. Frient, and J. Goulon, *Polyhedron*, 1983, **2**, 417; V. L. Goedken and J. A. Ladd, *J. Chem. Soc., Chem. Commun.*, 1981, 910.

8 E. M. Page, D. A. Rise, K. Hagen, L. Hedberg, and K. Hedberg, *Inorg. Chem.*, 1982, **21**, 3280.

9 M. G. B. Drew and R. Mandyezewski, *J. Chem. Soc. A*, 1970, 2815.

10 A. C. McDonnell, T. H. Hambley, M. R. Snow, and A. G. Wedd, *Aust. J. Chem.*, 1983, **36**, 253.

11 G. Bunzey, J. H. Enemark, J. K. Hoorie, and D. T. Sawyer, *J. Am. Chem. Soc.*, 1978, **100**, 3398.

12 F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 867.

13 J. R. Wasson, J. W. Hall, and W. E. Hatfield, *Transition Met. Chem.*, 1978, **3**, 195.

14 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Ithaca, New York, 1960.

15 R. Eisenberg, *Prog. Inorg. Chem.*, 1970, **12**, 295.

16 R. A. D. Wentworth, *Coord. Chem. Rev.*, 1973, **9**, 171.

17 A. Avdeef and J. P. Fackler, jun., *Inorg. Chem.*, 1975, **14**, 2002.

18 J. R. Dilworth, J. Hyde, P. Lyford, P. Vella, K. Venkatasubramanian, and J. A. Zubieta, *Inorg. Chem.*, 1979, **18**, 268.

19 G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 1966, **88**, 3235.

20 E. I. Stiefal, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *J. Am. Chem. Soc.*, 1966, **88**, 2956.

21 J. Hyde, L. Magin, and J. A. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1980, 204.

22 J. R. Dilworth, G. J. Leigh, F. B. Normanton, and J. A. Zubieta, Proc. Chem. Cr, Mo, W Conference, University of Sussex (1983), eds. J. R. Dilworth and M. F. Lappert, Royal Society of Chemistry, 1983.

23 E. I. Stiefel, K. F. Miller, A. E. Bruce, J. L. Corbin, J. M. Berg, and K. O. Hodgson, *J. Am. Chem. Soc.*, 1980, **102**, 3624.

24 J. M. Berg, D. J. Spira, K. O. Hodgson, A. E. Bruce, K. F. Miller, J. L. Corbin, and E. I. Stiefel, *Inorg. Chem.*, 1984, **23**, 3412.

25 G. R. Franzon and G. Birsch, *J. Am. Chem. Soc.*, 1973, **95**, 175.

26 N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc. A*, 1970, 2652.

27 G. W. Watt and R. J. Thompson, *Inorg. Synth.*, 1963, 7, 189.

Received 25*th July* 1985; *Paper* 5/1273