

Synthesis, spectroscopic and EXAFS studies of vanadium complexes of trithioether ligands and crystal structures of $[\text{VCl}_3(\text{[9]aneS}_3)]$ and $[\text{VI}_2(\text{thf})(\text{[9]aneS}_3)]$ ($[\text{9]aneS}_3 = 1,4,7\text{-trithiacyclononane})^\dagger$

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A series of vanadium-(II), -(III) and -(IV) macrocyclic thioether complexes has been synthesized and characterised by analytical, magnetic and spectroscopic methods. The new complexes reported are $[\{\text{V}(\text{[9]aneS}_3)\}_2(\mu\text{-Cl})_3\text{Cl}]$ ($[\text{9]aneS}_3 = 1,4,7\text{-trithiacyclononane}$), $[\text{VI}_2(\text{thf})(\text{[9]aneS}_3)]$, $[\text{VI}_2(\text{ttob})]$ (ttob = 2,5,8-trithia[9]-*o*-benzenophane), $[\text{VX}_3(\text{[9]aneS}_3)]$ (X = Cl, Br or I), $[\text{VX}_3(\text{[10]aneS}_3)]$ ($[\text{10]aneS}_3 = 1,4,7\text{-trithiacyclodecane}$), $[\text{VCl}_3(\text{ttob})]$, $[\text{VCl}_3(\text{[16]aneS}_4)]$ ($[\text{16]aneS}_4 = 1,5,9,13\text{-tetrathiacyclohexadecane}$), $[(\text{VX}_3)_2(\mu\text{-[18]aneS}_6)]$ (X = Cl or Br, $[\text{18]aneS}_6 = 1,4,7,10,13,16\text{-hexathiacyclooctadecane}$) and $[\text{VOCl}_2(\text{ttob})]$. The crystal structures of $[\text{VI}_2(\text{thf})(\text{[9]aneS}_3)]$ and $[\text{VCl}_3(\text{[9]aneS}_3)]$ and EXAFS structural data for $[\text{VX}_3(\text{[9]aneS}_3)]$ and $[\text{VX}_3(\text{[10]aneS}_3)]$ are presented and discussed. The acyclic trithioether complexes $[\text{VX}_3\{\text{MeC}(\text{CH}_2\text{SMe})_3\}]$ (X = Cl or Br) and the complex $[\text{VI}_2(\text{py})_4]$ are also reported.

Vanadium–sulfur chemistry has recently become an active area of research due *inter alia* to the existence of a vanadium nitrogenase system¹ and the involvement of vanadium sulfide species in the refining of crude oils.² It has been proposed that in the Fe/S/V cluster in the active site of vanadium nitrogenase the co-ordination at vanadium involves one nitrogen, two oxygen and three confacial sulfur atoms, similar to that at molybdenum in the crystallographically characterised iron–molybdenum cofactor of nitrogenase.¹ This proposal is supported by the fact that the EXAFS spectrum of the vanadium nitrogenase cofactor resembles that of the synthetic cluster $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{dmf})_3]^-$.³ In view of this work, noting that the only well characterised metal–sulfur site at which dinitrogen is bound and reduced is in the thioether complex *trans*-bis-(dinitrogen)(3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathia-cyclohexadecane)molybdenum,⁴ and in the knowledge that early transition metal thioether compounds are rare, we have initiated a study of vanadium thioether macrocyclic chemistry. In particular with regard to understanding the nature of the vanadium site in nitrogenase, we considered that as well as introducing the correct sulfur ligand environment at vanadium (three confacial S donors), macrocyclic trithioethers would also facilitate more stable complexes and may enable N- and O-donor ligands to be introduced at the other co-ordination sites. Accordingly, in this paper we report the preparation and spectroscopic characterisation of vanadium-(II), -(III) and -(IV) complexes involving trithioethers and also other macrocyclic and acyclic thioether ligands. Vanadium K-edge extended X-ray absorption fine structure (EXAFS) measurements have been used to determine V–S and V–X distances for several of these compounds and single crystal X-ray structural analyses of $[\text{VCl}_3(\text{[9]aneS}_3)]$ and $[\text{VI}_2(\text{thf})(\text{[9]aneS}_3)]$ are also reported. A preliminary communication on some aspects of this work has been published.⁵

Prior to this study the only vanadium thioether complexes to be structurally characterised were the vanadium(IV) species $[\text{VOCl}_2(\text{[9]aneS}_3)]$ ⁶ and $[\text{VOCl}_2(\text{[9]aneN}_2\text{S})\cdot\text{MeCN}]$ ⁷ ($[\text{9]aneN}_2\text{S} = 1\text{-thia-4,7-diazacyclononane}$), both of which were

obtained fortuitously from VCl_3 and have distorted octahedral geometry.

Results and Discussion

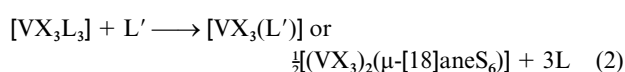
Preparations and spectroscopy

Vanadium(II) derivatives of thioether macrocycles have been prepared. Reaction of $[\text{VI}_2(\text{thf})_4]$ (thf = tetrahydrofuran) with 1 molar equivalent of $[\text{9]aneS}_3$ (1,4,7-trithiacyclononane) or ttob (2,5,8-trithia[9]-*o*-benzenophane) (L') in thf solution yields $[\text{VI}_2(\text{thf})(\text{[9]aneS}_3)]$ or $[\text{VI}_2(\text{thf})(\text{ttob})]$ respectively as a light blue solid [reaction (1)]. Infrared spectroscopy confirms the



presence of the thioether ligand as well as co-ordinated thf, while magnetic measurements are consistent with V^{II} . In addition, reaction of the triply chloride-bridged species $[\{\text{V}(\text{thf})_3\}_2(\mu\text{-Cl})_3][\text{AlCl}_2\text{Et}_2]$ ⁸ in CH_2Cl_2 with $[\text{9]aneS}_3$ gives the poorly soluble and highly air-sensitive complex $[\{\text{V}(\text{[9]aneS}_3)\}_2(\mu\text{-Cl})_3\text{Cl}]$, whose characterisation is on the basis of analytical and magnetic data.

Reaction of $[\text{VX}_3\text{L}_3]$ (L = MeCN, thf or Me_2PhPO ; X = Cl, Br or I) with 1 molar equivalent of L' [$L' = [\text{9]aneS}_3$, $[\text{10]aneS}_3$ (1,4,7-trithiacyclodecane) or ttob] or with 0.5 molar equivalent of $[\text{18]aneS}_6$ (1,4,7,10,13,16-hexathiacyclooctadecane) in anhydrous CH_2Cl_2 at room temperature under a dinitrogen atmosphere yields the neutral vanadium(III) species $[\text{VX}_3(L')]$ or $[(\text{VX}_3)_2(\mu\text{-[18]aneS}_6)]$ as a highly coloured solid in good yield. Similar reaction of $[\text{VX}_3(\text{thf})_3]$ (X = Cl or Br) with the tripodal ligand $\text{MeC}(\text{CH}_2\text{SMe})_3$ yields the neutral species $[\text{VX}_3\{\text{MeC}(\text{CH}_2\text{SMe})_3\}]$ {reaction (2); $L' = [\text{9]aneS}_3$, $[\text{10]aneS}_3$, ttob, $\text{MeC}(\text{CH}_2\text{SMe})_3$ or $\frac{1}{3}[\text{18]aneS}_6$ }.



The tetrathioether macrocycle 1,5,9,13-tetrathiacyclohexadecane ($[\text{16]aneS}_4$) reacted with $[\text{VCl}_3(\text{thf})_3]$ to give $[\text{VCl}_3(\text{[16]aneS}_4)]$, in which the S_4 ligand may be tridentate {as in $[\text{Mo}(\text{CO})_3(\text{[16]aneS}_4)]$ and $[\text{W}(\text{CO})_3(\text{Me}_8[\text{16]aneS}_4\text{-S,S',S''})]$ }^{9,10}

[†] Non-SI units employed: $\text{eV} \approx 1.60 \times 10^{-19} \text{ J}$, $\mu_B \approx 9.27 \times 10^{-24} \text{ J T}^{-1}$.

Table 1 Electronic spectroscopic data for vanadium(III) thioether macrocyclic compounds^a

Compound	Colour	$\tilde{\nu}_1/$ cm ⁻¹	$\tilde{\nu}_2/$ cm ⁻¹	$Dq/$ cm ⁻¹	$B^b/$ cm ⁻¹
[VCl ₃ ([9]aneS ₃)]	Pink	18 590	27 620	1932	690
[VBr ₃ ([9]aneS ₃)]	Brick red	17 890	24 020	1857	502
[VI ₂ ([9]aneS ₃)]	Brown-black	16 050	27 030	1783	770
[VCl ₃ ([10]aneS ₃)]	Pink	19 050	27 700	2048	640
[VBr ₃ ([10]aneS ₃)]	Orange	18 250	23 810	1866	445
[(VCl ₃) ₂ ([18]aneS ₆)]	Pink	19 380	28 010	2064	635
[(VBr ₃) ₂ ([18]aneS ₆)]	Red	17 930	23 320	1825	445
[VCl ₃ (MeCN) ₃] ^c	Green	14 400	21 400	1550	540
[VCl ₃ (thf) ₃] ^c	Orange	13 300	19 900	1400	553
[VCl ₆] ³⁻ ^c		16 650	18 350	1265	513
[V(CN) ₆] ³⁻ ^d		22 200	28 600	2385	550

^a Recorded as a solid diluted with BaSO₄ by diffuse reflectance.

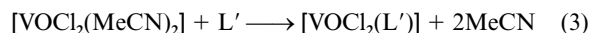
^b $C = 4.5B$. ^c Taken from ref. 11. ^d Taken from ref. 12.

Alternatively the fourth sulfur atom could ligate to another vanadium atom, as in $\{[\text{Cu}(\mu\text{-}\eta^1\text{:}\eta^3\text{-}[\text{14]aneS}_4)]_n\}$,¹¹ giving a polymer formulated as $\{[\text{VCl}_2[\mu\text{-}\eta^1\text{:}\eta^3\text{-}[\text{16]aneS}_4)]_n\}\text{Cl}_n$. Unfortunately the compound was too insoluble for studies in solution or to obtain crystals for a definitive structural study.

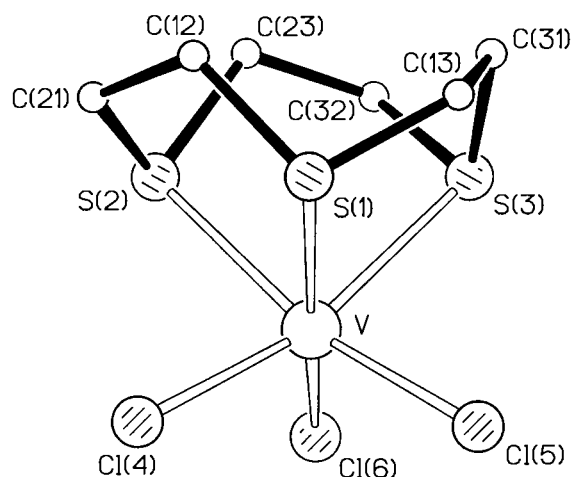
These thioether compounds are poorly soluble in common solvents; however, they are relatively stable in the solid state when contained in a dry, O₂-free atmosphere. The binuclear [18]aneS₆ complexes appear to be rather less stable to moist air than the trithioether compounds, decolourising readily upon exposure. The trithioether complexes are all constrained by the ligand geometry to be *fac* trisubstituted; however, in principle, [18]aneS₆ could yield either *mer*- or *fac*-trisubstituted isomers. In fact, comparison of the IR and UV/VIS spectroscopic data for these compounds with those for all of the other complexes prepared suggests that they too are *fac* trisubstituted. In each case the IR spectra confirm the presence of the thioether ligand and in addition the chloro and bromo derivatives show peaks in the region 200–450 cm⁻¹ which are tentatively assigned as $\nu(\text{V-Cl})$ or $\nu(\text{V-Br})$. Owing to their poor solubilities and sensitivity to moisture, FAB and electrospray mass spectra proved unhelpful. However, IR and UV/VIS spectroscopy and micro-analytical data were consistent with the proposed formulations.

The UV/VIS spectrum of a vanadium(III) (d²) complex in octahedral symmetry is expected to show three spin-allowed d–d transitions. These correspond to, in order of increasing energy: ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{T}_{1g}(\text{F})$ (ν_1), ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) and ${}^3\text{A}_{2g}(\text{F}) \leftarrow {}^3\text{T}_{1g}(\text{F})$ (ν_3). Typically ν_3 is not observed, since it is obscured by much more intense charge-transfer transitions. While the local symmetry at V^{III} in the compounds reported here is approximately C_{3v}, the absence of any discernible splitting of the d–d bands allows the spectra to be analysed in terms of O_h symmetry. The values of Dq and B were obtained from the appropriate Tanabe–Sugano diagram, and the data for the compounds in this work and some other octahedral vanadium(III) compounds for comparison are presented in Table 1. The individual values from such an analysis are not of high precision, but the derived trends are usually reliable. The ligand field strengths for the thioether species reported here are higher than for [VCl₃(thf)₃] or [VCl₃(MeCN)₃],¹² but lower than in the complex anion [V(CN)₆]³⁻.¹³ Also, Dq is higher in the vanadium(III) species than in the corresponding chromium(III) complexes.^{14–16}

The vanadium(IV) species [VOCl₂([9]aneS₃)]⁶ and [VOCl₂(ttob)] were prepared in high yield (>90%) as blue ([9]aneS₃) or turquoise (ttob) solids by the direct reaction of the vanadium(IV) precursor [VOCl₂(MeCN)₂] with the appropriate thioether L' in CH₂Cl₂ solution [reaction (3)]. Their IR spectra

**Table 2** Selected molecular dimensions in the [9]aneS₃ complexes of vanadium. Bond lengths are in Å, angles in °; estimated standard deviations in parentheses

	[VCl ₃ ([9]aneS ₃)]	[VI ₂ (thf)([9]aneS ₃)] Sample II
V–S(1)	2.469(2)	2.492(2)
V–S(2)	2.501(2)	2.490(2)
V–S(3)	2.515(2)	2.495(2)
V–X(4)	X = Cl 2.277(2)	X = I 2.7961(14)
V–X(5)	X = Cl 2.304(2)	X = I 2.8021(13)
V–X(6)	X = Cl 2.296(2)	X = O 2.133(5)
S(1)–V–S(2)	82.34(8)	84.03(8)
S(1)–V–S(3)	83.03(8)	84.71(8)
S(1)–V–X(4)	87.52(9)	90.02(6)
S(1)–V–X(5)	86.68(8)	90.86(7)
S(1)–V–X(6)	168.69(10)	172.9(2)
S(2)–V–S(3)	82.32(8)	83.45(8)
S(2)–V–X(4)	85.02(8)	89.23(6)
S(2)–V–X(5)	166.31(9)	169.92(7)
S(2)–V–X(6)	89.55(11)	90.1(2)
S(3)–V–X(4)	165.09(9)	171.38(7)
S(3)–V–X(5)	88.26(9)	87.44(6)
S(3)–V–X(6)	88.10(10)	90.7(2)
X(4)–V–X(5)	102.72(10)	99.48(4)
X(4)–V–X(6)	99.66(11)	93.9(2)
X(5)–V–X(6)	100.10(11)	94.4(2)

**Fig. 1** View of the structure of [VCl₃([9]aneS₃)] with the numbering scheme adopted

clearly show the V=O stretching band at *ca.* 960 cm⁻¹, as well as bands of the co-ordinated thioether. As expected for a vanadium(IV) (d¹) species, [VOCl₂(ttob)] is EPR active and shows a very broad resonance in the solid state ($g = 1.995$).

X-Ray crystallography

In view of the paucity of structural data on vanadium thioether compounds, single crystal X-ray determinations were undertaken on the vanadium(III) complex [VCl₃([9]aneS₃)] and the vanadium(II) compound [VI₂(thf)([9]aneS₃)].

The structure of [VCl₃([9]aneS₃)] (Fig. 1 and Table 2) shows the trithioether ligand bonded in a facial manner to the V^{III}, with the three chloride ligands completing the distorted octahedral geometry. A pseudo-threefold symmetry axis passes through the thioether ligand and the vanadium atom; the regularity of the ligand about this axis can be seen in Fig. 1, and mean dimensions in the ligand are listed in Table 3 with those of other complexes and in the free molecule. The angles subtended by the macrocycle at the vanadium atom, mean value 82.6(2)°, suggest that the nine-membered ring is too small to give an ideal octahedral co-ordination pattern. However, the

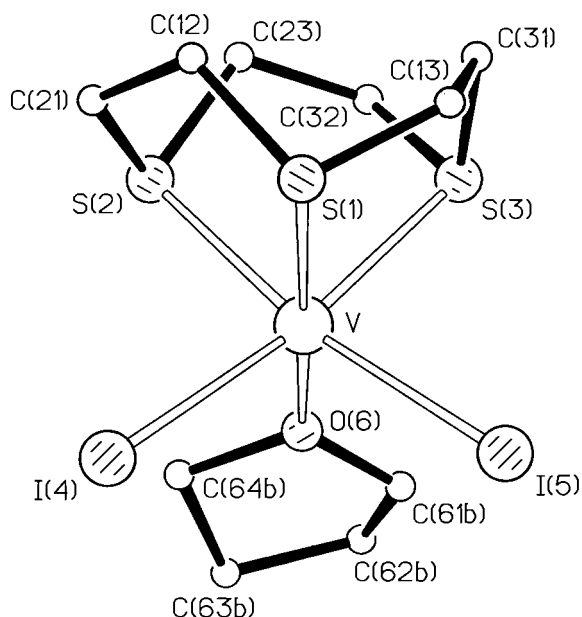


Fig. 2 View of the structure of $[\text{VI}_2(\text{thf})([9]\text{aneS}_3)]$, sample II, with the numbering scheme adopted. One of the two orientations of the disordered thf ligands is shown: the two molecules of $[\text{VI}_2(\text{thf})([9]\text{aneS}_3)]$, sample I, have very similar structures to that shown here

$\text{S}\cdots\text{S}$ distances in the complex are slightly shorter than in the free thioether molecule¹⁷ which has a very similar shape to that shown for the ligand; the angular requirements of the sulfur atoms are the most likely determining factor of the molecular geometry. The conformation of the molecule has been adjusted so that one of the lone pairs of electrons, in a tetrahedral arrangement, on each sulfur atom is pointing more directly at a common point (*viz.* the vanadium atom in the complex) than in the free molecule. The other co-ordinating atoms, chloride ions in this case, may also influence the distortions from the octahedral pattern.

Two polymorphs of $[\text{VI}_2(\text{thf})([9]\text{aneS}_3)]$ were examined by X-ray crystallography. The analysis of sample I of this complex (blue-green plates) shows two virtually identical molecules in the crystal but the intensity data were from a weakly diffracting crystal and the results were not precise so they are not recorded nor discussed here. Therefore, the second sample (greenish blue prisms), II, was examined and showed the same molecular complex (Fig. 2 and Tables 2 and 3) but with more satisfactory dimensions. In each sample, the V^{II} is co-ordinated to two terminal iodide ions, the oxygen atom of a thf ligand and the three sulfur atoms of the $[9]\text{aneS}_3$ molecule. In sample II the thf ligand is disordered with two distinct orientations of the five-membered ring; the oxygen atom site is common to both arrangements.

Mean dimensions of the thioether ligands and its co-ordination to the vanadium atom in several complexes are shown in Table 3. The V–S distances in these vanadium-(ii), -(iii) and -(iv) compounds appear to be almost independent of the formal oxidation state of the vanadium centre. Evidently, there is a balance between the σ and π components of the V–S bonding systems in these complexes which compensates for the variation of charge at the metal.

Comparison of V–S separations in crown thioether complexes with other types of V–S bonds

The shortest known V–S separations in monomeric complexes are in thiovanadyl groups *e.g.* in $[\text{VS}(\text{SPh})_4]^{2-}$ (2.078 Å)¹⁹ and $[\text{VS}(\text{SCH}_2\text{CH}_2\text{S})_2]^{2-}$ (2.087 Å).²⁰ The single-bond V–S separations in these anions are considerably longer, at 2.391 and 2.367 Å respectively, and these are typical of cases where the sulfur donor atom is from a thiolate(1–) group. Other examples

Table 3 Mean dimensions in the thioether ligands of $[9]\text{aneS}_3$ complexes of vanadium. Distances are in Å, angles in °. Standard deviations in parentheses

	$[\text{VCl}_3\text{-}([9]\text{aneS}_3)]$	$[\text{VI}_2(\text{thf})\text{-}([9]\text{aneS}_3)]$ Sample II	$[\text{VCl}_2\text{O-}([9]\text{aneS}_3)]^a$	$[9]\text{aneS}_3$ ¹⁷
Metal co-ordination				
V–S	2.495(14)	2.492(1)	2.53(4) ^a	
S–V–S	82.6(2)	84.1(4)	81.2(9)	
In the thioether ligand				
S–C _i ^b	1.805(1)	1.833(5)	1.803(6)	1.820(5)
S–C _o ^b	1.815(6)	1.812(5)	1.797(4)	1.823(5)
C–C	1.497(3)	1.509(8)	1.507(7)	1.510(6)
C–S–C	102.6(2)	102.0(2)	102.6(3)	102.8(3)
S–C _i –C _o	113.5(2)	113.2(4)	112.3(3)	113.0(4)
C _i –C _o –S	115.5(7)	115.7(3)	115.0(3)	117.0(4)
S \cdots S	3.29(1)	3.338(12)	3.293(7)	3.451(2)
Torsion angles				
S–C–C–S	–48.8(14)	–50.9(12)	–52.7(6)	58.5
C–C _o –S–C	–64.6(12)	–62.4(11)	–61.2(7)	55.1
C–S–C _i –C	131(2)	132.0(6)	132.9(4)	–131.1

^a The mean (from values in two independent molecules) of two V–S (*trans* to O) at 2.634 and 2.653 Å and four V–S (*trans* to Cl) distances in the range 2.463–2.481 Å. ^b Subscripts ‘i’ and ‘o’ indicate the in- and out-of-plane carbon atoms as identified by Blower and co-workers.¹⁸ In the vanadium complexes each VS_2C_2 chelate ring has an envelope shape in which one atom is displaced from the almost planar group of the other four atoms; the out-of-plane atoms in each of our molecules are C(13), C(32) and C(21); the free $[9]\text{aneS}_2$ molecule adopts a very similar shape.

include V–S at 2.378 Å in $[\text{VO}(\text{SCH}_2\text{CH}_2\text{S})_2]^{2-}$,²¹ 2.32 Å (mean) in $[\text{V}(\text{SC}_6\text{H}_4\text{Pr}^i\text{-}2,4,6)_3(\text{thf})_2]$,²² 2.290 Å (mean) in $[\text{V}\{\text{N}(\text{CH}_2\text{CH}_2\text{S})_3\}(\text{NH}_3)]$,²³ 2.263 Å (mean) in $[\text{V}\{\text{N}(\text{CH}_2\text{CH}_2\text{S})_3\}\text{-}(\text{NNMe}_2)]$ ²² and 2.381 Å (mean) in $[\text{VO}(\text{L-O,S})_2]$ (HL = 2-mercaptopyridine *N*-oxide).²⁴

The complex $[\text{V}(2\text{-SC}_2\text{H}_4\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{C}_6\text{H}_4\text{S-}2)(\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2)]$ ²⁵ is the only structurally characterised complex where vanadium is ligated by both thiolate and thioether donor functions. In it all the V–S separations fall within the narrow range 2.476–2.485 Å, suggested to be due to electron delocalisation through the phenyl rings.²⁵ These separations are considerably longer than those in vanadium thiolate complexes; they suggest that pure vanadium–thioether bonds should be longer still. In view of this the long V–S separations found in our crown thioether complexes [range 2.469(2)–2.515(2) Å] are not surprising.

The other class of complex to which crown thioether vanadium compounds may be compared comprises iron–vanadium–sulfur clusters, which may be regarded as structural models for the vanadium site of vanadium nitrogenase. The geometry about the vanadium atom in clusters and in crown thioether complexes is directly comparable as there are three *fac*-ligating sulfur atoms in each case; thus both V–S separations and S–V–S angles can be compared. The most straightforward comparison may be made between the structure of $[\text{VCl}_3([9]\text{aneS}_3)]$ and $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{dmf})_3]^-$ (containing vanadium essentially as V^{III}).²⁶ Both have local C_{3v} symmetry at vanadium, but the following remarks also apply to the other crown thioether complexes discussed in this paper and to other cluster complexes where dmf has been substituted by bipyridine or a diphosphine.²⁷

In $[\text{VCl}_3([9]\text{aneS}_3)]$ the mean V–S separation is 2.495(14) Å with a mean S–V–S angle of 82.6(2)°. The mean S \cdots S non-bonded distance is approximately 3.29(1) Å. In the cluster

Table 4 Vanadium K-Edge EXAFS structural data^a for vanadium(III) thioether macrocyclic compounds

Complex	$d(\text{V-S})^b/\text{\AA}$	$2\sigma^2/\text{\AA}^2$	$d(\text{V-X})^b/\text{\AA}$	$2\sigma^2/\text{\AA}^2$	R^d	Fit index ^e
$[\text{VCl}_3(\text{[9]aneS}_3)]$	2.498(4)	0.0116(7)	2.309(2)	0.0062(3)	19.8	3.5
$[\text{VCl}_3(\text{[9]aneS}_3)]^f$	2.495(14)		2.292(8)			
$[\text{VBr}_3(\text{[9]aneS}_3)]$	2.486(4)	0.0165(12)	2.472(2)	0.0093(2)	22.6	3.4
$[\text{VI}_3(\text{[9]aneS}_3)]$	2.486(4)	0.0083(8)	2.661(3)	0.0091(4)	24.9	6.6
$[\text{VCl}_3(\text{[10]aneS}_3)]$	2.411(11)	0.0200(24)	2.283(8)	0.0178(17)	20.2	5.5
$[\text{VBr}_3(\text{[10]aneS}_3)]$	2.482(7)	0.0105(18)	2.472(4)	0.0087(5)	23.6	9.1
	$d(\text{V-O})^b/\text{\AA}$					
$[\text{VCl}_3(\text{thf})_3]$	2.044(9)	0.0182(19)	2.344(6)	0.0138(7)	23.6	7.1
$[\text{VBr}_3(\text{thf})_3]$	2.036(5)	0.0098(9)	2.517(3)	0.0096(2)	21.0	4.4

^a Recorded in transmission mode on station 7.1, using powdered sample diluted with BN. ^b Standard deviations in parentheses. Note that the systematic errors in bond distances arising from data collection and analysis procedures are ± 0.02 – 0.03 \AA for well defined co-ordination shells. AFAC = 0.80 in all cases. ^c Debye–Waller factor. ^d Defined as $[(\chi^T - \chi^E)k^3 dk / \chi^E k^3 dk] \times 100\%$. ^e Defined as $\Sigma[(\chi^T - \chi^E)k_i^3]^2$. ^f Average bond distances from X-ray crystallographic data (see Table 2).

$[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{dmf})_3]^-$ the V–S separations are 2.338, 2.340 and 2.331 \AA and S–V–S angles are 101.4, 102.2 and 102.3°, the non-bonding S···S distances being around 3.6 \AA . The longer V–S separation in the crown thioether complexes is *not* due to the fact that the S_3 plane has larger S···S dimensions (in fact it has smaller dimensions). It reflects the much steeper nature of the pyramid (of which V is the apex and S_3 is the base) in the crown thioether complex. In the cluster the V is much more firmly embedded in the S_3 plane.

If the data for all crown thioether compounds and all clusters are considered, it is seen that V–S separations are longer (by 6–8%) and S–V–S angles are smaller (80 against 100°) in crown thioethers than in clusters. The V–S separations in clusters resemble far more closely typical V–S separations in thiolates.

Vanadium K-Edge EXAFS structural studies

Owing to the limited solubilities displayed by many of the compounds isolated, and their sensitivity to moisture, in most cases crystals suitable for an X-ray study could not be obtained. However, given the lack of structural data on compounds of this type, vanadium K-edge EXAFS data were used to provide important structural information for the metal–ligand bond lengths in the first co-ordination sphere, *i.e.* $d(\text{V-S})$ and $d(\text{V-X})$. The spectroscopic studies carried out in parallel provided key information concerning the donor sets involved in these products. Details of the refined EXAFS data for the complexes are given in Table 4 and Fig. 3 shows a typical example. Vanadium K-edge EXAFS spectra were also recorded for the $[\text{VX}_3(\text{thf})_3]$ (X = Cl or Br) model compounds and for $[\text{VCl}_3(\text{[9]aneS}_3)]$ in order to compare the V–S and V–X distances derived from this method with the *average* values obtained from X-ray crystallographic studies noted above. These model compounds also allow us to check that the data treatment and analyses are satisfactory. The EXAFS data for the thf adducts, $[\text{VX}_3(\text{thf})_3]$, were satisfactorily modelled by a first shell of three oxygens giving V–O distances of 2.04 \AA for both X = Cl and Br, with a second shell of three halides giving $d(\text{V-Cl}) = 2.34$ and $d(\text{V-Br}) = 2.52$ \AA . In the case of $[\text{VCl}_3(\text{[9]aneS}_3)]$ the data were satisfactorily modelled by an S_3Cl_3 donor set with $d(\text{V-Cl}) = 2.31$, $d(\text{V-S}) = 2.50$ \AA . These results correlate very well with the average V–S, V–O or V–X distances derived from the X-ray crystallographic studies, and provide further supporting evidence for the structures of the remaining compounds.

For $[\text{VX}_3(\text{[9]aneS}_3)]$ and $[\text{VX}_3(\text{[10]aneS}_3)]$ the EXAFS data were modelled for three sulfurs and three halogen atoms (Cl, Br or I as appropriate). In all cases the EXAFS data gave $d(\text{V-S})$ values very similar to those obtained crystallographically for vanadium(III)–thioether interactions (*ca.* 2.5 \AA) and significantly longer than $d(\text{V-Cl})$ (*ca.* 2.3 \AA). This is consistent with the interaction between the hard vanadium(III) centre and the thioether functions being weak, as might be anticipated

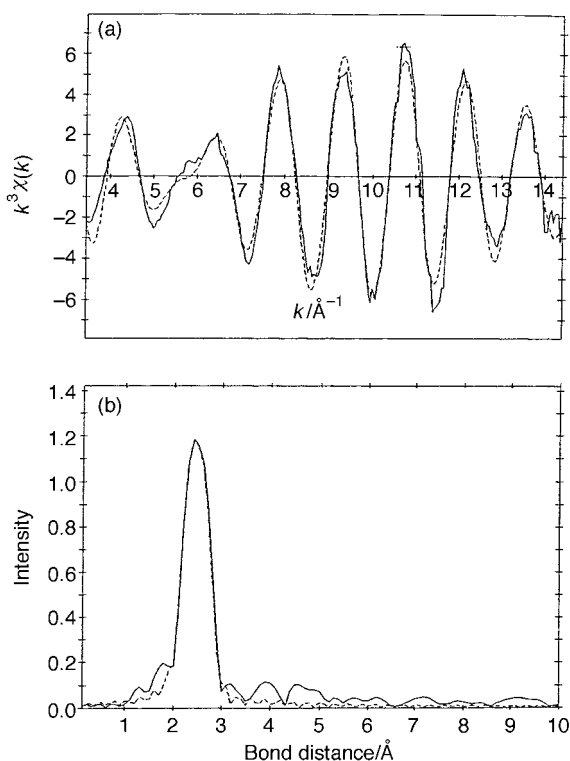


Fig. 3 (a) Background subtracted vanadium K-edge EXAFS data and (b) the corresponding Fourier transform for $[\text{VBr}_3(\text{[9]aneS}_3)]$ (solid line = experimental, dashed line = calculated data)

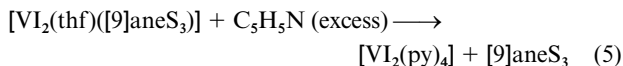
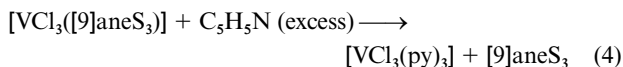
for such a hard metal–soft ligand combination. The V–Br and V–I bond lengths of *ca.* 2.45 and 2.66 \AA respectively are in accord with the trend expected on the basis of the increasing size of the halogen. Furthermore, the $\text{V}^{\text{III}}\text{-I}$ distances are shorter than the $\text{V}^{\text{II}}\text{-I}$ distances determined crystallographically for $[\text{VI}_2(\text{thf})(\text{[9]aneS}_3)]$ (see above), consistent with the increase in oxidation state in the former, and hence smaller metal ion radius.

We have also reported the preparation and structural characterisation (through EXAFS studies and X-ray crystallography) of a series of chromium(III) thioether and selenoether macrocyclic complexes.^{14,16} In the thioether species $d(\text{Cr-S})$ is *ca.* 2.4 \AA , while $d(\text{Cr-X})$ is 2.3 \AA for X = Cl and 2.45 \AA for X = Br. Thus the metal–thioether distance is significantly shorter than in the vanadium species reported here, while for a given halogen the metal–halogen distances are virtually the same.

Some reactions of [9]aneS₃ compounds

We have made a brief examination of the reactions of $[\text{VCl}_3(\text{[9]aneS}_3)]$ and $[\text{VI}_2(\text{thf})(\text{[9]aneS}_3)]$. We find that pyridine

displaces the thioether ligands from these complexes to give $[\text{VCl}_3(\text{py})_3]$ and $[\text{VI}_2(\text{py})_4]$ respectively [reactions (4) and (5)].



Neither thioether complex reacted with anhydrous HCl in thf and repeated attempts to obtain tractable products after reduction of these compounds with sodium or magnesium under N_2 or H_2 were unsuccessful.

Conclusion

These results illustrate that thioether ligands bond readily to vanadium; in particular [9]aneS₃ is capable of stabilising vanadium-(II), -(III) and -(IV) centres, although the V–S interaction in each case is relatively weak. It is notable that within the vanadium series the V–S distances *trans* to halide are relatively insensitive to the vanadium oxidation state. The introduction of O-donor coligands such as thf into these compounds indicates that a wider variety of coligands with the S₃ core can be anticipated in future studies.

Experimental

Infrared spectra were measured as Nujol mulls between CsI plates using Perkin-Elmer 883 or 983 spectrometers over the range 200–4000 cm^{-1} , UV/VIS spectra of samples diluted with BaSO₄ were recorded by diffuse reflectance using a Perkin-Elmer Lambda 19 spectrophotometer. Microanalytical data were obtained from the University of Surrey Microanalytical Service, the University of Southampton (C, H and N), and the Butterworth Laboratories Ltd. (S). Magnetic moments were measured at 20 °C by the Faraday method, using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as standard and making the usual diamagnetic corrections using Pascal's constants. The EXAFS measurements were made at the Daresbury Laboratory, operating at 2.0 GeV with typical currents of 200 mA. Vanadium K-edge data were collected on station 7.1 using a silicon(111) order-sorting monochromator, with harmonic rejection achieved by stepping off the peak of the rocking curve by 50% of full height level. Data were collected in transmission mode from samples diluted with boron nitride and mounted between Sellotape sheets in 1 mm aluminium holders.

The compounds PMe_2Ph , VCl_3 and VBr_3 were from Aldrich Chemical Co., as were some samples of [9]aneS₃ and [16]aneS₄; $[\text{VOCl}_2(\text{H}_2\text{O})_2]$ was from BDH Chemical Co. Samples of [9]aneS₃²⁸ and [16]aneS₄²⁹ as well as $\text{Me}_6[\text{16]aneS}_4$ and *ttob*,³⁰ were made by published procedures, as were the vanadium complexes $[\text{V}_2(\mu\text{-Cl})_3(\text{thf})_6][\text{AlCl}_2\text{Et}_2]$,⁷ $[\text{VCl}_3(\text{thf})_3]$,³¹ $[\text{VBr}_3(\text{thf})_3]$,³¹ $[\text{VCl}_3(\text{MeCN})_3]$,³² $[\text{VO}(\text{acac})_2]$,³³ $[\text{VI}_2(\text{thf})_4]$,³⁴ $[\text{VOCl}_2(\text{NCMe})_2]$,³⁵ and $[\text{VCl}_3(\text{OPMe}_2\text{Ph})(\text{PMe}_2\text{Ph})_2]$.³⁶ All reactions were performed in anhydrous solvents under an atmosphere of dry N_2 using standard Schlenk techniques.

Preparations

Vanadium(II) complexes. $\{[\text{V}(\text{[9]aneS}_3)_2(\mu\text{-Cl})_3]\text{Cl}$. The complex $\{[\text{V}(\text{thf})_3(\mu\text{-Cl})_2][\text{AlCl}_2\text{Et}_2]\}$ (0.65 g, 0.8 mmol) and [9]aneS₃ (0.21 g, 1.2 mmol) were heated under reflux in CH_2Cl_2 (100 cm^3) giving a purple solid which was filtered off, washed with dichloromethane ($2 \times 20 \text{ cm}^3$), diethyl ether and dried *in vacuo*. Yield 0.42 g, 85% (Found: C, 23.6; H, 4.0; S, 30.4. $\text{C}_6\text{H}_{12}\text{Cl}_2\text{S}_3\text{V}$ requires C, 23.9; H, 4.0; S, 31.8%). $\mu_{\text{eff}} = 3.5 \mu_{\text{B}}$.

$[\text{VI}_2(\text{thf})(\text{[9]aneS}_3)]$. Solutions of $[\text{VI}_2(\text{thf})_4]$ (0.59 g, 1.0 mmol) in thf (20 cm^3) and [9]aneS₃ (0.18 mmol) in thf (5 cm^3) were mixed. An immediate light blue precipitate was produced,

and this was filtered off, washed with thf and diethyl ether and dried *in vacuo*. Yield = 0.43 g, 77% (Found: C, 21.7; H, 3.6; S, 16.6. $\text{C}_{10}\text{H}_{20}\text{I}_2\text{OS}_3\text{V}$ requires C, 21.5; H, 3.6; S, 17.2%). $\mu_{\text{eff}} = 3.7 \mu_{\text{B}}$.

$[\text{VI}_2(\text{thf})(\text{ttob})]$. This complex was prepared in a similar manner and yield to the above, but using *ttob* instead of [9]aneS₃ (Found: C, 27.2; H, 3.5. $\text{C}_{16}\text{H}_{24}\text{I}_2\text{OS}_2\text{V}$ requires C, 30.3; H, 3.8%). $\mu_{\text{eff}} = 3.6 \mu_{\text{B}}$.

$[\text{VI}_2(\text{C}_5\text{H}_5\text{N})_4]$. A solution of pyridine (0.8 g, 10 mol) in thf (5 cm^3) was added to a solution of $[\text{VI}_2(\text{thf})_4]$ (0.59 g, 1 mmol) in thf (20 cm^3). Red crystals precipitated immediately. After an hour they were filtered off, washed with thf and ether and dried *in vacuo*. Yield 0.57 g, 0.92 mmol, 92% (Found: C, 39.1; H, 3.3; N, 8.8. $\text{C}_{20}\text{H}_{20}\text{I}_2\text{N}_4\text{V}$ requires C, 38.6; H, 3.2; N, 9.0%). $\mu_{\text{eff}} = 3.6 \mu_{\text{B}}$.

Vanadium(III) complexes. $[\text{VBr}_3(\text{thf})_3]$. This compound was made by refluxing VBr_3 in thf for 6 h, evaporating to dryness and recrystallising from thf–hexane in 85% yield (Found: C, 28.6; H, 4.5. Calc. for $\text{C}_{12}\text{H}_{24}\text{Br}_3\text{O}_3\text{V}$: C, 28.4; H, 4.7%).

$[\text{VI}_3(\text{thf})_3]$. A solution of $[\text{VI}_2(\text{thf})_4]$ (0.59 g, 1.0 mmol) in thf (40 cm^3) and I_2 (0.127 g, 0.5 mmol) in thf (10 cm^3) were mixed at 0 °C. Black crystals quickly precipitated. After the flask was cooled at –20 °C overnight they were filtered off and washed with thf and diethyl ether, yield 68% (Found: C, 22.4; H, 3.8; I, 59.7. $\text{C}_{12}\text{H}_{24}\text{I}_3\text{O}_3\text{V}$ requires C, 22.2; H, 3.7; I, 58.8%). $\mu_{\text{eff}} = 2.88 \mu_{\text{B}}$.

$[\text{VCl}_3(\text{[9]aneS}_3)]$. The complex $[\text{VCl}_3(\text{thf})_3]$ (0.75 g, 2.0 mmol) was treated with [9]aneS₃ (0.43 g, 2.0 mmol) in refluxing toluene, thf or CH_2Cl_2 (120 cm^3) for 1 h, giving a pink solid which was isolated by filtration, washed with thf and hexane, and dried *in vacuo*. Yield = 0.64 g, 94% (Found: C, 21.3; H, 3.6; S, 29.2. $\text{C}_6\text{H}_{12}\text{Cl}_3\text{S}_3\text{V}$ requires C, 21.3; H, 3.6; S, 28.5%). IR spectrum (Nujol): 1402s, 840m, 350m and 320w cm^{-1} . $\mu_{\text{eff}} = 2.55 \mu_{\text{B}}$. Similar reaction of $[\text{VCl}_3(\text{MeCN})_3]$ or $[\text{VCl}_3(\text{OPMe}_2\text{Ph})(\text{PMe}_2\text{Ph})_2]$ with [9]aneS₃ also yielded $[\text{VCl}_3(\text{[9]aneS}_3)]$ in high yield.

$[\text{VBr}_3(\text{[9]aneS}_3)]$. Method as for $[\text{VCl}_3(\text{[9]aneS}_3)]$ above, using $[\text{VBr}_3(\text{thf})_3]$ (0.142 g, 0.28 mmol) and [9]aneS₃ (0.05 g, 0.28 mmol), giving a brown solid. Yield = 0.09 g, 68% (Found: C, 15.3; H, 2.7; S, 19.4. $\text{C}_6\text{H}_{12}\text{Br}_3\text{S}_3\text{V}$ requires C, 15.5; H, 2.5; S, 20.4%). IR (Nujol mull): 1404s, 826m and 306w cm^{-1} [$\nu(\text{V-Br})$]. $\mu_{\text{eff}} = 2.59 \mu_{\text{B}}$.

$[\text{VI}_3(\text{[9]aneS}_3)]$. *Method 1.* The complex $[\text{VI}_2(\text{thf})_4]$ (0.40 g, 0.67 mmol) and I_2 (0.084 g, 0.33 mmol) were heated to reflux in thf solution (80 cm^3) and then filtered. To the cooled solution was added [9]aneS₃ (0.12 g, 0.67 mmol) in thf (20 cm^3), resulting in the immediate precipitation of a dark brown-black powder which was filtered off, washed with thf and diethyl ether and dried. Yield 0.2 g, 48% (Found: C, 12.1; H, 2.1. $\text{C}_6\text{H}_{12}\text{I}_3\text{S}_3\text{V}$ requires C, 11.8; H, 2.0%). IR (Nujol mull): 1404s and 826m cm^{-1} .

Method 2. Trimethylsilyl iodide (2 cm^3) was added to a mixture of $[\text{VCl}_3(\text{NCMe})_3]$ (0.27 g, 1.0 mmol) and [9]aneS₃ (0.18 g, 1 mmol) in MeCN (25 cm^3). The mauve precipitate dissolved and the mixture was distilled to 50% volume to expel SiMe_3Cl . The residue was then cooled to give a dark precipitate which was filtered off, washed with MeCN and diethyl ether and dried *in vacuo*. Yield 0.3 g, 74% (Found: C, 12.1; H, 2.1; S, 15.7. $\text{C}_6\text{H}_{12}\text{I}_3\text{S}_3\text{V}$ requires C, 11.8; H, 2.0; S, 15.7%). $\mu_{\text{eff}} = 2.80 \mu_{\text{B}}$.

$[\text{VCl}_3(\text{[10]aneS}_3)]$. Method as for $[\text{VCl}_3(\text{[9]aneS}_3)]$ above, using VCl_3 (0.34 mmol) and [10]aneS₃ (0.066 g, 0.34 mmol), giving a pink solid. Yield = 0.097 g, 81% (Found: C, 23.4; H, 3.9. $\text{C}_7\text{H}_{14}\text{Cl}_3\text{S}_3\text{V}$ requires C, 23.9; H, 4.0%). IR (Nujol mull): $\nu(\text{V-Cl})$ 440s (br) cm^{-1} .

$[\text{VBr}_3(\text{[10]aneS}_3)]$. Method as for $[\text{VCl}_3(\text{[9]aneS}_3)]$ above, using $[\text{VBr}_3(\text{thf})_3]$ (0.103 g, 0.20 mmol) and [10]aneS₃ (0.039 g, 0.20 mmol), giving an orange solid. Yield 0.064 g, 66% (Found: C, 17.0; H, 3.1. $\text{C}_7\text{H}_{14}\text{Br}_3\text{S}_3\text{V}$ requires C, 17.3; H, 2.9%). IR (Nujol mull): $\nu(\text{V-Br})$ 329w and 305 (br) cm^{-1} .

[VCl₃]₂(μ-[18]aneS₆). Method as for [VCl₃(9]aneS₃)] above, using VCl₃ (0.56 mmol) and [18]aneS₆ (0.025 g, 0.28 mmol), giving a pink solid. Yield 0.12 g, 64% (Found: C, 20.9; H, 3.5. C₆H₁₂Cl₃S₃V requires C, 21.3; H, 3.6%). IR (Nujol mull): 858m, 353 (br) m and 288w cm⁻¹.

[(VBr₃)₂(μ-[18]aneS₆)]. Method as for [VCl₃(9]aneS₃)] above, using [VBr₃(thf)₃] (0.05 g, 0.099 mmol) and [18]aneS₆ (0.018 g, 0.049 mmol), giving a brown solid. Yield 0.031 g, 67% (Found: C, 15.1; H, 2.6. C₆H₁₂Br₃S₃V requires C, 15.3; H, 2.5%). IR (Nujol mull): ν(V-Br) 315m and 296w cm⁻¹.

[VCl₃(ttob)]. The complex [VCl₃(thf)₃] (0.087 g, 0.23 mmol) and ttob (0.059 g, 0.23 mmol) were heated to reflux in CH₂Cl₂ solution (25 cm³) for 15 min. The resulting pink solid was filtered off, washed with CH₂Cl₂ and hexane and dried *in vacuo*. Yield 0.085 g, 90% (Found: C, 34.6; H, 3.9; S, 23.0. C₁₂H₁₆Cl₃S₃V requires C, 34.8; H, 3.9; S, 23.2%). μ_{eff} = 2.76 μ_B.

Vanadium(IV) complexes. [VOCl₂(9]aneS₃)]. *Method 1.* The complex [VOCl₂(MeCN)₂] (0.122 g, 0.55 mmol) was dissolved in CH₂Cl₂ (30 cm³) to give a blue solution, [9]aneS₃ (0.099 g, 0.5 mmol) was then added, and stirring for 1 h gave a blue precipitate which was filtered off, washed with thf and diethyl ether and dried *in vacuo*. Yield 0.16 g, 95% (Found: C, 22.5; H, 3.7; S, 29.5. Calc. for C₆H₁₂Cl₂OS₃V: C, 22.6; H, 3.7; S, 30.2%). IR spectrum (Nujol mull): ν(V=O) 962 cm⁻¹.

Method 2. The complex [VO(acac)₂] (0.294 g, 1.10 mmol) was dissolved in toluene (50 cm³), MeOH (0.23 cm³, 5.6 mmol) and SiMe₃Cl (0.70 cm³, 5.6 mmol) were added, giving a dark green solution. The compound [9]aneS₃ (0.200 g, 1.10 mmol) was then added and the resulting blue suspension was refluxed for 45 min before filtering. The residue was washed with CH₂Cl₂, thf and diethyl ether and dried *in vacuo*. Yield 0.29 g, 95% (Found: C, 22.6; H, 3.6; S, 29.7. Calc. for C₆H₁₂Cl₂OS₃V: C, 22.6; H, 3.7; S, 30.2%). μ_{eff} = 1.73 μ_B.

[VOCl₂(ttob)]. The complex [VOCl₂(MeCN)₂] (0.18 g, 0.82 mmol) and ttob (0.21 g, 0.82 mmol) were stirred in CH₂Cl₂ solution for 1 h to give a pale turquoise suspension. The precipitate was then filtered off, washed with CH₂Cl₂ and thf and dried *in vacuo*. Yield 0.29 g, 90% (Found: C, 36.3; H, 4.1; S, 24.2. C₁₂H₁₆Cl₂OS₃V requires C, 36.5; H, 4.1; S, 24.4%). μ_{eff} = 1.85 μ_B. IR spectrum (Nujol mull): ν(V=O) 982; ν(V-Cl) 415 cm⁻¹.

Reactions of [9]aneS₃ complexes

[VI₂(thf)(9]aneS₃)] with pyridine. A solution of pyridine (0.6 g, 7.5 mmol) in thf (5 cm³) was added to a suspension of [VI₂(thf)(9]aneS₃)] (0.41 g, 0.75 mmol) in thf (20 mmol). There was an immediate red colour. The mixture was refluxed for 4 h then the suspension of red product was cooled and the product filtered off, washed with thf and ether, dried *in vacuo* and identified by its IR spectrum as [VI₂(py)₄]. Yield 0.35 g (0.56 mmol, 75%). The filtrate was taken to dryness and the crude residue identified as [9]aneS₃ by its IR spectrum (80% yield).

[VCl₃(9]aneS₃)] with pyridine. In a similar reaction to the above, treatment of [VCl₃(9]aneS₃)] gave [VCl₃(py)₃] and [9]aneS₃ in 85% yield.

Neither [9]aneS₃ complex reacted with anhydrous HCl in thf even at reflux and repeated attempts to obtain tractable products after reduction of these compounds with sodium or magnesium under N₂ or H₂ in thf were unsuccessful.

X-Ray crystallography

The crystallographic data for the three samples are presented in Table 5.

[VCl₃(9]aneS₃)]. Ruby-red crystals suitable for X-ray analysis were obtained by mixing filtered solutions of [VCl₃-

(MeCN)₃] and [9]aneS₃ (0.05 mmol of each) in MeCN (125 cm³). The solution turned red over 15 min and red needles grew over 3 d. The same reaction carried out in thf, CH₂Cl₂ or MeOH did not give satisfactory crystals.

A ruby-red, square prism crystal, was mounted on a glass fibre, examined photographically, then transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters and measurement of diffraction intensities (1125 unique reflections to θ_{max} = 25°, 846 'observed' with $I > 2\sigma_I$). Intensities were corrected for absorption (by semiempirical ψ-scan methods) and to eliminate negative net intensities (by Bayesian statistical methods); no deterioration correction was necessary. The structure was determined by direct methods in SHELXS.³⁸ Refinement was by full-matrix least-squares methods, initially on F in SHELX,³⁹ then on F^2 in SHELXL.⁴⁰ Hydrogen atoms were included in idealised positions but with independent U_{iso} . All the non-hydrogen atoms were refined anisotropically. The polarity of the crystal was checked by refinement of the structure at $1-x$, $0.5-y$, $1-z$; this gave marginally lower R factors, but a significantly lower Flack parameter,⁴⁰ viz. 0.01(7) vs. 0.18(7).

Scattering factor curves for neutral atoms were taken from ref. 41. Computer programs used in this analysis have been noted above or in Table 4 of ref. 42, and were run on a DEC-AlphaStation 200 4/100 computer in the Nitrogen Fixation Laboratory, John Innes Centre.

[VI₂(thf)(9]aneS₃)]. Two polymorphs were obtained from the same recrystallisation solution, dark greenish blue plates (sample I) and dark greenish blue prisms (sample II). Crystals of each were mounted on glass fibres and sealed with epoxy resin. Photographic and diffractometric procedures similar to those described above were followed. Both crystals showed a decline in the intensities of three reflections monitored throughout the data collections, and the intensities of each were corrected accordingly. The structures of both were solved by direct methods in SHELXS³⁸ and refined, on F^2 in SHELXL.⁴⁰

In sample I there are two independent, virtually identical molecules in the crystal. The intensity data for this crystal were, overall, rather weak and there were few 'observed' data. The results from the refinement are not precise, and sample II was examined for better results. In sample II the thf ligand is disordered approximately equally in two distinct orientations; the O atom is common to both orientations and the planes of the four carbon atoms in the two arrangements differ by a rotation of ca. 45° about the V-O bond. The carbon atoms of the thf ligands were refined isotropically and their hydrogen atoms included in idealised positions, all parameters riding on those of the parent atoms. The remaining non-hydrogen atoms were refined anisotropically, and the hydrogen atoms in the [9]aneS₃ ligand included in calculated positions with freely refined U_{iso} .

CCDC reference number 186/1005.

EXAFS Refinements

Typically two or three data sets were collected for each complex and the analyses carried out on the averaged spectra. The raw data were background-subtracted using the program PAXAS⁴³ by fitting a six- or eight-order split polynomial to the pre-edge subtracted spectrum between $k = 2$ and 13–15 Å⁻¹. Curve fitting was carried out using the program EXCURV 92.⁴⁴ Ground state potentials of the atoms were calculated using Von Barth theory and phase shifts using Hedin-Lundqvist potentials. Two shells (3S and 3X) were fitted in each case. Refinements were also carried out using 6S or 6X, as well as other combinations, and in the case of X = Br or I the results clearly supported the S₃Br₃ or S₃I₃ donor sets expected. In the case of the chlorine derivatives, the very similar back scattering from S and Cl made the assignment of the donor set difficult on the basis of the EXAFS

Table 5 Crystallographic data for [VCl₃([9]aneS₃)] and [VI₂(thf)([9]aneS₃)]^a

Complex	[VCl ₃ ([9]aneS ₃)]		[VI ₂ (thf)([9]aneS ₃)]	
	Sample I	Sample II	Sample I	Sample II
Elemental formula	C ₆ H ₁₂ Cl ₃ S ₃ V	C ₁₀ H ₂₀ I ₂ OS ₃ V	C ₁₀ H ₂₀ I ₂ OS ₃ V	C ₁₀ H ₂₀ I ₂ OS ₃ V
<i>M</i>	337.6	557.2	557.2	557.2
Crystal system, space group (no.)	Tetragonal, <i>I</i> ₄ <i>cd</i> (no. 110)	Monoclinic, <i>P</i> ₂ <i>1</i> / <i>n</i> (equiv. to no. 14)	Monoclinic, <i>B</i> ₂ <i>1</i> / <i>c</i> (equiv. to no. 14)	Monoclinic, <i>B</i> ₂ <i>1</i> / <i>c</i> (equiv. to no. 14)
<i>a</i> /Å	17.2808(10)	7.8864(10)	7.8864(10)	16.0550(12)
<i>b</i> /Å	17.2808	33.284(4)	33.284(4)	8.6760(10)
<i>c</i> /Å	16.4654(11)	13.2548(14)	13.2548(14)	24.975(3)
β/°		95.144(10)	95.144(10)	91.681(8)
<i>U</i> /Å ³	4917.0(5)	3465.2(7)	3465.2(7)	3477.3(6)
<i>Z</i>	16	8	8	8
<i>D</i> _c /g cm ⁻³	1.824	2.136	2.136	2.128
<i>F</i> (000)	2720	2120	2120	2120
μ(Mo-Kα)/cm ⁻¹	19.2	44.8	44.8	44.7
Crystal colour, shape	Ruby-red, square prisms with good faces/edges	Dark greenish blue plates	Dark greenish blue plates	Dark greenish blue prisms
Crystal size/mm	0.035 × 0.035 × 0.52	0.88 × 0.24 × 0.04	0.88 × 0.24 × 0.04	0.23 × 0.14 × 0.12
On diffractometer:				
θ range for centred reflections/°	10–11	10–11	10–11	10–11
θ _{max} for data collection/°	25	20	20	23
<i>h</i> , <i>k</i> , <i>l</i> ranges	0–20, 0–20, 0–19	0–7, 0–32, –12 to 12	0–7, 0–32, –12 to 12	0–17, 0–9, –27 to 27
Crystal degradation (% overall)	0	39	39	12
Absorption: transmission factor range	0.042–0.063	0.58–0.79	0.58–0.79	0.84–0.99
Total no. reflection measured (not including absences)	2189	3478	3478	2511
<i>R</i> _{int} for equivalents	0.035	0.057	0.057	0.015
Total no. unique reflections	1125	3187	3187	2406
No. 'observed' reflections (<i>I</i> > 2σ _{<i>i</i>})	846	1710	1710	1811
Refinement:				
final <i>R</i> 1	0.052	0.133	0.133	0.055
final <i>wR</i> 2	0.069	0.261	0.261	0.083
no. reflections used	1125 (all data)	3184 (all but 3 suspect)	3184 (all but 3 suspect)	2406 (all data)
<i>R</i> 1 for the 'observed' data	0.037	0.081	0.081	0.037
goodness of fit (on <i>F</i> ²), <i>S</i>	1.003	1.057	1.057	1.062
reflections weighted, <i>w</i> =	σ ⁻² (<i>F</i> _o ²)	[σ ² (<i>F</i> _o ²) + (0.152 <i>P</i>) ²] ^{-1b}	[σ ² (<i>F</i> _o ²) + (0.152 <i>P</i>) ²] ^{-1b}	[σ ² (<i>F</i> _o ²) + 23.6 <i>P</i>] ^{-1b}
Final difference map highest peaks/ e Å ⁻³ , location	0.5, close to the V atom	1.5, near the I ligands	1.5, near the I ligands	1.3, close to an I ligand

^a Details in common: 293 K, λ(Mo-Kα) 0.710 69 Å. ^b $P = (F_o^2 + 2F_c^2)/3$.

data alone, although a better fit was obtained using two shells (3S and 3Cl) and, in addition, the UV/VIS and IR spectroscopic data provide very strong evidence for the donor sets chosen. The distances and Debye–Waller factors were refined for all the shells, as well as the Fermi energy difference. No attempt was made to refine the carbons of the ligand backbones since these occur over a range of distances and are not expected to be well defined.

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References

- R. R. Eady, *Chem. Rev.*, 1996, **96**, 3013 and refs. therein.
- J. F. Reynolds, W. R. Briggs and J. C. Fetzer, *Liq. Fuel Technol.*, 1985, **3**, 423.
- J. M. Arber, B. R. Dobson, R. R. Eady, P. Stevens, S. S. Hasnain, C. D. Garner and B. E. Smith, *Nature (London)*, 1987, **325**, 372.
- T. Yoshida, T. Adachi, T. Ueda, M. Kaminaka, N. Sasaki, T. Higuchi, T. Aoshima, I. Mega, Y. Mizobe and M. Hidai, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1040.
- M. C. Durrant, S. C. Davies, D. L. Hughes, C. Le Floc'h, R. L. Richards, J. R. Sanders, N. R. Champness, S. J. A. Pope and G. Reid, *Inorg. Chim. Acta*, 1996, **251**, 13.
- G. R. Willey, M. T. Lakin and N. W. Alcock, *J. Chem. Soc., Chem. Commun.*, 1991, 1414.
- U. Heinzel, A. Henke and R. Mattes, *J. Chem. Soc., Dalton Trans.*, 1997, 501.
- F. A. Cotton, S. A. Duraj, L. E. Manzer and W. J. Roth, *J. Am. Chem. Soc.*, 1985, **107**, 3850.
- P. K. Baker, M. C. Durrant, B. Goerd, S. D. Harris, D. L. Hughes and R. L. Richards, *J. Organomet. Chem.*, 1994, **469**, C22.
- P. K. Baker, M. C. Durrant, S. D. Harris, D. L. Hughes and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1997, 509.
- E. Dockal, L. Diaddario, M. Glick and D. Rorabacher, *J. Am. Chem. Soc.*, 1977, **99**, 4532.
- N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1989, p. 1161.
- A. P. B. Lever, *Inorganic Electronic Spectroscopy*, 2nd edn., Elsevier, Amsterdam, 1984.
- N. R. Champness, S. R. Jacob, G. Reid and C. S. Frampton, *Inorg. Chem.*, 1995, **34**, 396; S. J. A. Pope, N. R. Champness and G. Reid, *J. Chem. Soc., Dalton Trans.*, 1997, 1639.
- H.-J. Kuppers and K. Wieghardt, *Polyhedron*, 1989, **8**, 1770.
- W. Levason, G. Reid and S. M. Smith, *Polyhedron*, 1997, **16**, 5253.
- R. S. Glass, G. S. Wilson and W. N. Setzer, *J. Am. Chem. Soc.*, 1980, **102**, 5068.
- G. E. D. Mullen, M. J. Went, S. Wocadlo, A. K. Powell and P. J. Blower, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1205.
- J. R. Nichelson, J. C. Huffman, D. M. Ho and G. Christou, *Inorg. Chem.*, 1987, **26**, 3030.
- J. K. Money, K. Folting, J. C. Huffman, D. Collison, J. Temperley, F. E. Mabbs and G. Christou, *Inorg. Chem.*, 1986, **25**, 4583.
- J. K. Money, J. C. Huffman and G. Christou, *Inorg. Chem.*, 1985, **24**, 3294.
- C. R. Randall and W. H. Armstrong, *J. Chem. Soc., Chem. Commun.*, 1988, 986.
- S. C. Davies, D. L. Hughes, Z. Janas, L. Jerzykiewicz, R. L. Richards, J. R. Sanders and P. Sobota, *Chem. Commun.*, 1997, 261.

- 24 W. Tsagkalidis, D. Rodewald, D. Rehder and V. Vergopoulou, *Inorg. Chim. Acta*, 1994, **219**, 213.
- 25 W. Tsagkalidis, R. Rodewald and D. Rehder, *J. Chem. Soc., Chem. Commun.*, 1995, 165 and refs. therein.
- 26 S. M. Malinak, K. D. Demadis and D. Coucouvanis, *J. Am. Chem. Soc.*, 1995, **117**, 3126.
- 27 J. Kovacs and R. H. Holm, *Inorg. Chem.*, 1987, **26**, 711.
- 28 B. de Groot, G. R. Giesbrecht, S. J. Loeb and G. K. H. Shimizu, *Inorg. Chem.*, 1992, **30**, 17.
- 29 W. Rosen and D. H. Busch, *J. Am. Chem. Soc.*, 1969, **91**, 4694.
- 30 M. C. Durrant, S. Firth and R. L. Richards, *J. Chem. Soc., Perkin Trans.*, 1993, 445.
- 31 L. E. Manzer, *Inorg. Synth.*, 1982, **21**, 138.
- 32 A. T. Casey, R. J. H. Clark, R. S. Nyholm and D. E. Scaife, *Inorg. Synth.*, 1972, **13**, 165.
- 33 B. E. Byant and W. C. Fernelius, *Inorg. Synth.*, 1957, **5**, 115.
- 34 P. B. Hitchcock, D. L. Hughes, G. J. Leigh, J. R. Sanders, J. S. de Souza, C. J. McGarry and L. F. Larkworthy, *J. Chem. Soc., Dalton Trans.*, 1994, 3683.
- 35 J. Cave, P. R. Dixon and K. R. Seddon, *Inorg. Chim. Acta*, 1978, **30**, 349.
- 36 R. A. Henderson, A. Hills, D. L. Hughes and D. J. Lowe, *J. Chem. Soc., Dalton Trans.*, 1991, 1755.
- 37 G. W. A. Fowles and P. T. Greene, *J. Chem. Soc. A*, 1967, 1869.
- 38 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
- 39 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
- 40 G. M. Sheldrick, SHELXL 93, Program for crystal structure refinement, University of Göttingen, 1993.
- 41 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.
- 42 S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.
- 43 N. Binsted, PAXAS, Program for the analysis of X-ray absorption spectra, University of Southampton, 1988.
- 44 N. Binsted, J. W. Campbell, S. J. Gurman and P. C. Stephenson, EXCURV 92, SERC Daresbury Laboratory, 1992.

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