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Vanadium(IV) and Oxidovanadium(IV) and -(V) Complexes with Soft Thioether Coordination – Synthesis, Spectroscopic and Structural Studies

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$VOCl_3$ reacts with the thioethers $RS(CH_2)_2SR$ (R = Me, Et or *i*Pr) and 1,4-dithiane to form the first examples of V^V thioether complexes, the highly reactive, intensely coloured $[VOCl_3(dithioether)]$ which have been characterised by ^1H and ^{51}V NMR, IR and UV/Vis spectroscopy. Combining $VOCl_3$ with $[9]aneS_3$ gives $[VOCl_3(\kappa^2\text{-}[9]aneS_3)]$ which, upon treatment with $SbCl_5$ gives $[VOCl_2(\kappa^3\text{-}[9]aneS_3)][SbCl_6]$. Vanadium *K*-edge extended X-ray absorption fine structure (EXAFS) studies on three examples provided partial structural analyses for these very unstable compounds. Reaction of VCl_4 with $O(SiMe_3)_2$ in CH_2Cl_2/MeCN followed by addition of $RS(CH_2)_2SR$ (R = Me or Et) produced $[VOCl_2\{RS(CH_2)_2SR\}]$. The crystal structure of $[\{VOCl_2(MeSCH_2CH_2SMe)\}_4]$ reveals a unique tetrameric V_4O_4 core with each vanadium also coordinated to a chelating dithioether and two Cl ligands to complete the distorted octahedral geometry. Under rigorously anhydrous conditions VCl_4 reacts with $RS(CH_2)_2SR$ (R = Me, Et, *i*Pr, Ph), 1,4-dithiane or $[9]aneS_3$ to form $[VCl_4(thioether)]$ which are assigned as six-coordinate distorted octahedral species on the basis of their spectroscopic characterisation. In some cases trace hydrolysis of these compounds provides an alternative route to the $[VOCl_2(dithioether)]$ complexes.

Introduction

Vanadium has a very rich coordination chemistry owing in part to the accessibility of a range of oxidation states. However, the ease with which vanadium can undergo a redox switch between oxidation states, combined with its lability, leads to significant synthetic challenges in preparing pure materials, especially in the +4 and +5 oxidation states. These higher oxidation states of vanadium are dominated by oxido species and the majority of neutral ligand complexes known are with hard O- or N-donor ligands.[1–3] Examples of high oxidation state vanadium complexes with softer, neutral σ-donor ligands such as thio- or selenoethers are extremely rare – no V^V derivatives are known and the only structurally characterised example with V^{IV} is the distorted octahedral vanadyl species $[VOCl_2([9]aneS_3)]$.[4,5] The lower oxidation state V^{III} and V^{II} thioether complexes are well established,[5–8] but reports of V^{IV} thioethers contain very limited data.[9,10] We note that much early work on phosphane complexes of VCl_4 is now known to be erroneous (see for example ref.[11] for a thorough discussion of the problems) due to the failure to recognise the ease of reduction to V^{III} or the hydrolysis to $VOCl_2$ adducts, and the over-reliance on qualitative EPR spectra from incompletely characterised samples. In a recent paper concerned with $VOCl_3$ adducts with neutral N- or O-donor ligands,[3] we briefly noted that in dry CH_2Cl_2 solution $VOCl_3$ is reduced by SR_2 (R = Me, Et, *n*Bu or Ph), $PhSCH_2CH_2SPh$, Me_2Se or $MeSeCH_2CH_2SeMe$. In an effort to investigate more fully the chemistry of V^{IV} and V^V precursors with soft thioether ligands and to establish whether the ligand structure is important in determining the course of the reactions, we have conducted a systematic study of $VOCl_3$, $VOCl_2$ and VCl_4 with the dithioethers $RSCH_2CH_2SR$ (R = Me, Et, *i*Pr), 1,4-dithiane and the macrocyclic $[9]aneS_3$ and $[18]aneS_6$. We report here the results of this investigation including the IR, UV/Vis and NMR (for V^V) spectroscopic characterisation of the resulting complexes, structural studies via vanadium *K*-edge EXAFS measurements, and a crystal structure of an extremely unusual metallocyclic vanadyl(IV) species, $[\{VOCl_2(MeSCH_2CH_2SMe)\}_4]\cdot CH_2Cl_2$.

Results and Discussion

$VOCl_3$ Complexes: $VOCl_3$ and 2,5-dithiahexane react in anhydrous CH_2Cl_2 to give a dark red-brown solution from which $[VOCl_3(MeSCH_2CH_2SMe)]$ was obtained as a red-black powder by precipitation with *n*-hexane (Scheme 1). The freshly prepared complex is very soluble in chlorocarbons and extremely moisture-sensitive (turning into a blue oil in air), and decomposes even in the dark in ca. 48 h, becoming dull purple and completely insoluble in chlorocarbons. The red-black $[VOCl_3(RSCH_2CH_2SR)]$ (R = Et or

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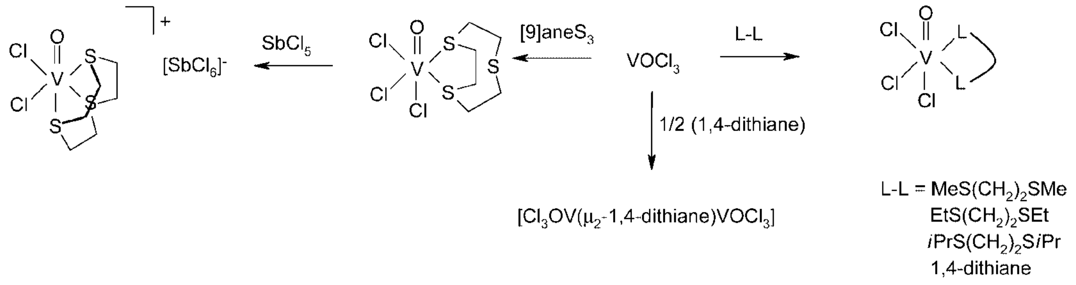


Scheme 1.

*i*Pr) are obtained similarly, although they are even less stable and decompose in a few hours, which prevented microanalytical data being obtained, but are spectroscopically very similar to the dithiahexane complex. In contrast, $VOCl_3$ in CH_2Cl_2 solution was immediately reduced by $PhSCH_2CH_2SPh$, *cis*-MeSCH=CHSMe or $MeS(CH_2)_3SMe$ to pinkish V^{III}-containing products (based upon their UV/Vis spectra). The red-black [$VOCl_3$(1,4-dithiane)] was obtained by treating a solution of 1,4-dithiane with a stoichiometric amount of $VOCl_3$ and precipitation with *n*-hexane, but using an excess of $VOCl_3$ gave the brown dinuclear [$(VOCl_3)_2$(1,4-dithiane)]. The reaction of thiacrowns with $VOCl_3$ is also very dependent on the ligand used. Both [9]aneS_3 and [18]aneS_6 react with excess $VOCl_3$ in CH_2Cl_2 to precipitate dark red-brown solids of composition [$VOCl_3$([9]aneS_3)] and [$(VOCl_3)_2$([18]aneS_6)] respectively, but [12]aneS_4 or [14]aneS_4 afford pale purple powders which lack any VO features in the IR spectra and their UV/Vis spectra suggest six-coordinate [VCl_3(thiacrown)], similar to complexes made directly from [$VCl_3(thf)_3$].[8] The [$VOCl_3$([9]aneS_3)] complex is stable for some weeks in the dark and the dry solid can be handled quickly in air, although it slowly turns blue in moist air (ca. 5 min) – the hydrolysis product was identified by IR and UV/Vis spectroscopy as [$VOCl_2$([9]aneS_3)].[4,5] Attempts to abstract chloride from [$VOCl_3$([9]aneS_3)] using $FeCl_3$ were unsuccessful, but when this reaction was repeated using $SbCl_5$, which is a much stronger Lewis acid, the brown-purple [$VOCl_2$([9]aneS_3)][$SbCl_6$] was formed in good yield. The complexes of the thiacrowns are very poorly soluble in chlorocarbons, which prevented solution spectroscopic studies.

The IR spectra of [$VOCl_3(RSCH_2CH_2SR)$] (Table 1) exhibit strong bands at ca. 970–1000 cm^{-1} assigned as ν(VO), and strong features at 400–300 cm^{-1} due to ν(VCl), which are similar to those observed in six-coordinate V^V complexes of N- and O-donor ligands.[3] The UV/Vis spectra of the solid compounds are dominated by intense L→V charge-transfer transitions above ca. 19000 cm^{-1} (usually with weak shoulders to lower energy), generally similar in band energies to those reported for N- or O-donor ligands,[3] suggesting that π(Cl)→V transitions are mainly responsible for the strong features. The insoluble materials produced by decomposition of the solids exhibited intense, poorly defined features across the visible region, presumably indicating mixed-valence materials. In anhydrous CH_2Cl_2 solution all three complexes exhibit single, quite sharp ^{51}V NMR resonances with chemical shifts only slightly (5–15 ppm) to low frequency of $VOCl_3$, and the spectra are unchanged on cooling the samples to 190 K. These values compare with much more negative resonances found for complexes with N- or O-donors[3,12] and are consistent with soft V–S coordination in these complexes. Hydrolysis in solution leads to the production of $[VOCl_4]^-$ and $[VO_2Cl_2]^-$, readily identified by their ^{51}V NMR resonances at δ +48 and –362 ppm respectively.[12] The ^1H NMR spectrum of [$VOCl_3(MeSCH_2CH_2SMe)$] at 295 K in CD_2Cl_2 shows single δ(Me) and δ(CH_2) resonances due to coordinated dithioether, to high frequency of those of the uncomplexed ligand, and the single δ(Me) and δ(CH_2) resonances indicate a single geometric isomer with the sulfur donor atoms *trans* to Cl, giving *fac* chlorines (Scheme 1). On cooling the solution to 190 K, pyramidal inversion at the sulfur

Table 1. Selected spectroscopic data on oxidovanadium complexes.

Complex	ν(VO) [cm^{-1}][a]	ν(VCl) [cm^{-1}][a]	δ(^{51}V)[b]	E_{max} [cm^{-1}][c]
[$VOCl_3(MeSCH_2CH_2SMe)$]	976	376, 350, 327	–14	14200 (sh), 18800, 21500 (sh), 27000
[$VOCl_3(EtSCH_2CH_2SEt)$]	977	366, 349, 323	–7	15000 (sh), 20800, 27800 (sh)
[$VOCl_3$(*i*PrSCH$_2$CH$_2$S*i*Pr)]	998	370, 330, 310	+5.5	15300 (sh), 20960, 28600
[$VOCl_3$(1,4-dithiane)]	988	374, 320	+18	16100 (sh), 20000, 27400
[$(VOCl_3)_2$(1,4-dithiane)]	1012	402(sh), 372, 338	+10.5	15530 (br), 18850, 23200, 27000 (sh)
[$VOCl_3$([9]aneS_3)]	974	371, 345	[d]	15000 (br), 19800 (br), 29410
[$VOCl_2$([9]aneS_3)][$SbCl_6$]	1020	418	[d]	15600 (br), 18660, 24400 (sh)
[$(VOCl_3)_2$([18]aneS_6)]	978	393, 372, 348	[d]	14600 (sh), 18700 (br), 30700
[$VOCl_2(MeSCH_2CH_2SMe)$]	975, 837	350, 319	–	13500 (sh), 19000, 27500
[$VOCl_2(EtSCH_2CH_2SEt)$]	985, 830	360, 304	–	13500 (sh), 18200, 27000

[a] Nujol mull. [b] CH_2Cl_2 solution relative to neat external $VOCl_3$ at 300 K. [c] Diffuse reflectance, diluted with $BaSO_4$. [d] Insufficiently soluble.

slows and four coordinated δ(Me) resonances and a complex pattern of overlapping $\delta(CH_2)$ signals are present, consistent with three invertomers (*meso-1, meso-2* and *DL*) in a complex lacking axial symmetry. In the presence of added ligand, separate resonances for "free" and coordinated dithioether are seen, showing ligand exchange is slow on the NMR timescale at ambient temperatures. The ^1H NMR spectra of the $[VOCl_3(RSCH_2CH_2SR)]$ (R = Et or *i*Pr) exhibit generally similar behaviour, although even at the lowest temperatures studied (190 K) the $^3J_{HH}$ couplings within the Et and *i*Pr groups are not resolved, only broad singlets are observed for the different protons – this broadening may be due to the proximity to the quadrupolar ^{51}V nucleus.

The dark red $[VOCl_3(1,4\text{-dithiane})]$ has similar physical and spectroscopic properties to the acyclic dithioether complexes, and is assigned a similar six-coordinate geometry, probably with chelating dithiane. The spectroscopic properties of the dark brown $[(VOCl_3)_2(1,4\text{-dithiane})]$ are rather different, notably υ(VO) is at 1020 cm^{-1}, in the range observed for five-coordinate $VOCl_3$ adducts.[3] 1,4-Dithiane often favours a bridging coordination mode[13] and this may account for the formation of a 2:1 complex uniquely with this ligand.

The $[VOCl_3([9]aneS_3)]$ complex is very poorly soluble in chlorocarbons, $MeNO_2$ or MeCN and decomposed by strong donor solvents such dmf, which has prevented solution spectroscopic studies. Three possible structures for this complex are the seven-coordinate $[VOCl_3(\kappa^3\text{-}[9]aneS_3)]$, six-coordinate $[VOCl_3(\kappa^2\text{-}[9]aneS_3)]$ or $[VOCl_2(\kappa^3\text{-}[9]aneS_3)]Cl$. The spectroscopic properties are similar to those of $[VOCl_3(RSCH_2CH_2SR)]$, and the EXAFS data (below) are consistent with $[VOCl_3(\kappa^2\text{-}[9]aneS_3)]$. The failure of the complex to react with $FeCl_3$ (to form $[VOCl_2(\kappa^3\text{-}[9]aneS_3)][FeCl_4]$) rules out the cationic formulation, and whilst seven-coordination is known for a very small number of V^V compounds, all seem to contain small bite-angle ligands such as $\kappa^2\text{-}NO_3$ or $\kappa^2\text{-}S_2CNR_2$[1] and it seems highly unlikely here. Hence the data support a $[VOCl_3(\kappa^2\text{-}[9]aneS_3)]$ formulation. The 2:1 $[18]aneS_6$ complex probably has a similar vanadium core. The dark brown-purple $[VOCl_2([9]aneS_3)][SbCl_6]$ formed by reaction of $VOCl_3$, $SbCl_5$ and $[9]aneS_3$ in anhydrous CH_2Cl_2 has υ(VO) at 1020 cm^{-1}, higher than that in the neutral $[VOCl_3([9]aneS_3)]$ (974 cm^{-1}) and a very strong, broad band at 343 cm^{-1} assigned as the T_{1u} mode of the $[SbCl_6]^-$ ion.

The instability of the $[VOCl_3(RSCH_2CH_2SR)]$ in solution and the insolubility of the macrocyclic complexes prevented all attempts to obtain crystals for X-ray structure determination. We therefore collected vanadium *K*-edge EXAFS data on three examples. Data were collected in transmission mode from freshly prepared (within 24 h) samples of $[VOCl_3(MeSCH_2CH_2SMe)]$, $[VOCl_3([9]aneS_3)]$ and $[VOCl_3(1,4\text{-dithiane})]$ diluted with BN (Experimental section). The data were all fitted to a four-shell model of 1 × O, 2 × Cl (*trans* S), 1 × Cl (*trans* O), and 2 × S, corresponding to a six-coordinate environment with the thioether sulfur atoms *trans* to Cl (see Experimental Section for details). The results are summarised in Table 2. Figure 1 shows a typical example of the background subtracted EXAFS data and the Fourier transform. The data on the three complexes are in excellent agreement. Few complexes of $VOCl_3$ have been structurally characterised but the *d*(V–O) of ca. 1.6 Å in the thioether complexes compares well with those in $[VO_2Cl_2]^-$ (1.58 (av) Å),[14] $[VOCl_2([9]aneS_3)]$ (1.579(4) Å)[4] and $[VOCl_3\{(2\text{-nitrophenyl})pyridine\text{-}2\text{-}$

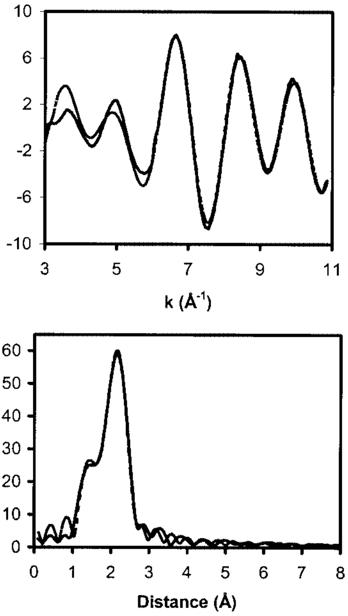


Figure 1. Vanadium *K*-edge k^3-weighted EXAFS (top) and Fourier-transformed EXAFS (bottom) for $[VOCl_3(1,4\text{-dithiane})]$/boron nitride. Solid lines refer to data, dashed lines to calculated fit.

Table 2. Vanadium *K*-edge EXAFS data.[a]

Complex	*d*(V–O) [Å] (O)	$2\sigma^2$ [$Å^2$] [b]	*d*(V–Cl) [Å] (2Cl)	$2\sigma^2$ [$Å^2$] [b]	*d*(V–Cl) [Å] (Cl)	$2\sigma^2$ [$Å^2$][b]	*d*(V–S) [Å] (2S)	$2\sigma^2$ [$Å^2$][b]	E_f[c]	*R*%[d]
$[VOCl_3(MeSCH_2CH_2SMe)]$	1.583(5)	0.002(1)	2.249(6)	0.009(2)	2.385(18)	0.009(2)	2.68(4)	0.053(11)	–10.8(9)	29.1
$[VOCl_3(1,4\text{-dithiane})]$	1.581(6)	0.003(1)	2.220(4)	0.003(5)	2.49(4)	0.036(12)	2.66(5)	0.08(3)	–12.6(9)	20.0
$[VOCl_3([9]aneS_3)]$	1.593(6)	0.003(1)	2.265(9)	0.013(2)	2.442(16)	0.013(4)	2.69(3)	0.052(9)	–10.5(11)	32.0

[a] Standard deviations in parentheses. [b] Debye–Waller factor. [c] The difference between the calculated Fermi level energy and the theoretically known values for the element. [d] Defined as $[\int(\chi^T - \chi^E)k^3\,dk / \int \chi^E k^3\,dk] \times 100$ (where T is theoretical and E is experimental).

carboxamide}] (1.572(1) Å].[14] For comparison *d*(V–O) in solid molecular $VOCl_3$ (133 K) is 1.562(7) Å and *d*(V–Cl) 2.125(3) and 2.124(2) Å.[15] Two V–Cl shells were refined, the slightly shorter distances corresponding to the two chlorines *trans* to S, and the longer distance due to the one chlorine *trans* to V=O. The V–S distances at ca. 2.66–2.69 Å are significantly longer than $V–S_{trans\text{Cl}}$ in both $[\{VOCl_2(MeSCH_2CH_2SMe)\}_4]$ (2.48 Å) (Table 3) and $[VOCl_2([9]aneS_3)]$ (2.47 Å). The $Ti–S_{trans–Cl}$ distances in $[TiCl_4(\text{dithioether})]$ are 2.60–2.65 Å.[16] The similarity of the distances within the three V^V complexes and the best fit statistical data also support the six-coordinate S_2Cl_3O donor sets for $[VOCl_3([9]aneS_3)]$ and $[VOCl_3(1,4\text{-dithiane})]$ proposed above based upon the spectroscopic data.

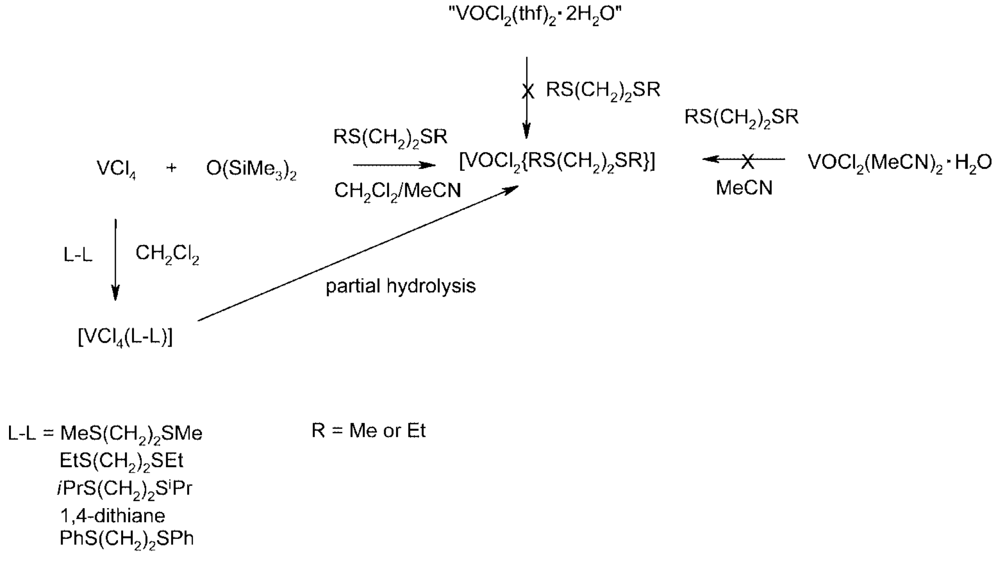
Table 3. Selected bond lengths [Å] and angles [°] for $[\{VOCl_2(MeSCH_2CH_2SMe)\}_4]\cdot CH_2Cl_2$.[a]

V1–O1	1.640(3)	V1–O1c	2.004(3)
V1–Cl1	2.288(1)	V1–Cl2	2.311(1)
V1–S1	2.662(1)	V1–S2	2.482(2)
S1–C1	1.810(6)	S1–C2	1.808(6)
S2–C3	1.813(5)	S2–C4	1.783(6)
O1–V1–O1c	93.7(2)	O1–V1–Cl1	106.97(11)
O1c–V1–Cl1	90.89(9)	O1–V1–Cl2	98.29(10)
O1c–V1–Cl2	166.15(8)	Cl1–V1–Cl2	92.30(5)
O1–V1–S2	92.25(11)	O1c–V1–S2	90.50(9)
Cl1–V1–S2	160.60(5)	Cl2–V1–S2	82.08(5)
O1–V1–S1	168.56(11)	O1c–V1–S1	77.40(8)
Cl1–V1–S1	80.58(5)	Cl2–V1–S1	89.83(4)
S2–V1–S1	80.85(5)	V1–O1–V1b	168.6(2)

[a] Symmetry operations: *b* = *y*, – *x*, 2 – *z*; *c* = –*y*, *x*, 2 – *z*.

$VOCl_2$ Complexes: Red-brown crystals of $[\{VOCl_2(MeSCH_2CH_2SMe)\}_4]$ were initially obtained by storing a dilute CH_2Cl_2 solution of VCl_4 and $MeSCH_2CH_2SMe$ in a freezer for a few days, and were found to have the unique tetranuclear structure described below. The crystals clearly form by hydrolysis and red-brown powders of $[\{VOCl_2(RSCH_2CH_2SR)\}_4]$ (R = Me or Et) can be isolated in modest yield by storing dilute CH_2Cl_2 solutions of VCl_4 and $RSCH_2CH_2SR$ (after removal of precipitated $[VCl_4(RSCH_2CH_2SR)]$ by filtration) in a freezer for 1–2 weeks (Scheme 2). Hydrolysis does not stop at these species and after several months blue oils form. The robust (blue) $[VOCl_2([9]aneS_3)]$ can be made by hydrolytic oxidation of $[VCl_3([9]aneS_3)]$,[4] or by decomposition of $[VOCl_3([9]aneS_3)]$ (above), but these routes are not viable for the acyclic dithioethers. However, reaction of VCl_4 with one mol-equiv. of $O(SiMe_3)_2$ in anhydrous CH_2Cl_2 containing a small amount of MeCN, followed by addition of $RSCH_2CH_2SR$ produced the $[\{VOCl_2(RSCH_2CH_2SR)\}_4]$ in good yield. The MeCN presumably stabilises the $VOCl_2$ intermediate, since the reaction in neat CH_2Cl_2 does not work. Excess MeCN should be avoided since it reduces VCl_4 to V^{III}.[17] The $[\{VOCl_2(RSCH_2CH_2SR)\}_4]$ are readily hydrolysed in solution and decomposed by alcohols or acetone, but the pure, dry solids can be handled quickly in air. They are paramagnetic with $\mu_{\text{eff}} = 1.8\,\mu_B$ and exhibit ν(V=O) at 975, 837 (R = Me) or 985, 830 (R = Et) cm^{-1} (Table 1) consistent with the V–O···V bridged structure (below).

Many vanadyl compounds are known; the majority are blue or green, discrete five-coordinate square pyramids or distorted octahedra (5 + 1 coordination), or sometimes chain polymers with *trans* O=V···O=V··· links.[1,2] A limited number of orange-brown polymers with polydentate Schiff bases are also known.[1,18] The structure of $[\{VOCl_2(MeSCH_2CH_2SMe)\}_4]$ is quite different (Table 3, Figure 2) and has a tetranuclear V_4O_4 core. The structure can either be described as based upon square pyramidal $VOCl_2(MeSCH_2CH_2SMe)$ units with apical chlorine, linked through asymmetric *cis* oxygen bridges into a tetramer, or as a puckered square with vanadium at the corners and asymmetric [V–O 1.640(3), 2.004(3) Å], non-linear [V–O–V 168.6(2)°] oxygen bridges along the edges. The coordination about each vanadium is completed by two terminal chlorines and a chelating dithioether [S–V–S angle 80.85(5) °]



Scheme 2.

which has the *DL* configuration. In addition to the disparate V–O distances (the differences are 0.4 Å), the bond lengths around the vanadium centres reveal that the *trans* influence of the ligands on this hard metal is O > Cl > S. Thus V–$S_{trans\text{O}}$ 2.662(1) Å, whilst V–$S_{trans\text{Cl}}$ 2.482(2) Å and V–$Cl_{trans\text{O}}$ 2.311(1) Å, V–$Cl_{trans\text{S}}$ 2.288(1) Å. For comparison, the bond lengths in the six-coordinate (5 + 1) [$VOCl_2$([9]aneS_3)] are V–O 1.579(4), V–Cl 2.295(5), and V–S 2.634(5), 2.470(5) Å.[4] A search of the CCDB revealed that the structure of the [{VO(SNNS)}$_4$] [SNNS = the dianion of *N*,*N′*-bis(*o*-mercaptophenyl)ethylendiamine] also contains a V_4O_4 core, but with a boat conformation.[19] The closest analogue to the structure of [{$VOCl_2$($MeSCH_2CH_2SMe$)}$_4$] appears to be [{$TiOCl_2$([15]crown-5)}$_4$], a hydrolysis product of [$TiCl_4$([15]crown-5)], which contains a planar Ti_4O_4 ring with coordination at each Ti completed by two terminal chlorines and a κ^2-crown ether.[20]

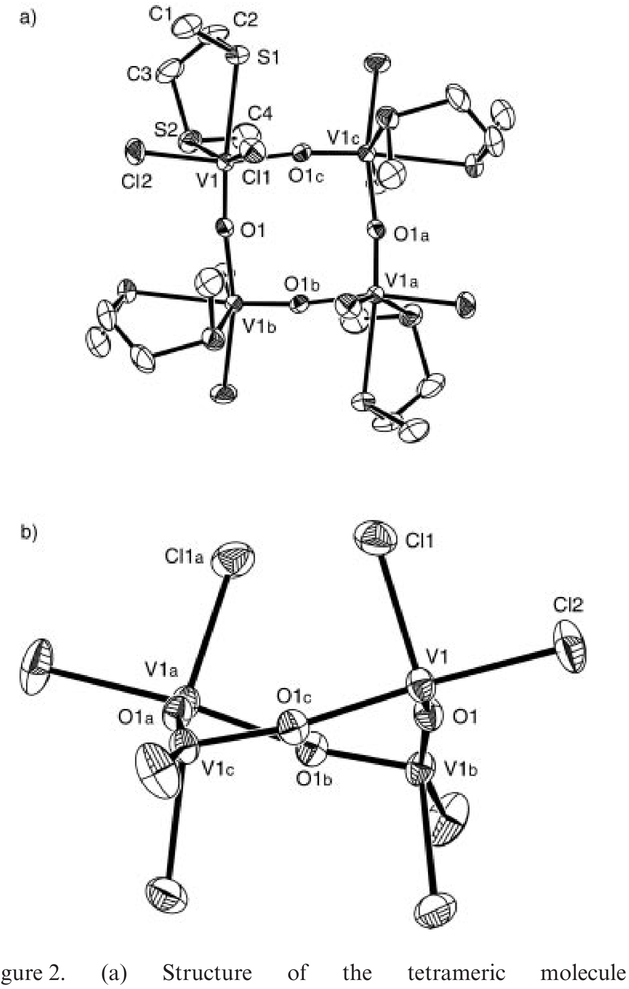


Figure 2. (a) Structure of the tetrameric molecule [{$VOCl_2$($MeSCH_2CH_2SMe$)}$_4$]·CH_2Cl_2. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operations: *a* = –*x*, – *y*, *z*; *b* = *y*, – *x*, 2 – *z*; *c* = –*y*, *x*, 2 – *z*; (b) edge view of the V_4O_4 core within the tetramer.

VCl_4 Complexes: The reactions of the dithioethers $RSCH_2CH_2SR$ (R = Me, Et, *i*Pr), 1,4-dithiane and $MeS(CH_2)_3SMe$ in a 1:1 mol. ratio in rigorously anhydrous CH_2Cl_2 solution at or below ambient temperatures formed dark violet [VCl_4(dithioether)], which precipitated from the solutions. Using excess dithioether, addition of neat ligand to concentrated solutions of VCl_4 (which generates considerable heat) or gently heating CH_2Cl_2 solutions, produced lighter coloured materials, which contained substantial amounts of V^{III}. Gentle reflux of the CH_2Cl_2 preparative solutions in the presence of excess ligand produced complete reduction to pale lilac six-coordinate V^{III} complexes. Using the weaker donor $PhSCH_2CH_2SPh$ produced an unstable dark purple solid [VCl_4($PhSCH_2CH_2SPh$)], but the related ligand $PhS(CH_2)_3SPh$ does not form a V^{IV} complex; under similar reaction conditions it produced a pale lilac powder with the UV/Vis spectrum of a V^{III} complex (E_{max} 11970, 18500, 28570 cm^{-1}).[21] The reaction of VCl_4 with [9]aneS_3 in CH_2Cl_2 precipitates the purple solid [VCl_4([9]aneS_3)] which is insoluble in common solvents and when dry may be handled quickly in air without visible decomposition. Refluxing a mixture of VCl_4 with [9]aneS_3 in CH_2Cl_2 results in the known bright pink complex [VCl_3([9]aneS_3)].[5] Repeated attempts to isolate [$VCl_4(SR_2)_2$] (R = Me, Et, *n*Bu or Ph) by reaction of VCl_4 with SR_2 in a 1:≤2 molar ratio in anhydrous CH_2Cl_2 solution failed. Excess thioether brings about immediate reduction to V^{III}, as described previously.[7,22,23]

The solid [VCl_4(dithioether)] are extremely moisture-sensitive, evolving yellow fumes in air and turning green-blue. However, in contrast to the V^V [$VOCl_3$(dithioether)] complexes, they are stable in the dry box for several weeks. The complexes are very poorly soluble in chlorocarbons (cf. [$TiCl_4$(dithioether)])[16] and decomposed by acetone, alcohols or thf. The complexes are paramagnetic with magnetic moments μ_{eff} = 1.7–1.9 μ_B, consistent with d^1 V^{IV}. The diffuse reflectance spectra show broad features at ca. 19000–20000 cm^{-1} with a weaker shoulder to low energy (ca. 17000 cm^{-1}). The original work on these complexes assigned these features as d–d transitions and ascribed the splitting to the low symmetry (C_{2v}).[9] However, a d–d assignment seems at odds with the very intense colours and we propose that these bands are charge transfer π(Cl)→V (main band) and π(S)→V (shoulder), respectively. These assignments are supported by approximate calculations based upon the optical electronegativity model.[21,24,25] The spectrum of $[VCl_6]^{2-}$ contains the $^2T_{2g} \rightarrow {}^2E_g$ transition at 15500 cm^{-1} and the lowest charge-transfer band, π(Cl)→V(t_{2g}) at 20500 cm^{-1}.[24] The lowest energy charge-transfer band (E_{max}) for a d^1 complex in octahedral symmetry is predicted by the Equation (1):

$$E_{max}/\text{cm}^{-1} = 30000\{\chi_{opt}(\text{L}) - \chi_{opt}(\text{M})\} - (14/3)B \qquad (1)$$

Using the normal Pauling electronegativities for Cl and S, and estimating the Racah parameter (*B*) for Cl = 650 cm^{-1}, leads to a prediction of π(Cl)→V(t_{2g}) ca. 20000 cm^{-1} and π(S)→V(t_{2g}) ca. 17000 cm^{-1}. The very significant low energy shift in the charge-transfer bands between [$TiCl_4$(dithioether)][16] and [VCl_4(dithioether)] is also consistent with the much greater ease of reduction of the vanadium complexes.

Conclusions

The results reported here constitute the first detailed characterisation of a series of soft, neutral thioether ligand complexes of V^{IV} and V^{V}. The architecture of the thioether ligands plays a significant role in governing the vanadium oxidation state produced and the relative stabilities of the complexes. Soft donor ligand complexes of V^{V} are extremely unusual (phosphanes, arsanes, selenoethers and some thioethers bring about immediate reduction to V^{IV} and/or V^{III}).[3,7,10] The tetrameric structure observed for $[\{VOCl_2(MeSCH_2CH_2SMe)\}_4]$ is a new structure type for vanadyl(IV), and contrasts with the discrete distorted octahedral geometry in the (coordinatively saturated) $[VOCl_2([9]aneS_3)]$. The successful isolation of these complexes indicate that under appropriate conditions and with judicious choice of ligand architecture, it may be possible to obtain limited examples of analogues with other soft donor ligands (e.g. selenoethers or arsanes).

Experimental Section

All reactions were conducted under anhydrous conditions and under dry dinitrogen using standard vacuum line Schlenk and glovebox techniques. $VOCl_3$ and VCl_4 (Aldrich) were used as received. Solvents were dried by distillation from CaH_2 (CH_2Cl_2) or Na/benzophenone ketyl (hexane and diethyl ether). The thioethers $RSCH_2CH_2SR$ (R = Me, Et, *i*Pr, Ph) and $MeS(CH_2)_3SMe$ were made by literature methods[26] and dried and stored over molecular sieves. 1,4-dithiane, $[9]aneS_3$ and $[18]aneS_6$ were obtained from Aldrich and were dried by melting in vacuo immediately before use. Physical measurements were made as described previously[3] and microanalytical data were obtained from the microanalytical laboratory of Strathclyde University. All measurements were made on freshly prepared samples and the samples of the majority of the compounds were prepared several times and checked for consistency of the spectroscopic data.

$[VOCl_3(MeSCH_2CH_2SMe)]$: A solution of $VOCl_3$ (0.23 g, 1.3 mmol) in dry CH_2Cl_2 (5 mL) was added to a solution of 2,5-dithiahexane (0.16 g, 1.3 mmol) in dry CH_2Cl_2 (20 mL). The dark red solution was concentrated to ca. 5 mL in vacuo, dry *n*-hexane (5 mL) added and the red-black solid isolated by filtration, and dried in vacuo. Yield 0.18 g, 46%. $C_4H_{10}Cl_3OS_2V$ (295.5): calcd. C 16.3, H 3.4; found C 16.1, H 3.6. ^1H NMR (300 MHz, CD_2Cl_2, 300 K): δ = 2.5 (s, 3 H, CH_3), 3.0 (s, 2 H, CH_2); (193 K): δ = 2.36, 2.39, 2.47, 2.60 (s, CH_3), 3.15–3.33 (br. m, CH_2) ppm. ^{51}V NMR (CH_2Cl_2, 300 K): δ = –14 ($w_{1/2}$ = 800 Hz, sharpens on cooling but shift unchanged) ppm. UV/Vis (CH_2Cl_2): E_{max} (ε_{mol}, $cm^{-1} dm^3 mol^{-1}$) = 17120 (sh), 20160 (930), 21050 (1150), 25600 (1500), 31050 (sh), 33330 (2700) cm^{-1}.

$[VOCl_3(EtSCH_2CH_2SEt)]$: This compound was best made by adding excess $VOCl_3$ to the ligand in CH_2Cl_2 and pumping to dryness in vacuo in the dark. Yield 65%. As made it is a red-black powder, very soluble in chlorocarbons. Even in the dark in the glove box the complex decomposes in less than 24 h becoming insoluble in chlorocarbons. ^1H NMR (300 MHz, CD_2Cl_2, 300 K): δ = 1.46 (br. s, 3 H, CH_3), 2.96 (br. s, 2 H, CH_2), 3.20 (br. s, 2 H, CH_2) ppm. ^{51}V NMR (CH_2Cl_2, 300 K): δ = –7.1 ($w_{1/2}$ = 850 Hz); (223 K): δ = –7.5 ($w_{1/2}$ = 700 Hz) ppm.

$[VOCl_3(iPrSCH_2CH_2SiPr)]$: This complex was made similarly to the one above, obtained as a red-black powder, yield 62%. ^1H NMR (300 MHz, CD_2Cl_2, 300 K): δ = 1.2 (br., 6 H, CH_3), 1.40 (br., H, CH), 3.0 (br. s, 2 H, CH_2); (190 K): δ = 1.17, 1.18 (sh), 1.31, 1.39, 2.95, 3.08 (all broad and with no couplings resolved) ppm. ^{51}V NMR (CH_2Cl_2, 300 K): δ = –5.4 ($w_{1/2}$ = 700 Hz); (213 K): δ = –6.1 ($w_{1/2}$ = 700 Hz) ppm. UV/Vis (CH_2Cl_2): E_{max} = 15300 (sh), 20960, 28600, 30500 cm^{-1}.

$[VOCl_3(1,4\text{-dithiane})]$: A solution of $VOCl_3$ (0.23 g, 1.3 mmol) in dry CH_2Cl_2 (5 mL) was added to a solution of freshly sublimed 1,4-dithiane (0.16 g, 1.3 mmol) in dry CH_2Cl_2 (20 mL). The dark red solution was concentrated to ca. 5 mL in vacuo, dry *n*-hexane (5 mL) added and the red-black solid isolated by filtration, and dried in vacuo. Yield 0.22 g, 58%. $C_4H_8Cl_3OS_2V$ (293.5): calcd. C 16.4, H 2.8; found C 16.3, H 3.2. ^1H NMR (300 MHz, CD_2Cl_2, 300 K): δ = 3.34 (br., CH_2); (190 K): δ = 3.63 (br., 2 H), 3.05 (br., 2 H) ppm. ^{51}V NMR (CH_2Cl_2, 300 K): δ = +18 ($w_{1/2}$ = 300 Hz); (213 K): δ = +38. UV/Vis (CH_2Cl_2): E_{max} = 16000 (sh), 18100, 21200, 26000 cm^{-1}.

$[(VOCl_3)_2(1,4\text{-dithane})]$: 1,4-Dithiane (0.12 g, 1.0 mmol) was freshly sublimed in vacuo and then dissolved in dry CH_2Cl_2 (15 mL) and added to a solution of $VOCl_3$ (0.36 g, 2.0 mmol) in dry CH_2Cl_2 (10 mL). The very dark brown solution was stirred for 1 h at room temperature and then concentrated in vacuo to ca. 5 mL. Dry *n*-hexane (5 mL) was added by cannula and the dark brown powder which separated was filtered off and dried in vacuo. Yield 0.32 g, 67%. $C_4H_8Cl_6O_2S_2V_2$ (466.8): calcd. C 10.3, H 1.7; found C 10.3, H 1.1. ^1H NMR (300 MHz, CD_2Cl_2, 300 K): δ = 3.1 (s, CH_2) ppm. ^{51}V NMR (CH_2Cl_2, 300 K): δ = +10.5 ($w_{1/2}$ = 100 Hz), little changed on cooling ppm. UV/Vis (CH_2Cl_2): E_{max} = 18200 (sh), 21370, 27170 cm^{-1}.

$[VOCl_3([9]aneS_3)]$: $[9]aneS_3$ (0.09 g, 0.5 mmol) was dissolved in dry CH_2Cl_2 (15 mL) and added to a solution of $VOCl_3$ (0.09 g, 0.5 mmol) in dry CH_2Cl_2 (10 mL). A dark red-brown solid separated immediately. The dark suspension was concentrated to ca. 5 mL in vacuo, and the red-brown solid filtered off, rinsed with dry *n*-hexane (5 mL) and dried in vacuo. Yield 0.17 g, 94%. $C_6H_{12}Cl_3OS_3V$ (353.6): calcd. C 20.4, H 3.4; found C 20.5, H 3.7. {When the dry solid is exposed to air it turns pale green-blue in ca. 5 min and this product was identified as $[VOCl_2([9]aneS_3)]$. IR (Nujol): $\tilde{\nu}$ = 960 cm^{-1} (VO), 344, 307 (sh) (VCl) cm^{-1}. UV/Vis (*dr* in $BaSO_4$): E_{max} = 14450, 25000 sh, 30120 cm^{-1}.}

$[VOCl_2([9]aneS_3)][SbCl_6]$: $VOCl_3$ (0.09 g, 0.5 mmol) and $SbCl_5$ (0.15 g, 0.5 mmol) were dissolved in dry CH_2Cl_2 (15 mL), and stirred for 10 min, after which a solution of $[9]aneS_3$ (0.09 g, 0.5 mmol) in CH_2Cl_2 (10 mL) was added by syringe. The mixture slowly became brown and then deep purple in colour and after about 30 min contained a deep purple-brown precipitate in a pale yellow solution. The solid was filtered off, rinsed with CH_2Cl_2 (5 mL) and dried in vacuo. Yield 0.30 g, 91%. $C_6H_{12}Cl_8OS_3SbV$ (652.7): calcd. C 11.0, H 1.9; found C 10.7, H 2.2. IR (Nujol): $\tilde{\nu}$ = 1020 ν(VO), 418 (VCl), 343 $\nu(SbCl_6)$ cm^{-1}.

$[(VOCl_3)_2([18]aneS_6)]$: Was made similarly to the $[9]aneS_3$ complex above using a 2.5:1 ratio of $VOCl_3$:$[18]aneS_6$ giving a dark red-brown powder. Yield 75%. $C_{12}H_{24}Cl_6O_2S_6V_2$ (707.3): calcd. C 20.4, H 3.4; found C 20.5, H 3.7.

$[\{VOCl_2(MeSCH_2CH_2SMe)\}_4]$. Method 1: VCl_4 (0.19 g, 1.0 mmol) was dissolved in a mixture of anhydrous CH_2Cl_2 (20 mL) and MeCN (0.5 mL), $Si(OMe_3)_2$ (0.18 g, 1.0 mmol) added, and the solution stirred for 15 min. $MeSCH_2CH_2SMe$ (0.12 g, 1.0 mmol) was then added, the solution stirred for 1 h and then concentrated in vacuo to ca. 5 mL. The brown solid was separated by filtration and dried in vacuo. Yield 0.15 g, 45%.

Method 2: VCl_4 (0.38 g, 2.0 mmol) was dissolved in anhydrous CH_2Cl_2 (15 mL) and $MeSCH_2CH_2SMe$ (0.24 g, 2.0 mmol) in CH_2Cl_2 (10 mL) added producing a very dark solution and some precipitate. The solid was filtered off and the solution stirred at room temperature under nitrogen for 24 h, and then refrigerated for 1 week. The brown solid formed was filtered off and dried in vacuo. Yields variable – typically 10–15%. $C_4H_{10}Cl_2OS_2V \cdot CH_2Cl_2$ (345.2): calcd. C 17.4, H 3.5; found C 17.2, H 3.7. μ_{eff} (298 K) = 1.81 μ_B.

[$VOCl_2(EtSCH_2CH_2SEt)$]: Was made similarly by Method 1 above. Yield 55%. $C_6H_{14}Cl_2OS_2V$ (288.0): calcd. C 25.0, H 4.9; found C 24.6, H 5.3. μ_{eff} (298 K) = 1.80 μ_B.

[$VCl_4(MeSCH_2CH_2SMe)$]: VCl_4 (0.38 g, 2.0 mmol) was dissolved in anhydrous CH_2Cl_2 (15 mL) and $MeSCH_2CH_2SMe$ (0.24 g, 2.0 mmol) in CH_2Cl_2 (10 mL) added producing a very dark solution and some precipitate. Concentration in vacuo to ca. 5 mL, followed by filtration produced a dark solid which became a purple-black powder on drying in vacuo. Yield 0.50 g, 80%. $C_4H_{10}Cl_4S_2V$ (315.0): calcd. C 15.2, H 3.2; found C 14.8, H 3.8. IR (Nujol): $\tilde{\nu}$ = 379 (sh), 362 (br), 316 (sh) (VCl) cm^{-1}. UV/Vis (*dr* in $BaSO_4$): E_{max} = 17240 (sh), 19500, 29400, 38500 cm^{-1}. μ_{eff} (298 K) = 1.70 μ_B.

[$VCl_4(EtSCH_2CH_2SEt)$]: Dark purple powder made similarly to the above. Yield 85%. $C_6H_{14}Cl_4S_2V$ (343.1): calcd. C 21.0, H 4.1; found C 21.4, H 4.3. IR (Nujol): $\tilde{\nu}$ = 365 (br), 346, 295 (sh) (VCl) cm^{-1}. UV/Vis (*dr* in $BaSO_4$): E_{max} = 17000 (sh), 19650, 28400, 37750 cm^{-1}. μ_{eff} (298 K) = 1.68 μ_B.

[VCl_4(*i*$PrSCH_2CH_2S$*i*Pr)]: Dark purple powder made similarly. Yield 70%. $C_8H_{18}Cl_4S_2V \cdot CH_2Cl_2$ (456.0): calcd. C 23.7, H 4.4; found C 22.9, H 4.0. IR (Nujol): $\tilde{\nu}$ = 389, 344 (br), 290 (VCl) cm^{-1}. UV/Vis (*dr* in $BaSO_4$): E_{max} = 17850 (sh), 19600, 29400, 39525 cm^{-1}. μ_{eff} (298 K) = 1.70 μ_B.

[VCl_4(1,4-dithiane)]: Dark red-black powder was made similarly. Yield 55%. $C_4H_8Cl_4S_2V$ (313.0): calcd. C 15.4, H 2.6; found C 15.3, H 2.9. IR (Nujol): $\tilde{\nu}$ = 384, 351, 312 (VCl) cm^{-1}. UV/Vis (*dr* in $BaSO_4$): E_{max} = 17600 (sh), 20000, 28250 cm^{-1}. μ_{eff} (298 K) = 1.73 μ_B.

[$VCl_4\{MeS(CH_2)_3SMe\}$]: Dark purple powder. Yield 85%. $C_5H_{12}Cl_4S_2V$ (329.0): calcd. C 18.3, H 3.7; found C 18.3, H 3.9. IR (Nujol): $\tilde{\nu}$ = 368 (br) 330 (br) (VCl) cm^{-1}. UV/Vis (*dr* in $BaSO_4$): E_{max} = 17000 (sh), 20100, 29100, 39600 cm^{-1}.

[$VCl_4(PhSCH_2CH_2SPh)$]: A cold solution of VCl_4 (0.19 g, 1.0 mmol) in CH_2Cl_2 (30 mL) was added slowly to a solution of $PhSCH_2CH_2SPh$ (0.25 g, 1.0 mmol) in CH_2Cl_2 (10 mL) with vigorous stirring. An intensely purple solution was produced, which was immediately concentrated to 10 mL in vacuo, and the dark solid which precipitated isolated by filtration, and dried in vacuo. Yield 0.28 g, 63%. If the solution is stirred for 1 h before work-up significant amounts of V^{III} (UV/Vis evidence) are present. $C_{14}H_{14}Cl_4S_2V \cdot CH_2Cl_2$ (524.1): calcd. C 34.4, H 3.5; found C 34.5, H 3.5. IR (Nujol): $\tilde{\nu}$ = 372, 344 (br), 304 (VCl) cm^{-1}. UV/Vis (*dr* in $BaSO_4$): E_{max} = 17250 (sh), 19200, 29400 cm^{-1}.

X-ray Crystallography: Crystals of [$\{VOCl_2(MeSCH_2CH_2SMe)\}_4$]·$CH_2Cl_2$ were obtained from a CH_2Cl_2 solution by cooling to about –20 °C for several days (see text). Data collection used a Nonius Kappa CCD diffractometer with confocal mirror monochromated Mo-K_α X-radiation (λ = 0.71073 Å) and with the crystal held at 120 K in a cooled nitrogen gas stream. Structure solution was straightforward[27–29] with H atoms introduced into the model in calculated positions except for the dichloromethane solvate where no H atoms were included. The inclusion of the TWIN/BASF[28] commands made a small improvement to the data fit. Selected bond lengths and angles are given in Table 3 with crystallographic data in Table 4.

Table 4. Crystallographic data for [$\{VOCl_2(MeSCH_2CH_2SMe)\}_4$]·$CH_2Cl_2$.

Formula	$C_{17}H_{42}Cl_{10}O_4S_8V_4$
M	1125.25
Crystal system	tetragonal
Space group (no.)	$I\bar{4}$ (82)
a [Å]	12.3183(17)
b [Å]	12.3183(17)
c [Å]	13.964(3)
U [Å^3]	2118.8(6)
Z	2
μ(Mo-K_α) [mm^{-1}]	1.906
F(000)	1132
Total no. reflections	8567
Unique reflections	2424
R_{int}	0.051
No. of parameters, restraints	103, 2
R_1[a] [$I_o > 2\sigma(I_o)$]	0.041
R_1 [all data]	0.052
wR_2[a] [$I_o > 2\sigma(I_o)$]	0.086
wR_2 [all data]	0.091

[a] $R_1 = \Sigma|| F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

CCDC-642012 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

EXAFS Data Collection and Treatment: Vanadium *K*-edge EXAFS data were collected at ambient temperature on station 7.1 of the Daresbury SRS fitted with a silicon 110 monochromator and operating in transmission mode. Data were recorded from samples prepared <24 h previously, sealed in foil-wrapped flasks under N_2 and stored in the cold. Samples of the complexes were diluted ca. 1:3 with dry, powdered BN and pressed between Kapton windows in 1 mm thick cells. Two or three data sets were collected from each sample and then averaged. Background subtraction was performed with the PAXAS[30] package and the k^3-weighted EXAFS were fitted using Excurve.[31] The [$VOCl_3\{MeS(CH_2)_2SMe\}$], [$VOCl_3$(1,4-dithiane)] and [$VOCl_3(\kappa^2$-[9]aneS_3)] EXAFS were modelled with a cluster of C_s symmetry with oxygen and one Cl on the mirror plane and an overall geometry close to octahedral. The models were tested for both five- and six-coordination, the best fit statistical data supporting six-coordination with S_2Cl_3O donor sets.

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