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Studies on Chromium(III) and Vanadium(III) Complexes with Crown Ether and Crown Thioether Coordination – Synthesis, Properties and Structural Systematics

Charlotte D. Beard,[a] Loretta Carr,[a] Martin F. Davis,[a] John Evans,[a] William Levason,[a] Louise D. Norman,[a] Gillian Reid,*[a] and Michael Webster[a]

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A series of six-coordinate chloro Cr^{III} and V^{III} complexes involving crown ether, crown thioether and mixed ether/thioether crowns, $[MCl_3(crown)]$ (M = Cr or V; crown = 12-crown-4, 15-crown-5,18-crown-6, $[12]aneS_4$, $[15]aneS_5$, $[9]aneS_2O$, $[15]aneS_2O_3$, $[18]aneS_3O_3$) has been prepared by the reaction of $[MCl_3(thf)_3]$ with rigorously dried crown in anhydrous CH_2Cl_2. In the presence of small amounts of water the monoaquo species $[MCl_3(H_2O)(15\text{-crown-}5)]$ and $[MCl_3(H_2O)(18\text{-crown-}6)]$ are obtained. The products have been characterised by IR and UV/Visible spectroscopy, microanalyses and for $[CrCl_3(H_2O)(18\text{-crown-}6)]$, $[VCl_3(H_2O)(15\text{-crown-}5)]$ and $[CrCl_3([15]aneS_5)]$, by X-ray crystallography. The unexpected affinity of specifically the 15-crown-5 and 18-crown-6 complexes to pick up H_2O is rationalised in terms of the strain within the two adjacent five-membered chelate rings in the anhydrous (κ^3-coordinated) species, and a wider survey of the structures reported for six-coordinate M^{III} crown complexes (M = Sc – Cr) with $RECH_2CH_2ER$ (E = O or S) reveals that while the S–M–S angles in five-membered chelate rings are typically around 82°, those involving O–M–O are very substantially more acute at around 75°. Thus, the $[MCl_3(\kappa^3\text{-crown ether})]$ complexes are much less stable and can alleviate some of this significant ring strain by switching to κ^2-crown coordination with the H_2O ligand completing the six coordination. In contrast, the crown thioether complexes have much less tendency to do this and hence appear to be more stable. Furthermore, using the structurally related (dimethylene linkages) mixed thia/oxa crowns to probe the M–O vs. M–S binding competitively, strongly indicates that the Cr^{III} and V^{III} preferentially coordinate to the thioether rather than the ether donor atoms, contrary to normal expectation based upon HSAB theory.

Introduction

The coordination chemistry of crown ether ligands is dominated by the group 1 and 2 metals and the lanthanides.[1–3] Two main types of metal–crown ether complex are known – primary coordination, where the crown bonds directly to the metal by some or all of the ether oxygen atoms, and secondary coordination, where the crown is not directly bonded to the metal, but interacts through H bonding with the metal complex. Relatively few studies of transition metal crown ether complexes have been reported. For the early 3d metals, scandium(III) forms primary coordination complexes under anhydrous conditions, including $[ScCl_2(15\text{-crown-}5)][SbCl_6]$, $[ScCl(15\text{-crown-}5)(MeCN)][SbCl_6]_2$, $[ScCl_2(18\text{-crown-}6)][SbCl_6]$ and $[Sc(12\text{-crown-}4)_2]^{3+}$, whilst in the presence of water secondary coordination occurs as in $[ScCl_3(H_2O)_3]\cdot$crown (crown = 15-crown-5, 18-crown-6).[4–6] Titanium(IV) halides produce the very moisture sensitive $[TiX_4(\kappa^2\text{-crown})]$ (crown = 12-crown-4, 15-crown-5, 18-crown-6; X = Cl or Br) and $[TiCl_3(15\text{-crown-}5)(MeCN)][SbCl_6]$; two hydrolysis products $[Ti_2Cl_6(\mu\text{-}O)(18\text{-crown-}6)_2]$ and $[Ti_4(\mu\text{-}O)_4Cl_8(15\text{-crown-}5)_4]$ have also been structurally characterised.[7–9]

Titanium(III), vanadium(III) and chromium(III) are represented by some scattered structurally characterised complexes, viz. $[MCl_3(H_2O)(18\text{-crown-}6)]$ (M = Ti or V),[10,11] $[VCl_2(15\text{-crown-}5)][VOCl_4]$,[12] $[CrCl_3(H_2O)(15\text{-crown-}5)]$,[13] and $[CrCl_3(H_2O)_3]\cdot(15\text{-crown-}5)$,[14] but the systematic chemistry with these trivalent metals has not been investigated. We have also been probing the chemistry of early transition-metal centres with softer thioether ligands and macrocycles in order to explore the effects of combining these soft ligands with hard metals. In this context we have described previously the preparations and properties of a series of neutral Cr^{III} and V^{III} halide complexes of the form $[MX_3(L)]$ (X = Cl or Br; L = $[9]aneS_3$, $[10]aneS_3$ [1,4,7-trithiacyclodecane] or $[18]aneS_6$ [1,4,7,10,13,16-hexathiacyclooctadecane]) and the cationic $[CrX_2([n]aneS_4)]PF_6$ (*n* = 14 or 16) ($[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane, $[16]aneS_4$ = 1,5,9,13-tetrathiacyclohexadecane).[15] The crystal structure of $[CrCl_3(\kappa^3\text{-}[18]aneS_6)]$ has also been described by Grant and co-workers.[16] Chromium(III) complexes with thioether-containing ligands, e.g.

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[a] School of Chemistry, University of Southampton,
Southampton SO17 1BJ, UK
E-mail: g.reid@soton.ac.uk

$[CrCl_3\{RS(CH_2)_2NH(CH_2)_2SR\}]$ (R = Me, Et, *n*Bu, *n*-decyl) have also been shown to be important catalyst precursors which, when combined with methylaluminoxane, promote the selective trimerisation of ethene to produce 1-hexene.[17] The nature of the ligand plays an important role in determining the product distribution in these processes.

Here we report the results of our systematic studies on the synthesis, characterisation and structures of complexes of the three crown ethers 12-crown-4, 15-crown-5 and 18-crown-6, the thiamacrocycles $[12]aneS_4$ (1,4,7,10-tetrathiacyclododecane) and $[15]aneS_5$ (1,4,7,10,13-pentathiacyclopentadecane) and the mixed thia-oxa macrocycles $[9]aneS_2O$ (1-oxa-4,7-dithiacyclononane), $[15]aneS_2O_3$ (1,4,7-trioxa-10,13-dithiacyclopentadecane) and $[18]aneS_3O_3$ (1,4,7-trioxa-10,13,16-trithiacyclooctadecane) with Cr^{III} and V^{III} chlorides. The macrocyclic ligands were specifically chosen to provide a direct comparison between ether and thioether coordination and the mixed S/O systems to probe the ligation to S or O competitively. The crystal structures of three complexes are reported and an analysis of the structural parameters of these species, together with the structurally characterised examples in the literature reveal some quite marked trends in the angles subtended at the metal. These are discussed in terms of donor atom type, ring size and complex stability.

Results and Discussion

The reaction of $[MCl_3(thf)_3]$ with rigorously dry (either by prolonged heating in vacuo or by pre-treatment with $SOCl_2$ in refluxing CH_2Cl_2) 15-crown-5 in CH_2Cl_2 under anhydrous conditions yields pink-purple (Cr) and pink (V) powders $[MCl_3(\kappa^3\text{-15-crown-5})]$, whilst in the presence of small amounts of water the products are $[MCl_3(H_2O)(\kappa^2\text{-15-crown-5})]$. The structure of $[CrCl_3(H_2O)(\text{15-crown-5})]$ has been reported[13] and consists of a pseudo-octahedral chromium centre bonded to three facial chlorines, a water molecule and κ^2 to the crown. The anhydrous and aqua complexes are readily distinguishable by their IR spectra (the presence or absence of water bands), have distinguishable spectra in the fingerprint region and also differ in the far IR ν(M–Cl) vibrations (Experimental Section). The anhydrous $[MCl_3(\kappa^3\text{-15-crown-5})]$ readily convert to $[MCl_3(H_2O)(\kappa^2\text{-15-crown-5})]$ upon stirring in CH_2Cl_2 solution with small amounts of added water under N_2 (larger amounts of water completely displace the crown – see below). Crystals of $[VCl_3(H_2O)(\kappa^2\text{-15-crown-5})]$ were obtained from CH_2Cl_2/hexane. The structure shows (Figure 1, Table 1) the V coordinated to three facial Cl atoms 2.309(2)–2.335(2) Å, one H_2O ligand [2.064(5) Å] and two adjacent ether O atoms from the crown [2.070(4) and 2.122(4) Å]. The O–V–O angle within the chelate ring is 76.23(18)°. The O5···O6···O4a angle is a plausible 102.3°. The structure of $[VCl_3(H_2O)(\kappa^2\text{-18-crown-6})]$ reported by Atwood and co-workers shows similar geometric parameters.[8] Although the H atoms bonded to the water O6 were not convincingly identified, there are only two suitable O···O distances for O–H···O H-bonding interactions. Thus O6···O5 [2.784(6) Å] is an intramolecular H-bond and O6···O4a [2.676(6) Å, a: *y*, *x*, –*z*] an intermolecular interaction to crown O atoms.

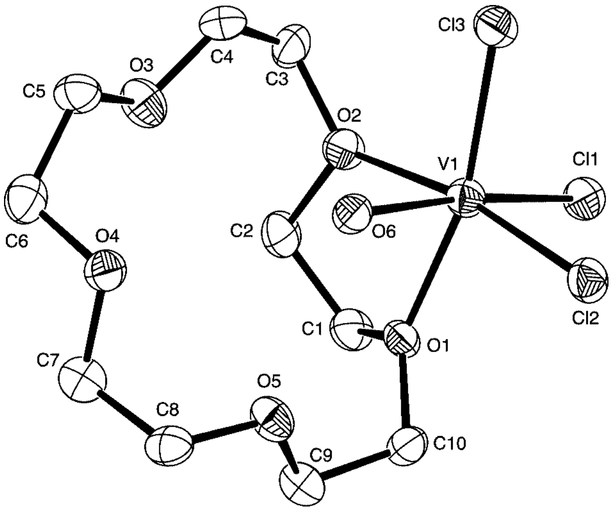

Figure 1. View of the structure of $[VCl_3(H_2O)(\text{15-crown-5})]$ with numbering scheme adopted. H atoms have been omitted for clarity and the ellipsoids are drawn at the 50% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for $[VCl_3(H_2O)(\text{15-crown-5})]\cdot 3/4CH_2Cl_2$.

V1–O1	2.070(4)	V1–Cl1	2.319(2)
V1–O2	2.122(4)	V1–Cl2	2.335(2)
V1–O6	2.064(5)	V1–Cl3	2.309(2)
O6–V1–O1	82.72(19)	O6–V1–O2	88.12(18)
O1–V1–O2	76.23(18)	O6–V1–Cl3	89.08(14)
O1–V1–Cl3	166.19(14)	O2–V1–Cl3	92.46(14)
O6–V1–Cl1	172.78(14)	O1–V1–Cl1	90.07(15)
O2–V1–Cl1	89.73(14)	Cl3–V1–Cl1	97.90(8)
O6–V1–Cl2	89.08(13)	O1–V1–Cl2	94.00(13)
O2–V1–Cl2	170.10(14)	Cl3–V1–Cl2	96.98(8)
Cl1–V1–Cl2	91.89(8)		

Stirring a CH_2Cl_2 solution of this complex overnight with a further added water leads to deposition of blue crystals. These were shown (unit cell determination) to be the V^{IV} species $[VOCl_2(H_2O)_2]\cdot(\text{15-crown-5})$ whose structure has been determined previously and shows secondary bonding interactions between the H_2O ligands on the vanadyl centre and the crown ether.[18]

The corresponding reactions of $[MCl_3(thf)_3]$ with 12-crown-4 gave $[MCl_3(\kappa^3\text{-12-crown-4})]$. Similarly, reaction of $[MCl_3(thf)_3]$ with 18-crown-6 affords $[MCl_3(\kappa^3\text{-18-crown-6})]$ and $[MCl_3(H_2O)(\kappa^2\text{-18-crown-6})]$ (the latter with M = Cr was characterised by an X-ray study – below), while using a 2:1 ratio of M/crown gives the binuclear $[(MCl_3)_2(\text{18-crown-6})]$. The anhydrous $[MCl_3(\kappa^3\text{-18-crown-6})]$ are particularly moisture sensitive, much more so than $[MCl_3(\kappa^3\text{-12-crown-4})]$, which may indicate that the water is first associated with the "free" O atoms of the crown and then transferred to the metal, which will be less easy in the smaller ring. The structure of $[CrCl_3(H_2O)(\text{18-crown-6})]$ shows two independent molecules in the asymmetric unit, one of which is shown in Figure 2, Table 2. The Cr^{III} is in a distorted octahedral environment, coordinated to three facial Cl atoms, two adjacent ether O atoms from the crown and a water molecule. For the Cr1 molecule (see Figure 2) each of the O13 H atoms is involved in an intramolecular H bond to a crown O atom [O13···O4 2.813(4), O13···O6 2.842(4) Å]. A similar situation applies to the Cr2 containing-molecule and O14. The Cr–O distances within the crown are ca. 2.05 Å, while the Cr–OH$_2$ distances are slightly shorter in each case. The O–Cr–O angles within the chelate rings are notable at only 79.22(11) and 76.93(12)°. The structural features in this species parallel those in [CrCl$_3$(H$_2$O)(κ^2-15-crown-5)] reported by Dehnicke and co-workers,[13] which shows intramolecular H-bonding interactions between the coordinated H$_2$O ligand and two of the uncoordinated O atoms of the crown.

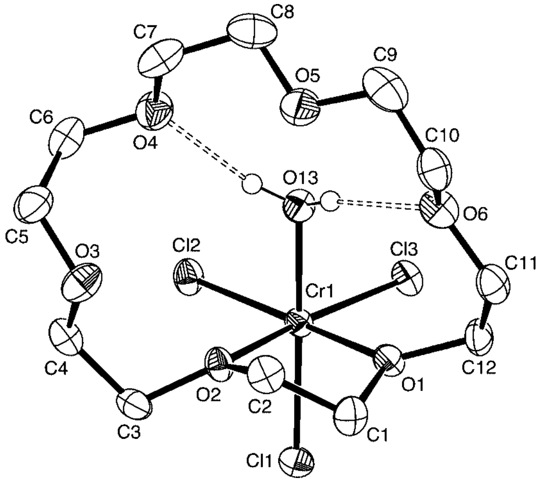

Figure 2. View of the structure of one of the two independent [CrCl$_3$(H$_2$O)(18-crown-6)] molecules with numbering scheme adopted. H atoms on C have been omitted for clarity and the ellipsoids are drawn at the 50% probability level. The other molecule is very similar.

As before, the anhydrous and the aqua complexes can be distinguished by their IR spectra, and the IR spectra of the dinuclear complexes are quite distinct in the fingerprint region. All of the M^{III} complexes contain pseudo-octahedral metal centres, as shown by their diffuse reflectance spectra (Table 3) (some solution spectra were obtained but a combination of poor solubility and extreme moisture sensitivity of the dilute solutions meant they were poorly reproducible and are not quoted).

The d^3 chromium complexes typically showed two d–d bands assigned (in O_h symmetry) as $^4A_{2g}\rightarrow{}^4T_{2g}$ and $^4A_{2g}\rightarrow{}^4T_{1g}(F)$, respectively, and a third band was usually evident of the edge of intense features in the UV, which may be the $^4A_{2g}\rightarrow{}^4T_{1g}(P)$ transition (Table 3).[19] Although the actual metal-centre symmetry is lower than O_h, no clearly resolved splitting of the bands was observed, although the lowest energy feature was often asymmetric. The band maxima show small shifts consistent with the ligand field strengths Cl < O$_{crown}$ < H$_2$O. For the d^2 vanadium complexes the two transitions observed are assigned to $^3T_{1g}\rightarrow{}^3T_{2g}$, and $^3T_{1g}\rightarrow{}^3T_{1g}(P)$, respectively, based on O_h symmetry and trends are discussed below.

Table 2. Selected bond lengths [Å] and angles [°] for [CrCl$_3$(H$_2$O)(18-crown-6)].

Cr1–O1	2.060(3)	Cr1–Cl1	2.3047(13)
Cr1–O2	2.047(3)	Cr1–Cl2	2.2704(12)
Cr1–O13	2.034(3)	Cr1–Cl3	2.2780(12)
Cr2–O7	2.072(3)	Cr2–Cl4	2.3017(13)
Cr2–O8	2.069(3)	Cr2–Cl5	2.2892(12)
Cr2–O14	2.016(3)	Cr2–Cl6	2.2717(12)
O13–Cr1–O2	86.41(12)	O13–Cr1–O1	86.05(12)
O2–Cr1–O1	79.22(11)	O13–Cr1–Cl2	89.84(9)
O2–Cr1–Cl2	94.26(8)	O1–Cr1–Cl2	172.49(9)
O13–Cr1–Cl3	90.94(9)	O2–Cr1–Cl3	169.63(8)
O1–Cr1–Cl3	90.60(8)	Cl2–Cr1–Cl3	95.75(4)
O13–Cr1–Cl1	173.43(9)	O2–Cr1–Cl1	87.82(9)
O1–Cr1–Cl1	89.78(9)	Cl2–Cr1–Cl1	93.73(5)
Cl3–Cr1–Cl1	94.18(5)	O14–Cr2–O8	85.70(12)
O14–Cr2–O7	86.76(12)	O8–Cr2–O7	76.93(12)
O14–Cr2–Cl6	88.74(9)	O8–Cr2–Cl6	171.29(10)
O7–Cr2–Cl6	96.08(9)	O14–Cr2–Cl5	90.23(9)
O8–Cr2–Cl5	91.43(9)	O7–Cr2–Cl5	168.16(9)
Cl6–Cr2–Cl5	95.29(4)	O14–Cr2–Cl4	174.83(9)
O8–Cr2–Cl4	91.73(9)	O7–Cr2–Cl4	88.29(9)
Cl6–Cr2–Cl4	93.27(5)	Cl5–Cr2–Cl4	94.33(5)

Grant and co-workers have described the reaction of CrCl$_3$·6H$_2$O with the thioether macrocycles [12]aneS$_4$ and [15]aneS$_5$ in refluxing MeCN; however, unsurprisingly, in the presence of water the substitutions are not clean and no pure products were isolated.[16] We have obtained the thioether macrocyclic complexes [CrCl$_3$(κ^3-[12]aneS$_4$)] and [CrCl$_3$(κ^3-[15]aneS$_5$)] readily and in good yield from [CrCl$_3$(thf)$_3$] and the thiamacrocycle in anhydrous CH$_2$Cl$_2$ solution and isolated them as purple/blue solids. Despite the softer nature of the ligand donor atoms, once isolated these compounds show a much reduced tendency to pick up H$_2$O in the metal coordination sphere cf. the crown ethers above (IR evidence). [VCl$_3$(κ^3-[12]aneS$_4$)] was obtained similarly.

A crystal structure of [CrCl$_3$([15]aneS$_5$)] confirms (Figure 3, Table 4) the distorted octahedral coordination at Cr through three facial Cl atoms and three facial and mutually adjacent S atoms of the macrocycle, d(Cr–Cl) = 2.2849(8)–2.3028(9) Å; d(Cr–S) = 2.4161(10)–2.4942(8) Å, the bond lengths and angles compare well with those in the crystallographically characterised neutral [CrCl$_3$([18]aneS$_6$)][16] and the cationic *cis*-[CrX$_2$([14]aneS$_4$)]PF$_6$.[15] The UV/Visible spectra show clearly that the thioether donors present a stronger ligand field than the O–donor ligands, giving the overall order Cl$^-$ < O$_{crown}$ < H$_2$O < S$_{thiacrown}$ (Table 3).

The mixed thia-oxa macrocyclic complexes [MCl$_3$(κ^3-[9]-aneS$_2$O)], [MCl$_3$(κ^3-[15]aneS$_2$O$_3$)] and [MCl$_3$(κ^3-[18]-aneS$_3$O$_3$)] were obtained from similar reactions as purple/blue (Cr) or pink (V) coloured solids. These compounds have a much lower tendency to pick up H$_2$O compared to the crown ether complexes.

The diffuse reflectance UV/Visible spectra for the thia and thia-oxa macrocyclic complexes are also consistent

Table 3. UV/Visible data [cm^{-1}].[a]

Complex[b]	$^4A_{2g}\rightarrow{}^4T_{2g}$	$^4A_{2g}\rightarrow{}^4T_{1g}$(F)	$^4A_{2g}\rightarrow{}^4T_{1g}$(P)
$[CrCl_3(thf)_3]$	13666 (sh), 14450	19680	27320
$[CrCl_3$(12-crown-4)]	13510	19050	–
$[CrCl_3$(15-crown-5)]	13195	19230	27930
$[CrCl_3(H_2O)$(15-crown-5)]	13660	19650	29250 (sh)
$[CrCl_3$(18-crown-6)]	13200 (sh), 13500	19380	28900 (sh)
$[CrCl_3(H_2O)$(18-crown-6)]	13570	19685	29270 (sh)
$[(CrCl_3)_2$(18-crown-6)]	13400, 13960 (sh)	19450	–
$[CrCl_3([12]aneS_4)]$	14050	19840	29900 (sh)
$[CrCl_3([15]aneS_5)]$	14290	19380	30490 (sh)
$[CrCl_3([9]aneS_2O)]$	14880	19970	–
$[CrCl_3([15]aneS_2O_3)]$	14450	20000	30860 (sh)
$[CrCl_3([18]aneS_3O_3)]$	14350	19660	30300
Complex[b]	$^3T_{1g}\rightarrow{}^3T_{2g}$	$^3T_{1g}\rightarrow{}^3T_{1g}$(P)	
$[VCl_3(thf)_3]$	12820	20490	
$[VCl_3$(12-crown-4)]	11870	18900	
$[VCl_3$(15-crown-5)]	11500 (sh), 12830	19380	
$[VCl_3(H_2O)$(15-crown-5)]	11300 (sh), 12690	19190	
$[VCl_3$(18-crown-6)]	12900	18950	
$[VCl_3(H_2O)$(18-crown-6)]	11900 (sh), 13400	19800	
$[(VCl_3)_2$(18-crown-6)]	12320	19230	
$[VCl_3([12]aneS_4)]$	12690	18250	
$[VCl_3([9]aneS_2O)]$	13440	18880	
$[VCl_3([15]aneS_2O_3)]$	12940, 13400 (sh)	19850	
$[VCl_3([18]aneS_3O_3)]$	12800	19690	

[a] Spectra recorded by diffuse reflectance; frequencies quoted have errors estimated as +/– 100 cm^{-1}. [b] For Cr^{III} ν_1 gives 10Dq directly; for both Cr^{III} and V^{III} semi-quantitative fitting of the spectra (in O_h symmetry) to the appropriate Tanabe–Sugano diagram gave consistent trends, i.e. the average 10 Dq increases with incorporation of S-donor atoms and is accompanied by a small decrease in the B parameter.[19]

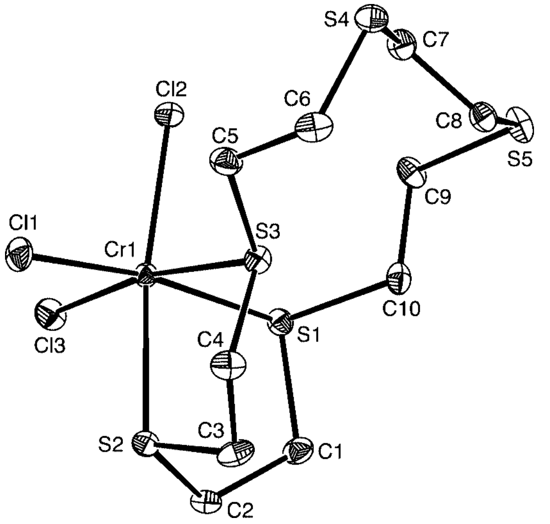

Figure 3. View of the structure of $[CrCl_3([15]aneS_5)]$ with numbering scheme adopted. H atoms are omitted for clarity and the ellipsoids are drawn at the 50% probability level.

with distorted octahedral geometries. For the $[MCl_3([9]aneS_2O)]$ complexes, S_2O coordination of the macrocycle is imposed, giving the metal an S_2OCl_3 donor set overall, and as expected, the UV/Visible spectra of $[MCl_3([9]aneS_2O)]$ (Table 3) much more closely resemble those of the thioether crown analogues (S_3Cl_3 donor set) rather than the crown ether analogues (O_3Cl_3 donor set). Importantly, comparison of the energies of the d-d transitions in the Cr^{III} thiaoxa species clearly shows that even the $[15]aneS_2O_3$ and $[18]aneS_3O_3$ systems involve S-coordination (although this technique does not readily discriminate between S_3 vs. S_2O vs. SO_2 coordination). Unfortunately, despite repeated efforts to obtain single crystals of one or more of the complexes with these ligands to provide definitive proof of the metal donor set, we have not been successful.

Table 4. Selected bond lengths [Å] and angles [°] for $[CrCl_3([15]aneS_5)]$.

Cr1–Cl1	2.2849(8)	Cr1–S1	2.4942(8)
Cr1–Cl2	2.2885(9)	Cr1–S2	2.4166(9)
Cr1–Cl3	2.3028(9)	Cr1–S3	2.4261(10)
Cl1–Cr1–Cl2	96.13(3)	Cl1–Cr1–Cl3	94.45(3)
Cl2–Cr1–Cl3	99.08(3)	Cl1–Cr1–S2	87.74(3)
Cl2–Cr1–S2	171.22(3)	Cl3–Cr1–S2	88.43(3)
Cl1–Cr1–S3	90.21(3)	Cl2–Cr1–S3	88.46(3)
Cl3–Cr1–S3	170.64(3)	S2–Cr1–S3	83.64(3)
Cl1–Cr1–S1	172.12(3)	Cl2–Cr1–S1	91.71(3)
Cl3–Cr1–S1	83.62(3)	S2–Cr1–S1	84.58(3)
S3–Cr1–S1	90.68(2)		

Analysis of Structural Data

Evidence from this work shows that the κ^3-coordinated crown ether complexes may be obtained only under stringently anhydrous conditions, with traces of water leading to partial hydrolysis and isolation of the mono-aqua complexes, with the crown now only κ^2-coordinated. On the other hand, the thiamacrocycles readily yield S_3-coordinated species, which appear to be considerably less susceptible to hydrolysis. At first sight this seems surprising because on the basis of Pearson's HSAB theory, one would anticipate that the crown ether ligands (O-donor) would result in more stable complexes than the softer thioether macrocycles. In order to explain these results we have therefore examined the structural parameters in these species, together with the crystallographically determined parameters in all other reported six-coordinate (octahedral) complexes of early transition metals (Sc, Ti, V and Cr) with ether and thioether ligands of the form $RE(CH_2)_2ER$ and $RE(CH_2)_2E(CH_2)_2ER$ (E = O or S; R = alkyl) and S- or O-donor macrocycles involving dimethylene linkages. The results obtained using the Cambridge Crystallographic Database[20,21] are presented in Figure 4, which shows histograms depicting the E–M–E angles within the five-membered chelate rings for E = O (a) and for E = S (b). The average O–M–O angles in these species are 74.8°, with values ranging from 68.6–79.0°, while the average S–M–S chelate angles are 82.2°, with values ranging from 75.7–86.8°. The data obtained from the three crystal structures presented above are consistent with the data in Figure 4. This surprisingly large difference is consistent with the crown ether complexes being more strained, and may well explain why the κ^3-crown complexes are so readily hydrolysed – incorporating two adjacent very acute five-membered chelates leads to a very strained species which will readily scavenge another donor ligand such as H_2O and convert to κ^2-crown to relieve the strain within the coordination sphere. In contrast, the S–M–S chelate angles of ca. 82° are closer to the idealised 90° angle in a regular octahedron. In support of this we note that the O–Cr–O angles in *mer*-$[CrCl_3(thf)_3]$ are 86.0(1) and 86.5(1)° – the monodentate thf ligands remove chelate constraints as a consideration, and hence presumably reflect the preferred relative positioning of the ligands.[22]

The magnitude of the chelate angle subtended at the metal M is a consequence of both the M–E distances and the E–C distances. The M–S distances are ca. 0.4 Å longer than *d*(M–O) in these species. The reason for the large difference in E–M–E angles presumably originates from the difference between *d*(O–C) (typically ca. 1.47 Å) vs. *d*(S–C) (typically ca. 1.83 Å) – thus an O–C–C–O linkage is too short to accommodate idealised octahedral angles at a coordinated early transition metal without introducing significant angle strain at the O and the C atoms.

We previously reported the preparation and properties of the Ti^{IV} complex $[TiCl_4(\kappa^2\text{-}[15]aneS_2O_3)]$, the ^1H NMR spectrum of which unexpectedly showed that coordination to Ti is through the two thioether S atoms, not the ether O atoms.[9] This result, together with the results of the present studies, suggest that the substantially different ring-strain effects introduced upon chelation of $–OCH_2CH_2O–$ cf. $–SCH_2CH_2S–$ linkages plays a dominant role in determining the donor set at Ti and offsets the fact that the thioethers are softer donor ligands than the ethers.

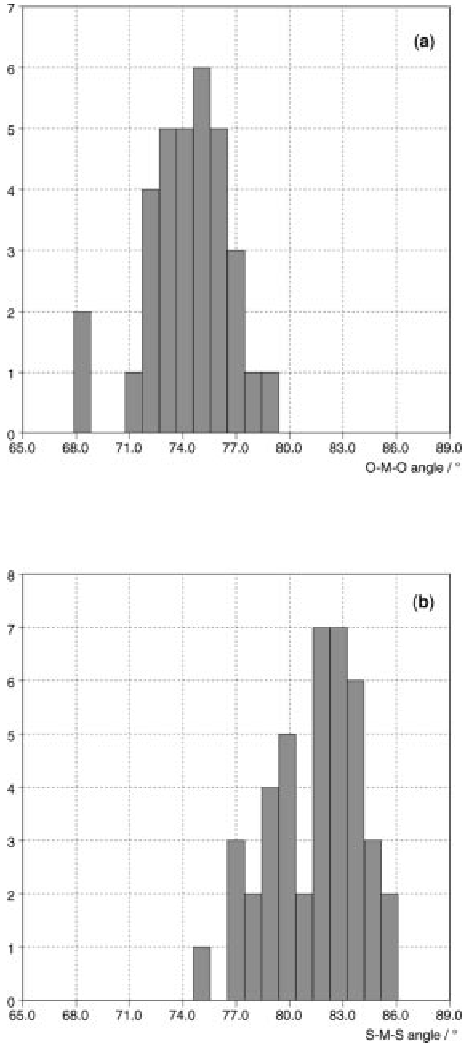

Figure 4. Histograms showing the crystallographically determined E–M–E angles within saturated five-membered chelate rings on an octahedral metal centre (M = Sc, Ti, V, Cr). (**a**) E = O, mean O–M–O angle 74.8(2.4)°. The lowest angles are for $[Sc(CH_2SiMe_3)_3(12\text{-crown-}4)]$ which contains two adjacent five-membered chelate rings.[28] (b) E = S, mean S–M–S angle 82.2(2.6)°. The lowest angles are for those complexes involving the macrocycle $[9]aneS_3$ containing three adjacent five-membered chelate rings.

Conclusions

We describe here a series of neutral chloro Cr^{III} and V^{III} complexes with crown ether, crown thioether and mixed thia-oxa crown ligands. The κ^3-crown ether complexes show a marked tendency to dissociate one O atom and pick up a H_2O ligand – an observation also noted for other early transition-metal crown ether complexes both by ourselves and by other workers. Furthermore, competitive binding studies using mixed S/O crowns with various ring sizes, but still maintaining the dimethylene linking groups strongly suggest that *S*-coordination is preferred.

This work has shown that despite the prediction that the hard, oxophilic early transition metals are likely to coordinate more favourably with ether-based ligands than the softer thioethers, ring strain within the resulting five-membered chelates plays a critical role and destabilises the crown ether complexes cf. the crown thioether analogues in these systems. This result suggests that the linkage between the O atoms of crown ether ligands may be of fundamental importance in determining complex stability and that judicious choice of crown design (ring size and substitution pattern) may influence significantly the stability of transition metal–crown ether complexes and allow a much wider range of transition metal complexes with this important family of ligands to be prepared. Work is underway in our laboratories currently to investigate this more fully. Finally, we note that these considerations are not relevant to the *endo*-coordinated crowns in the seven-coordinate species such as $[ScCl_2(\kappa^5\text{-15-crown-5})]^+$, $[ScCl(\kappa^5\text{-15-crown-5})(MeCN)]^{2+}$ [4–6] and $[VCl_2(\kappa^5\text{-15-crown-5})]^+$,[12] since in these species the crown occupies five positions in a pentagonal plane, with idealised O–M–O angles of 72° which can be easily accommodated by the five-membered chelate rings.

Experimental Section

Physical Measurements: Infrared spectra were recorded as Nujol mulls between CsI discs with a Perkin–Elmer 983G spectrometer over the range 4000–180 cm^{-1}. UV/Visible spectra were obtained in diffuse reflectance mode from samples diluted with $BaSO_4$ using a Perkin–Elmer Lambda19 spectrometer or as solutions in CH_2Cl_2 using quartz cells. Microanalyses were performed by the University of Strathclyde micro-analytical service. In some cases the compounds retained some CH_2Cl_2 which was evident from the microanalyses, IR and by ^{1}H NMR spectroscopy; partial CH_2Cl_2 is also evident in some of the crystal structures. $[CrCl_3(thf)_3]$ was made by the literature route.[23] $[VCl_3(thf)_3]$ and the macrocycles 12-crown-4, 15-crown-5, 18-crown-6, [12]aneS_4 and [15]aneS_5 were obtained from Aldrich. The mixed thia-oxa crowns, [9]aneS_2O, [15]aneS_2O_3 and [18]aneS_3O_3 were prepared by the literature methods.[24] The anhydrous crown ethers were obtained either by prolonged heating in vacuo or by refluxing the crown with thionyl chloride in CH_2Cl_2. The aqua complexes either used the crowns treated as above and subsequent addition of small amounts of water, or using crowns which were "dried" by pumping in vacuo at room temperature for a few hours (under these conditions ^{1}H NMR and IR spectra provide evidence for retention of some water). The anhydrous crowns were stored in Schlenk flasks and manipulated in a dry box. All complexes were manipulated in a dry box (<5 ppm water).

Chromium(III) Complexes

$[CrCl_3(12\text{-crown-4})]$: $[CrCl_3(thf)_3]$ (0.4 g, 1.1 mmol) in dry CH_2Cl_2 (5 mL) was combined with dry 12-crown-4 (0.2 g, 1.1 mmol) in dry CH_2Cl_2 (5 mL). A precipitate was formed; this was then filtered off and dried in vacuo. The product was a pink solid. Yield 0.10 g, 24%. $C_8H_{16}Cl_3CrO_4\cdot 1/2CH_2Cl_2$ (377.0): calcd. C 27.1, H 4.5; found C 27.5, H 4.9. IR (Nujol): $\tilde{\nu}$ = 1299 (s), 1261 (m), 1228 (m), 1145 (s), 1063 (s), 1026 (vs), 934 (m), 908 (s), 838 (s), 363 (sh), 356 (s), 340 (sh) cm^{-1}.

$[CrCl_3(15\text{-crown-5})]$: $[CrCl_3(thf)_3]$ (0.13 g, 0.34 mmol) in dry CH_2Cl_2 (5 mL) was added to anhydrous 15-crown-5 (0.07 g, 0.34 mmol) in dry CH_2Cl_2 (5 mL) and the solution was stirred for 30 min. A solid was produced and then filtered off and dried in vacuo. Pink solid. Yield 0.06 g, 38%. $C_{10}H_{20}Cl_3CrO_5\cdot CH_2Cl_2$ (463.5): calcd. C 28.5, H 4.8; found C 27.5, H 5.8. IR (Nujol): $\tilde{\nu}$ = 1304 (m), 1263 (m), 1231 (m), 1147 (s), 1126 (s), 1111 (s), 1081 (s), 1064 (vs), 1021 (vs), 934 (s), 928 (sh), 906 (sh), 841 (s), 798 (s), 728 (s), 380 (sh), 362 (s), 349 (s) cm^{-1}.

$[CrCl_3(H_2O)(15\text{-crown-5})]$: $[CrCl_3(thf)_3]$ (0.10 g, 0.27 mmol) in dry CH_2Cl_2 (5 mL) was added to 15-crown-5 (0.17 g, 0.28 mmol) in dry CH_2Cl_2 (5 mL) and the solution was stirred for 1 h. The precipitate was filtered off and dried in vacuo. The product was a pink solid. Yield 0.05 g, 37%. $C_{10}H_{22}Cl_3CrO_6$ (396.6): calcd. C 30.3, H 5.6; found C 29.5, H 6.1. IR (Nujol): $\tilde{\nu}$ = 3300 (br), 1630 (m), 1303 (m), 1249 (m), 1140 (s), 1120 (s), 1110 (s), 1073 (vs), 1035 (vs), 1006 (m), 933 (s), 919 (m), 854 (s), 828 (w), 786 (w), 365 (sh), 343 (m), 321 (m) cm^{-1}.

$[CrCl_3(18\text{-crown-6})]$: $[CrCl_3(thf)_3]$ (0.3 g, 0.8 mmol) in dry CH_2Cl_2 (5 mL) was combined with dry 18-crown-6 (0.2 g, 1.0 mmol) in dry CH_2Cl_2 (5 mL). The solution was stirred for 5 min the solid produced was then filtered off and dried in vacuo. The product produced was a pink solid. Yield 0.05 g, 10%. $C_{12}H_{24}Cl_3CrO_6\cdot 1/2CH_2Cl_2$ (465.1): calcd. C 32.3, H 5.4; found C 32.5, H 6.0. IR (Nujol): $\tilde{\nu}$ = 1306 (m), 1260 (w), 1120 (s), 1166 (s), 1022 (s), 937 (m), 922 (m), 822 (m), 797 (m), 377 (m), 352 (s) cm^{-1}.

$[CrCl_3(H_2O)(18\text{-crown-6})]$: $[CrCl_3(thf)_3]$ (0.14 g, 0.37 mmol) in dry CH_2Cl_2 (10 mL) was combined with 18-crown-6 (0.1 g, 0.4 mmol) in dry CH_2Cl_2 (10 mL). The solution was stirred for 1 h. Addition of dry *n*-hexane (5 mL) produced a precipitate, which was then filtered off and dried in vacuo. The product produced was a pink solid. Yield 0.03 g, 19%. $C_{12}H_{26}Cl_3CrO_7$ (440.7): calcd. C 32.7, H 6.0; found C 31.9, H 7.0. IR (Nujol): $\tilde{\nu}$ = 3300 (br), 1617 (m), 1299 (w), 1261 (m), 1148 (m), 1093 (vs), 1046 (sh), 1019 (s), 951 (w), 865 (s), 810 (m), 356 (m), 323 (m) cm^{-1}.

$[(CrCl_3)_2(18\text{-crown-6})]$: $[CrCl_3(thf)_3]$ (0.19 g, 0.50 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL) and a solution of dry 18-crown-6 (0.06 g, 0.23 mmol) in anhydrous CH_2Cl_2 (10 mL) added and the mixture stirred for 30 min. The solution was concentrated in vacuo to 10 mL, and dry hexane (10 mL) added dropwise to the vigorously stirred solution. After stirring for 10 min the purple solid which had separated was filtered off and dried in vacuo. Yield 0.09 g, 67%. $C_{12}H_{24}Cl_6Cr_2O_6$ (581.0): calcd. C 24.8, H 4.2; found C 25.7, H 5.9. IR (Nujol): $\tilde{\nu}$ = 1346 (w), 1306 (w), 1258 (m), 1210 (w), 1147 (sh), 1092 (s), 1064 (s), 1018 (s), 936 (m), 921 (sh), 852 (m), 821 (m), 707 (m), 587 (w), 367 (sh), 350 (s) cm^{-1}.

$[CrCl_3([12]aneS_4)]$: [12]aneS_4 (0.03 g, 0.13 mmol) was dissolved in CH_2Cl_2 (5 mL) and combined with a solution of $[CrCl_3(thf)_3]$ (0.05 g, 0.13 mmol) in CH_2Cl_2 (5 mL). The solution turned blue immediately and a small amount of blue precipitate formed. The solution was concentrated further to ca. 3 mL in vacuo. The resulting blue solid was then filtered off and dried in vacuo. Yield 0.04 g, 76%. $C_8H_{16}Cl_3CrS_4$ (398.8): calcd. C 24.1, H 4.0; found C 24.4, H 4.6. IR (Nujol): $\tilde{\nu}$ = 1300 (w), 1262 (m), 1093 (m), 1017 (m), 951 (w), 923 (w), 861 (m), 802 (m), 744 (m), 366 (m), 329 (w) cm^{-1}.

$[CrCl_3([15]aneS_5)]$: Prepared similarly to $[CrCl_3([12]aneS_4)]$ using [15]aneS_5. Purple solid. Yield 88%. $C_{10}H_{20}Cl_3CrS_5$ (459.0): calcd. C 26.2, H 4.4; found 25.6, H 4.9. IR (Nujol): $\tilde{\nu}$ = 1260 (s), 1096 (s), 1021 (s), 800 (m), 340 (m), 315 (sh) cm^{-1}.

$[CrCl_3([9]aneS_2O)]$: Prepared similarly to $[CrCl_3([12]aneS_4)]$ using [9]aneS_2O. Purple solid. Yield 58%. $C_6H_{12}Cl_3CrOS_2\cdot 1/4thf$ (340.67): calcd. C 24.7, H 4.1; found 25.0, H 4.0. IR (Nujol): $\tilde{\nu}$ = 1297 (w), 1200 (w), 1188 (w), 1056 (m), 1012 (m), 989 (s), 934 (m), 912 (s), 836 (m), 772 (w), 686 (w), 487 (w), 358 (s), 343 (sh) cm^{-1}.

$[CrCl_3([15]aneS_2O_3)]$: Prepared similarly to $[CrCl_3([12]aneS_4)]$ using [15]aneS_2O_3. Purple solid. Yield 40%. $C_{10}H_{20}Cl_3CrO_3S_2$ (410.8): calcd. C 29.2, H 4.9; found C 28.9, H 5.3. IR (Nujol): $\tilde{\nu}$ = 1304 (m), 1260 (m), 1095 (s), 1021 (s), 917 (w), 868 (w), 802 (m), 366 (m), 345 (w) cm^{-1}.

$[CrCl_3([18]aneS_3O_3)]$: $[CrCl_3(thf)_3]$ (0.18, 0.52 mmol) was dissolved in anhydrous CH_2Cl_2 (15 mL) and added to a solution of

[18]aneS_3O_3 (0.16 g, 0.52 mmol) in anhydrous CH_2Cl_2 (15 mL), when an intensely blue solution formed immediately which rapidly deposited a blue solid. The mixture was stirred for 30 min, dry hexane (10 mL) was added dropwise and the mixture stirred for a further 1 h. The deep blue solid was filtered off and dried in vacuo. Yield 0.16 g, 82%. $C_{12}H_{24}Cl_3CrO_3S_3\cdot1/2CH_2Cl_2$ (513.3): calcd. C 29.2, H 4.9; found C 28.9, H 5.3. IR (Nujol): $\tilde{\nu}$ = 1348 (w), 1295 (m), 1260 (m), 1130 (sh), 1101 (s), 1070 (sh), 1023 (s), 914 (w), 849 (w), 801 (s), 470 (w), 355 (sh), 345 (s) cm^{-1}.

Vanadium(III) Complexes

[VCl_3(12-crown-4)]: [VCl_3(thf)$_3$] (0.38 g, 1.0 mmol) and dry 12-crown-4 (0.18 g, 1.0 mmol) were combined in dry CH_2Cl_2 (10 mL). The pink powder that precipitated was filtered off after 2 h and dried in vacuo. Yield 0.28 g, 33%. $C_8H_{16}Cl_3O_4V$ (333.5): calcd. C 28.8, H 4.8; found C 28.8, H 5.6. IR (Nujol): $\tilde{\nu}$ = 1298 (s), 1261 (w), 1231 (m), 1145 (s), 1066 (s), 1027 (s), 937 (m), 909 (s), 837 (s), 483 (m), 364 (m), 339 (s) cm^{-1}.

[VCl_3(15-crown-5)]: Prepared similarly to [VCl_3(12-crown-4)] using anhydrous 15-crown-5. Pink powder. Yield 0.15 g, 25%. $C_{10}H_{20}Cl_3O_5V\cdot CH_2Cl_2$ (462.5): calcd. C 28.5, H 5.2; found C 27.5, H 5.3. IR (Nujol): $\tilde{\nu}$ = 1304 (m), 1262 (w), 1228 (w), 1149 (m), 1113 (m), 1080 (sh), 1068 (vs), 1027 (s), 933 (m), 918 (m), 846 (m), 793 (m), 367 (m), 342 (s), 324 (s) cm^{-1}.

[$VCl_3(H_2O)$(15-crown-5)]: [VCl_3(thf)$_3$] (0.17 g, 0.48 mmol) in dry CH_2Cl_2 (5 mL) was added to 15-crown-5 (0.11 g, 0.48 mmol) in dry CH_2Cl_2 (5 mL) and the solution was stirred for 1 h. The pink precipitate was filtered off and dried under vacuo. Yield 0.15 g, 38%. $C_{10}H_{22}Cl_3O_6V\cdot CH_2Cl_2$ (480.5): calcd. C 27.5, H 5.0; found C 27.5, H 6.1. IR (Nujol): $\tilde{\nu}$ = 3300 (br), 1630 (m), 1303 (m), 1260 (m), 1140 (s), 1120 (s), 1110 (s), 1073 (vs), 1035 (vs), 1006 (m), 933 (s), 919 (m), 854 (s), 828 (w), 786 (w), 362 (sh), 331 (m), 321 (m) cm^{-1}.

[VCl_3(18-crown-6)]: [VCl_3(thf)$_3$] (0.37 g, 1.0 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL) and added to a solution of 18-crown-6 (0.26 g, 1.0 mmol) in anhydrous CH_2Cl_2 (10 mL), and the purple-pink solution stirred for 1 h. The pink solid which separated on concentration of the solution to ca. 15 mL in vacuo, was filtered off and dried. Yield 0.21 g, 50%. $C_{12}H_{24}Cl_3O_6V\cdot CH_2Cl_2$ (506.5): calcd. C 30.8, H 5.2; found C 31.2, H 6.5. IR (Nujol): $\tilde{\nu}$ = 1350 (w), 1297 (m), 1261 (m), 1240 (w), 1100 (sh), 1057 (s), 1033 (s), 928 (s), 833 (s), 799 (s), 485 (w), 432 (w), 359 (sh), 340 (s) cm^{-1}.

[$VCl_3(H_2O)$(18-crown-6)]: The filtrate from the [VCl_3(18-crown-6)] preparation above was treated with 0.1 mL H_2O and stirred for 1 h, concentrated in vacuo to ca. 10 mL to give a pink solid which was filtered off and dried in vacuo. Yield 35%. $C_{12}H_{26}Cl_3O_7V$ (439.6): calcd. C 32.8, H 6.0; found C 32.4, H 6.3. IR (Nujol): $\tilde{\nu}$ = 3400 (br), 1630 (m), 1290 (m), 1256 (m), 1150 (sh), 1093 (br.,s), 1000 (s), 952 (s), 920 (m), 837 (m), 808 (m), 389 (w), 333 (s), 310 (sh) cm^{-1}.

[$(VCl_3)_2$(18-crown-6)]: Prepared similarly to [VCl_3(18-crown-6)] from anhydrous 18-crown-6 and two mol. equiv. [VCl_3(thf)$_3$]. Pink solid. Yield 45%. $C_{12}H_{24}Cl_6O_6V_2$ (578.9): calcd. C 24.9, H 4.2; found C 24.4, H 4.4. IR (Nujol): $\tilde{\nu}$ = 1298 (m), 1275 (m), 1097 (sh), 1056 (s), 1031 (s), 930 (m), 833 (m), 794 (w), 365 (sh), 341 (s) cm^{-1}.

[VCl_3([12]aneS_4)]: Prepared similarly to [VCl_3(18-crown-6)], using [12]aneS_4. Pink solid. Yield 30%. $C_8H_{16}Cl_3S_4V$ (397.8): calcd. C 24.2, H 4.1; found C 25.1, H 5.3. IR (Nujol): $\tilde{\nu}$ = 1345 (w), 1260 (s), 1090 (s), 1041 (m), 1015 (s), 925 (w), 841 (m), 801 (s), 677 (w), 361 (w), 346 (m) cm^{-1}.

[VCl_3([9]aneS_2O)]: Prepared similarly to [VCl_3(18-crown-6)] using [9]aneS_2O. Pink solid. Yield 52%. $C_6H_{12}Cl_3OS_2V$ (321.6): calcd. C 22.4, H 3.8; found C 22.4, H 3.7. IR (Nujol): $\tilde{\nu}$ = 1300 (w), 1260 (m), 1182 (w), 1096 (s), 1072 (sh), 1051 (m), 1013 (s), 998 (w), 976 (w), 935 (m), 910 (m), 797 (s), 483 (w), 356 (sh), 339 (m) cm^{-1}.

[VCl_3([15]aneS_2O_3)]: [VCl_3(thf)$_3$] (0.21 g, 0.55 mmol) was dissolved in anhydrous CH_2Cl_2 (15 mL) and added to a solution of [15]aneS_2O_3 (0.14 g, 0.55 mmol) in anhydrous CH_2Cl_2 (10 mL), and the purple-pink solution stirred for 1 h. The pink solid which separated on standing was filtered off and dried in vacuo. Yield 0.12 g, 54%. $C_{10}H_{20}Cl_3O_3S_2V\cdot2CH_2Cl_2$ (579.5): calcd. C 24.8, H 4.2; found C 24.6, H 4.9. IR (Nujol): $\tilde{\nu}$ = 1290 (m), 1260 (m), 1208 (w), 1190 (m), 1126 (s), 1116 (s), 1064 (s), 1015 (sh), 917 (m), 905 (m), 811 (s), 796 (sh), 485 (w), 416 (w), 360 (s), 322 (s) cm^{-1}.

[VCl_3([18]aneS_3O_3)]: [VCl_3(thf)$_3$] (0.11 g, 0.29 mmol) was dissolved in anhydrous CH_2Cl_2 (15 mL) and added to a solution of

Table 5. Crystallographic parameters.[a]

Complex	[$CrCl_3(H_2O)$(18-crown-6)]	[$CrCl_3$([15]aneS_5)]	[$VCl_3(H_2O)$(15-crown-5)]$\cdot3/4CH_2Cl_2$
Formula	$C_{12}H_{26}Cl_3CrO_7$	$C_{10}H_{20}Cl_3CrS_5$	$C_{10}H_{22}Cl_3O_6V\cdot0.75(CH_2Cl_2)$
M_r	440.68	458.91	459.26
Crystal system	monoclinic	orthorhombic	trigonal
Space group	$P2_1/c$ (no. 14)	$Pna2_1$ (no. 33)	$P3_221$ (no. 154)
a [Å]	15.663(3)	12.942(3)	12.153(2)
b [Å]	13.0981(16)	8.4682(15)	12.153(2)
c [Å]	19.216(4)	16.040(3)	22.773(3)
α [°]	90	90	90
β [°]	109.352(8)	90	90
γ [°]	90	90	120
U [Å^3]	3719.5(11)	1757.8(6)	2912.9(9)
Z	8	4	6
μ(Mo-K_α) [mm^{-1}]	1.074	1.684	1.150
R_{int}	0.1258	0.0393	0.1990
Total no. reflections	43927	13098	27190
Unique reflections	8505	3972	4408
No. of parameters	428	172	209
R_1 [$I_o > 2\sigma(I_o)$]	0.0580	0.0292	0.0681
R_1 (all data)	0.1402	0.0380	0.1787
wR_2 [$I_o > 2\sigma(I_o)$]	0.1062	0.0537	0.1180
wR_2 (all data)	0.1314	0.0567	0.1490

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

[18]aneS_3O_3 (0.09 g, 0.29 mmol) in anhydrous CH_2Cl_2 (10 mL), and the pale purple-pink solution stirred for 1 h. The solution was concentrated in vacuo to 10 mL, and dry hexane (10 mL) was added dropwise to the vigorously stirred solution. After stirring for 10 min the pale pink solid which had separated was filtered off and dried in vacuo. Yield 0.07 g, 52%. $C_{12}H_{24}Cl_3O_3S_3V$ (469.8): calcd. C 30.7, H 5.2; found C 31.2, H 5.6. IR (Nujol): $\tilde{\nu}$ = 1346 (w), 1300 (m), 1258 (s), 1210 (w), 1100 (s), 1072 (s), 1033 (s), 919 (m), 848 (w), 805 (s), 477 (m), 355 (sh), 343 (s) cm^{-1}.

X-ray Crystallography: Details of the crystallographic data collection and refinement parameters are given in Table 5. Crystals of [$CrCl_3(H_2O)$(18-crown-6)], [$CrCl_3$([15]aneS_5)] and [$VCl_3(H_2O)$(15-crown-5)]·3/4CH_2Cl_2 were obtained by layering CH_2Cl_2 solutions of the complexes with hexane. Data collection used a Nonius Kappa CCD diffractometer (T = 120 K) and with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Structure solution and refinement were routine.[25,26] H atoms bonded to C were introduced in calculated positions (C–H 0.99 Å). H atoms on the water molecules (O13 and O14) were located in [$CrCl_3(H_2O)$(18-crown-6)] from later electron-density maps and introduced into the model and refined using DFIX commands on the four O–H distances [target 0.84(2) Å]. Refinement converged leaving satisfactory H–O–H and H–O–Cr angles. Water H atoms were not identified on O6 in the V compound. The U_{iso} for H atoms was either a common refined parameter or 1.2U_{eq} of the bonded C atom (in [$CrCl_3$([15]aneS_5)] only). The absolute structures of the crystals used for [$VCl_3(H_2O)$(15-crown-5)] and [$CrCl_3$([15]aneS_5)] were established from the Flack parameter.[27] Selected bond lengths and angles are given in Table 1, 2 and 4.

CCDC-607029 (for Cr/O), -607030 (for V), and -607031 (for Cr/S) contain 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.

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