REVIEW

J. Chem. Research (S),
2002, 467–472
J. Chem. Research (M),
2002, 1001–1022

Early transition metal complexes of polydentate and macrocyclic thio- and seleno-ethers

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Recent work on the syntheses, structures and properties of complexes of polydentate and macrocyclic thio- and seleno-ether ligands with Groups 3-6 metals in positive oxidation states (≥3) is described.

Keywords: thioether, selenoether, early transition metal

Introduction

Thio- and seleno-ethers are soft, neutral, moderate σ donor ligands (although both π donor and π acceptor components of the bonding have sometimes been suggested, evidence for either is sparse, and only applies to very specific systems). The majority of their reported complexes are with later transition metals in medium oxidation states or with low valent organometallic or carbonyl compounds across the d-block.[1–5] More recently complexes with p-block metals and metalloids have been described, in many of which the thio- or selenoether forms weak "secondary" bonds to the central element.[6] Early transition metals in positive oxidation states are generally large, hard acceptors which form strong complexes with charged ligands and hard neutral O- or N- donors. Complexes of early transition metals with simple thioethers, usually SR_2, tetrahydrothiophen, or more rarely $RS(CH_2)_2SR$, were first reported many years ago,[1–3] but in most cases their intractable nature and hydrolytic instability, resulted in limited spectroscopic data, and structural data were very rare. In this article we review some relatively recent work (mostly post 1985) on complexes of the Group 3–6 metals in positive oxidation states (≥ 3) with thio- and seleno-ethers. The coverage is not comprehensive, excludes mixed donor ligands and concentrates on acyclic bi- and poly-dentates and macrocycles. No complexes of these metal centres with softer telluroethers have yet been characterised,[5] and the only structurally authenticated examples of a coordinated telluroether function are in complexes of Ti(IV) with dianionic Te-bridged bis(aryloxo) ligands.[7] In addition to their inherent interest, some of these complexes may provide single source precursors for metal-sulfide or metal-selenide films by CVD methods.

Group 3 and the f-block

There are no reports of scandium(III) or yttrium(III) complexes. The first structurally authenticated lanthanide thioether complex is $[La([9]anS_3)I_3(MeCN)_2]$ made from $[LaI_3(MeCN)_4]$ and $[9]aneS_3$ in diethyl ether.[8] The structure determination of the lanthanum complex reveals a distorted square antiprism with La-S = 3.0635(4)–3.1263(4) Å. The corresponding green U(III) complex $[U([9]aneS_3)I_3(MeCN)_2]$ is made similarly from $[UI_3(MeCN)_4]$ and is isostructural but with U-S = 3.0146(9)–3.0779(9) Å.[8] The authors suggest that since the U-S distances are markedly shorter than the corresponding La-S, whereas the corresponding M-I and M-NCMe differ by ca 0.03 Å, there may be a π-acceptor component to the U-S bond.[8] However, examination of the S-C bonds reveals no significant difference between free $[9]aneS_3$ [9] and $[La([9]aneS_3)I_3(MeCN)_2]$, with those in the uranium complex marginally shorter on average. If π-acceptance occurs into the C-S σ^* orbitals, the C-S bonds should lengthen in the U complex. A more likely explanation is that U(III) is softer than La(III) and the shorter U-S bonds reflect a stronger σ interaction. Dark green $[U(BH_3Me)_4(MeSCH_2CH_2SMe)]$ can be described as either 14-coordinate U, or if the tridentate H_3BMe groups are conceptually treated as monatomic ligands, distorted octahedral.[10] Competitive NMR experiments show that the affinity of the $U(BH_3Me)_4$ fragment for neutral ligands increases $MeOCH_2CH_2OMe < MeSCH_2CH_2SMe < Me_2NCH_2CH_2NMe_2 < Me_2PCH_2CH_2PMe_2$.[10]

Group 4

Titanium(IV) complexes of both thio- and seleno-ethers are well established, but much less is known about zirconium(IV) or hafnium(IV) complexes and complexes of lower oxidation states are unexplored. All three metal(IV) centres form $[MX_4L_2]$ (M = Ti, Zr or Hf; X = Cl or Br, L = Me_2S, Me_2Se, Et_2S, Et_2Se, $(CH_2)_4S$ *etc*) by direct reaction of the appropriate MX_4 with excess L in CH_2Cl_2, toluene or alkanes.[11–15] The products are very moisture sensitive and appear to be exclusively *cis* isomers, in contrast to the Sn(IV) analogues for which both *cis* and *trans* isomers are known.[6] This is rationalised by invoking $X(p\pi) \rightarrow M(d\pi)$ π-donation which is maximised in the *cis* isomer (and is not possible in tin). The structures of various examples including $[TiCl_4\{(CH_2)_4S\}_2]$, $[TiCl_4(R_2Se)_2]$ (R = Me or Et) and $[ZrCl_4(Me_2S)_2]$ show they are distorted (*cis*) octahedral monomers with <X-M-X all greater than 90°, and with $M\text{-}X_{transX} > M\text{–}X_{transL}$ consistent with a *trans* influence X > S,Se, the reverse of that found with late transition metals. The reaction of $TiCl_4$ with $MeE(CH_2)_nEMe$ (E = S or Se, n = 2 or 3), $PhE(CH_2)_2EPh$ and $o\text{-}C_6H_4(EMe)_2$) in n-hexane result in yellow or red $[TiCl_4(L\text{-}L)]$ irrespective of the Ti:L-L ratio used.[16] Similar red $[TiBr_4(L\text{-}L)]$ and two rare examples of TiI_4 complexes, the red-purple $[TiI_4(L'\text{-}L')]$ (L′-L′ = $MeSe(CH_2)_2SeMe$ or $o\text{-}C_6H_4(SeMe)_2$) were made from CH_2Cl_2 solution. X-ray structures of $[TiCl_4\{MeE(CH_2)_3EMe\}]$, $[TiCl_4\{MeS(CH_2)_2SMe\}]$ and $[TiCl_4\{o\text{-}C_6H_4(SeMe)_2\}]$ revealed distorted *cis* octahedral molecules. Multinuclear VTNMR studies showed that in solution at ambient temperatures the chloride complexes are undergoing rapid pyramidal inversion at the Group 16 atoms, whilst for the bromides and iodides, ligand dissociation is also present. Whilst inversion and dissociation slow on cooling for the complexes with X = Cl or Br, even at 200K the iodides are still undergoing rapid ligand dissociation. The complexes are very unstable to moisture and a dinuclear product of trace hydrolysis, $[Cl_3Ti\{MeS(CH_2)_2SMe\}]_2(\mu\text{-}O)$ was also structurally characterised.[16] In contrast to some diphosphines or diarsines[17] there was no evidence that dithio- or diseleno-ethers can form eight-coordinate $[TiX_4(L\text{–}L)_2]$.

However, the larger $ZrCl_4$ or $HfCl_4$ form both 1:1 and 1:2 complexes with dithioethers and diselenoethers.[14,18] It is difficult to obtain pure samples of the complexes directly from the

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* To receive any correspondence.

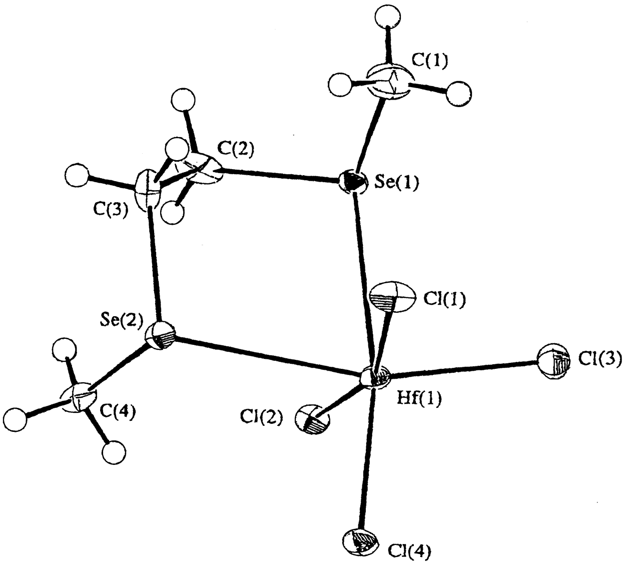

Fig. 1 The structure of [$HfCl_4\{MeSe(CH_2)_2SeMe\}$] from ref. 14 by permission of the Royal Society of Chemistry.

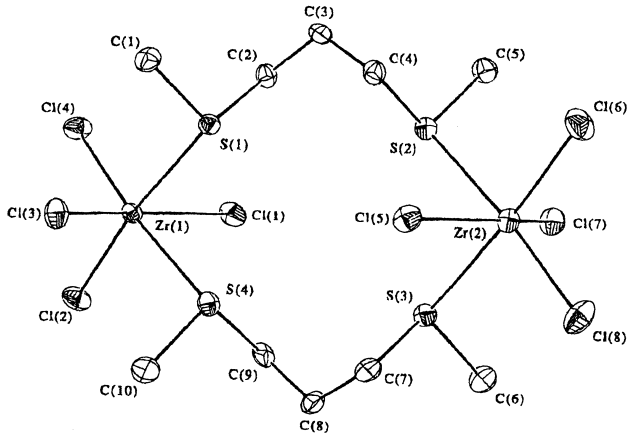

Fig. 2 The structure of [$ZrCl_4\{MeS(CH_2)_3SMe\}$] from ref. 14 by permission of the Royal Society of Chemistry.

polymeric MCl_4, and displacement of hard donor ligands such as the tetrahydrofuran in [$ZrX_4(thf)_2$] is unsuccessful. A better route is reaction of [$MCl_4(Me_2S)_2$] with L–L in CH_2Cl_2. If a 1:1 ratio of MCl_4: L–L (L–L = $MeE(CH_2)_nEMe$, E = S or Se, n = 2 or 3) is used the products were white or cream [MCl_4(L–L)] which are very poorly soluble in non-coordinating solvents, decomposed by O or N-donor solvents, and readily hydrolysed in air.[14] The X-ray structure of [$HfCl_4\{MeSe(CH_2)_2SeMe\}$] reveals the expected distorted octahedral monomer (Fig. 1), but [$ZrCl_4\{MeS(CH_2)_3SMe\}$] is dimeric with bridging dithioethers (Fig. 2). The data also reveal d[Zr-S(Se)] are markedly longer than d(Zr-Cl), consistent with weak binding of the Group 16 ligand (also observed in the Ti complexes). The formation of the dinuclear structure with $MeS(CH_2)_3SMe$ may reflect the weaker tendency to chelation in the 6-membered ring, but may also be (poor) solubility driven. In contrast to the results with TiX_4, the reaction of [$MCl_4(SMe)_2$] (M = Zr or Hf) with three equivalents of $MeE(CH_2)_2EMe$ (E = S or Se) in CH_2Cl_2 gave [$MCl_4\{MeE(CH_2)_2EMe\}_2$] and structures of [$MCl_4\{MeS(CH_2)_2SMe\}_2$] show 8-coordinate flattened dodecahedral molecules (Fig. 3).[14] The d(M-Cl) and d(M-S) are both *ca* 0.1 Å longer in the 8-coordinate complexes compared with the 6-coordinate analogues, which we attribute to steric crowding. The 8-coordinate complexes are also generally too insoluble for NMR studies, but the 6- and 8- coordinate compounds can be distinguished in the far IR spectra by the ν(M-Cl) frequencies which are typically 50 cm^{-1} lower in the latter.

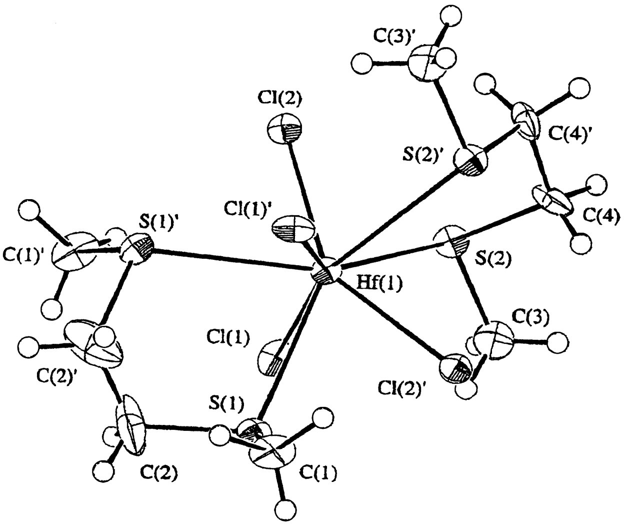

Fig. 3 The structure of [$HfCl_4\{MeS(CH_2)_2SMe\}_2$] from ref. 14 by permission of the Royal Society of Chemistry.

The reactions of TiX_4 (X = Cl or Br) with $MeC(CH_2EMe)_3$ (E = S or Se) produced poorly soluble and very moisture sensitive [$TiX_4\{MeC(CH_2EMe)_3\}$].[19] Ambient temperature ^1H and $^{13}C\{^1H\}$ NMR studies in anhydrous CH_2Cl_2 show simple spectra due to fast dynamic processes, but on cooling to 190K the spectra show the presence of diastereoisomers resulting from bidentate coordinated $MeC(CH_2EMe)_3$ and hence 6-coordinated titanium. The structure of the analogous *cis* octahedral [$TiBr_4\{MeC(CH_2AsMe_2)_3\}$] has been confirmed by an X-ray study.[17] Insoluble [$ZrCl_4\{MeC(CH_2EMe)_3\}$] have been obtained[19] but the structures are unknown, although 7-coordination for the larger metal centre is a possibility.

The yellow *fac* octahedral imido-complex [$TiCl_2(NBu^t)$-$\{[9]aneS_3\}$] is made from [$TiCl_2(NBu^t)(py)_3$] and 1,4,7-trithiacyclononane,[20] and comparison of the d(Ti-Cl) bond lengths with those in the [9]aneN_3 or Me_3[9]aneN_3 analogues confirms the low *trans* influence of the thioether donors. The reaction of [9]aneS_3 or [10]aneS_3 with TiX_4 (X = Cl, Br or I) formed [$TiX_4\{[n]aneS_3\}$] of which only the complex [$TiCl_4\{[9]aneS_3\}$] was soluble enough for NMR studies.[21,22] These revealed a complex second order pattern suggesting 7-coordination with tridentate thiamacrocycle, but as yet attempts to grow cystals for an X-ray study have failed.[21] The white [$ZrCl_4\{[n]aneS_3\}$] (n = 9, 10) are formed from [$ZrCl_4(SMe_2)_2$] and the ligand in CH_2Cl_2 and once isolated are insoluble in non-donor solvents.[21] However crystals of [$ZrCl_4\{[9]aneS_3\}$] were obtained by allowing CH_2Cl_2 solutions of the reactants to diffuse together, and the structure (Fig. 4) reveals 7-coordinate zirconium.[14]

Both $TiCl_4$ in $CHCl_3$ (slowly) and $ZrCl_4$ in CH_2Cl_2 (rapidly) cleave $PhSe(CH_2)_2SePh$ with formation of PhSeSePh.[14,16]

Lower oxidation state complexes are little known but include the purple air and moisture sensitive [$TiCl_3\{[9]aneS_3\}$],[22] prepared from [$TiCl_3(MeCN)_3$] and [9]aneS_3 in MeCN.

Group 5

Despite the larger number of accessible oxidation states, the Group 16 ligand chemistry of these metals is less developed than that of Group 4. The deep blue V(IV) complex

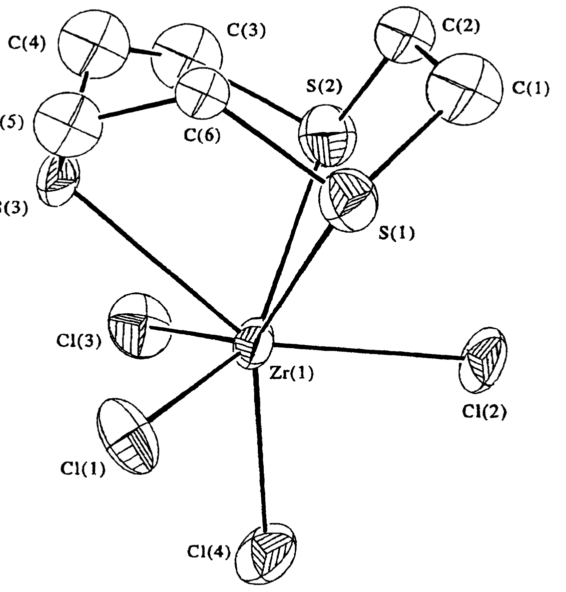

Fig. 4 The structure of [$ZrCl_4${[9]aneS_3}] from ref. 14 by permission of the Royal Society of Chemistry.

[$VOCl_2${[9]aneS_3}], originally obtained (presumably by adventitious air-oxidation) from VCl_3 and [9]aneS_3 in MeCN,[23] can be made directly from [$VOCl_2(MeCN)_2$] or [$VO(acac)_2$]/Me_3SiCl and [9]aneS_3.[24,25] The structure of [$VOCl_2${[9]aneS_3}] reveals a distorted 6-coordinate vanadium centre with a short d(V-O) of 1.579(4) Å and long d(V–S) = 2.634(5) (*trans* O), 2.470(5) Å (*trans* Cl).[23] The trithiacrown 2,5,8-trithia[9]-*o*-benzophane (ttob) forms a similar complex.[25] The reaction of [$VX_3(thf)_3$] (X = Cl, Br or I) with [9]aneS_3, [10]aneS_3, ttob or $MeC(CH_2SMe)_3$ produced the [VX_3(trithioether)] complexes as pink (Cl), orange (Br) or brown (I), air- and moisture sensitive solids. The X-ray structure of [VCl_3{[9]aneS_3}] and vanadium K-edge EXAFS data on the others are consistent with strong V–Cl (*ca* 2.3 Å) and weak V-S (*ca* 2.5 Å) bonds.[24,25] Analysis of the UV-visible spectra showed that thioethers produce relatively weak ligand fields on V(III). Attempts to reduce [VCl_3{[9]aneS_3}] were unsuccessful but the [9]aneS_3 is readily displaced by pyridine. Larger thiacrowns produce [VCl_3{[16]aneS_4}] in which the ligand may be tridentate and [{VCl_3}$_2${[18]aneS_6}] probably containing a bis(tridentate) bonding mode.[25] Some selenoether analogues have been obtained,[26] but are less stable. Blue [VI_2(thf)(L_3)] (L_3 = [9]aneS_3, ttob) were obtained from [$VI_2(thf)_4$] and the ligands, and the structure of the former shows the expected 6-coordination at V(II) (Fig. 5).[25] The mean d(V–S) distances differ little between the three complexes [$VOCl_2${[9]aneS_3}], [VCl_3{[9]aneS_3}] and [VI_2(thf){[9]aneS_3}] despite the different oxidation states, although it should be recognised that the identities of the co-ligands differ.

The reaction of $NbCl_5$ with [14]aneS_4 in benzene produced [$(NbCl_5)_2${[14]aneS_4}] which has the structure shown in Fig. 6.[27,28] Related complexes [$(NbCl_5)_2L_4$] (L_4 = [16]aneS_4, [20]aneS_4), [$(NbCl_5)_4L_4$] (L_4 = [14]aneS_4, [16]aneS_4, [20]aneS_4), [$(NbCl_5)_x${[24]aneS_6}] (x = 3, 6) and [$(NbCl_5)_4${[28]aneS_8}] have been made similarly and characterised by analysis. It is assumed that each $NbCl_5$ group coordinates to a single sulfur atom. Mononuclear, probably 8-coordinate Nb(IV) complexes, [NbX_4{$MeS(CH_2)_2SMe$}$_2$] (X = Cl, Br or I) were reported many years ago,[18] but need structural authentication, and it is possible than 6-coordinate analogues could be prepared.

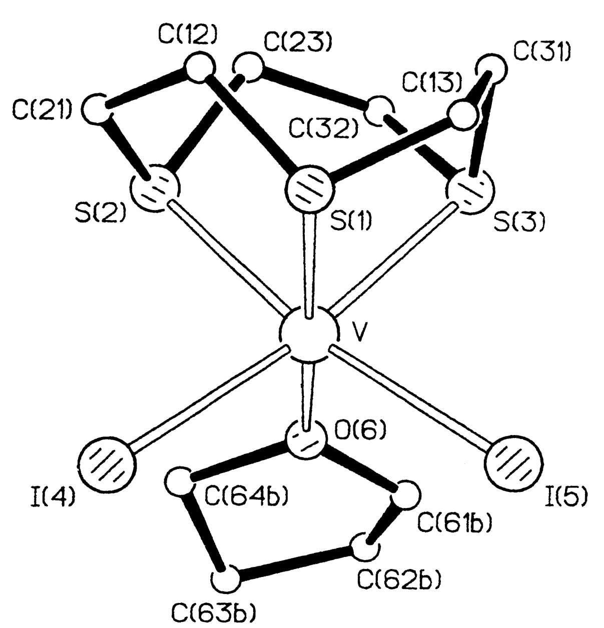

Fig. 5 The structure of [VI_2(thf){[9]aneS_3}] from ref. 25 by permission of the Royal Society of Chemistry.

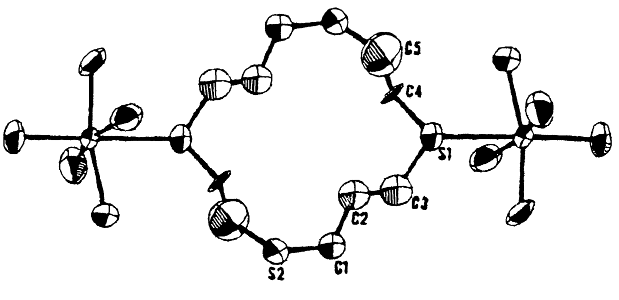

Fig. 6 The structure of [$(NbCl_5)_2${[14]aneS_4}] from ref. 28 by permission of the American Chemical Society.

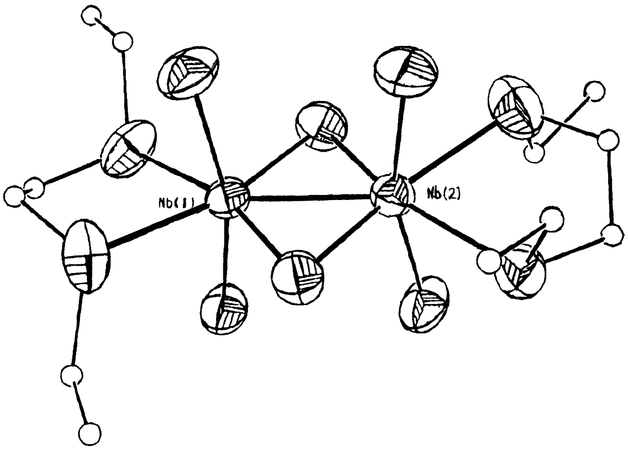

Fig. 7 The structure of [Nb_2Cl_6{$EtS(CH_2)_2SEt$}$_2$] from ref. 29 by permission of the American Chemical Society.

Metal-metal bonded chloride-bridged dimers of both Nb(III)/Ta(III) and Nb(IV)/Ta(IV) with mono- and diphosphine ligands are well characterised, but the systems with sulfur ligands are more complicated due to the ability of these metals to extract sulfur from the ligands. Since X-ray crystallography cannot distinguish S^{2-} from Cl^- bridges some ambiguity surrounds several of the reports.[29] Limiting the discussion to dithioethers, reported complexes include $[Nb_2Cl_6(L–L)_2]$ and $[Ta_2Cl_6(L–L)_2]$ (L–L = $MeS(CH_2)_2SMe$, $EtS(CH_2)_2SEt$).[30,31] However, whilst dark red $[Nb_2Cl_6\{EtS(CH_2)_2SEt\}_2]$ has been confirmed as an Nb(III)-Nb(III) dimer ($\sigma^2\pi^2$) (Fig. 7) with a metal-metal bond distance of 2.682(3) Å, in excellent agreement with diphosphine analogues,[29] the previously reported[31] green "$[Ta_2Cl_6\{EtS(CH_2)_2SEt\}_2]$" with d(Ta-Ta) = 2.846(5) Å (and very similar "$[M_2Cl_6(SMe_2)_4]$" (M = Nb or Ta)) seem likely to be the sulfur bridged $[Ta_2S_2Cl_4\{EtS(CH_2)_2SEt\}_2]$ and thus a Ta(IV)-Ta(IV) complex (σ^2).[29] It is significant that a minor (5%) green product was noted in the original synthesis[31] of red $[Nb_2Cl_6\{EtS(CH_2)_2SEt\}_2]$, and the products formed in these systems may contain either μ-S or μ-Cl linkages and the species isolated will depend on the precise reaction conditions. Di- or poly-selenoether complexes of Nb or Ta are unknown.

Group 6

There is an extensive range of thioether, selenoether and telluroether substituted carbonyl and carbonyl halide complexes of the Group 6 metals, which fall outside this article.[2,5] For chromium the remaining complexes are of Cr(III), with the exception of one Cr(V) compound. Treatment of $[CrCl_3(NBu^t)\{MeO(CH_2)_2OMe\}]$ with [9]aneS_3 and $AgCF_3SO_3$ in CH_2Cl_2 produced green $[CrCl_2(NBu^t)\{[9]aneS_3\}]CF_3SO_3$ which has μ = 1.7 B.M. and an isotropic ESR signal at g = 1.990, both consistent with Cr(V).[32] The structure (Fig. 8) is the expected *fac* octahedron with relatively long Cr-S bonds (2.396(av) *trans* Cl, 2.500(1) Å *trans* N). Chromium(III) complexes of acyclic bi- and poly-dentates include[33,34] $[CrX_3L^3]$ (X = Cl, Br or I; L^3 = $MeC(CH_2SMe)_3$, $S(CH_2CH_2CH_2SMe)_2$), $[Cr\{S(CH_2CH_2CH_2SMe)_2\}_2][BF_4]_3$, and $[Cr(MeSCH = CHSMe)_3][BF_4]_3$. All are moisture sensitive solids, poorly soluble in non-coordinating solvents. Triselenoether complexes $[CrX_3L'^3]$ (X = Cl or Br, L'^3 = $MeC(CH_2SeMe)_3$, $Se(CH_2CH_2CH_2\ SeMe)_2$) are prepared from $[CrX_3(thf)_3]$ and the ligands under rigorously anhydrous conditions.[35]

There are a number of thiacrown complexes, mostly of type $[CrX_3(L)]$ (X = Cl, sometimes Br; L = [9]aneS_3, [10]aneS_3, [11]aneS_3, [18]aneS_6, [20]aneS_6) which are 6-coordinate with X_3S_3 donor sets.[36–38] Also reported are $[\{CrX_3\}_2\{[18]aneS_6\}]$,[36] and $[Cr(CF_3SO_3)_3\{[9]aneS_3\}]$.[37] The best route is reaction of $[CrX_3(thf)_3]$ with the thiacrown in a non-coordinating solvent, the volatile thf is easily removed under reduced pressure. In some cases $CrX_3.6H_2O$ has been used,[38] but this route fails to give isolable products with many thiacrowns, and a starting material containing a hard strong donor (H_2O) is a poor choice when synthesising soft donor complexes of a hard metal centre. The complexes are poorly soluble in non-coordinating solvents and hydrolyse easily. The structure of $[CrCl_3\{[18]aneS_6\}]$ reveals a *fac* octahedral geometry with [18]aneS_6 bonded through three neighbouring sulfurs,[38] and Cr K-edge EXAFS data have been reported for other examples.[36] If the reactions of $[CrX_3(thf)_3]$ (X = Cl, Br sometimes I) and thiacrowns are conducted in the presence of a halide abstractor such as $TlPF_6$ or $AgPF_6$, the products are $[CrX_2(L)]PF_6$ (L = [14]aneS_4, [16]aneS_4),[36,39] and there are analogues with [16]aneSe_4.[35] The X-ray structures of $[CrX_2\{[14]aneS_4\}]PF_6$ (X = Cl or Br)[36,39] show *cis* octahedral cations (Fig. 9) and structural data for these and also the [16]aneSe_4 complexes have been obtained via Cr K-edge EXAFS.[35,36] The absence of splittings of the d-d spectral bands of the [16]aneS_4 and [16]aneSe_4 complexes suggest these are also *cis* isomers. Analysis of the UV-visible spectra of the solid chromium(III) complexes show that S or Se ligands exert relatively weak ligand fields in these complexes, a result of the hard/soft acceptor/donor combination.[35,36] Solution spectra of some of the complexes in dmso have given similar values but these results should be viewed with some reserve since partial or total displacement of the thiacrown by the strong donor solvent cannot be ruled out. An explosive pink solid formulated as $[Cr\{[9]aneS_3\}_2](ClO_4)_3$ has been reported[37] to form on heating solid [9]aneS_3 with $[Cr(H_2O)_6](ClO_4)_3$,[37] but lacks detailed characterisation.

Molybdenum complexes of polydentate and macrocyclic thioethers have been reported in oxidation states III–VI based

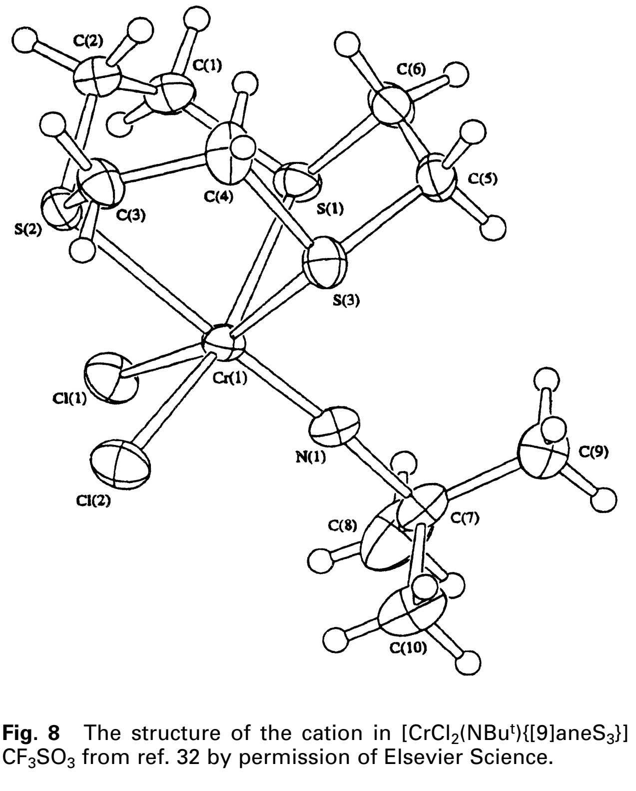

Fig. 8 The structure of the cation in $[CrCl_2(NBu^t)\{[9]aneS_3\}]CF_3SO_3$ from ref. 32 by permission of Elsevier Science.

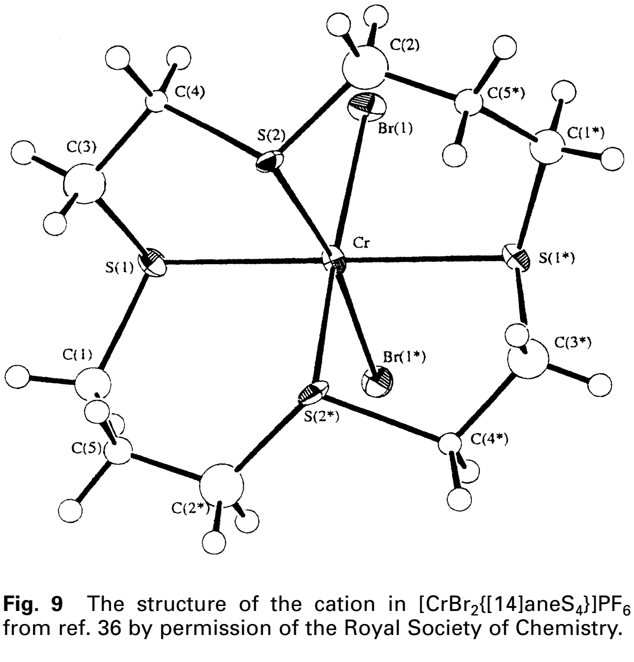

Fig. 9 The structure of the cation in $[CrBr_2\{[14]aneS_4\}]PF_6$ from ref. 36 by permission of the Royal Society of Chemistry.

respectively upon $MoCl_3$, $MoCl_4$, $MoOCl_3$ and MoO_2Cl_2,[40–42] there are some tungsten(V) analogues based upon $WOCl_3$,[42] and a few selenoether compounds.[43] In these earlier studies the characterisation of the complexes relied upon analysis and limited spectroscopic data, and the structures proposed, especially those with coordination numbers >6 or as ligand bridged oligomers, are uncertain. Authentication of these by X-ray crystallography is required to place the area on a firm basis.

Red-brown $[MoCl_3\{[n]aneS_3\}]$ (n = 9 or 10)[44,45] are made from $[MoCl_3(thf)_3]$ and $[n]aneS_3$ in CH_2Cl_2. Orange fac-$[MoCl_3L]$ (L = $Me_8[16]aneS_4$) was obtained from $[\{MoCl_2(CO)_4\}_2]$ and $Me_8[16]aneS_4$ apparently via a disproportionation (Mo(III) and Mo(0)) reaction.[46] The Mo(0)-$Me_8[16]aneS_4$ system was studied in considerable detail by Yoshida and co-workers in connection with dinitrogen ligation. The ligand also supports *trans*-$[MoCl_2\{Me_8[16]aneS_4\}]^{0,+,2+}$ which are related by electrochemically reversible one electron redox couples.[47] The X-ray structures of *trans*-$[MoBr_2\{Me_8[16]aneS_4\}]$ (d(Mo-S) = 2.436(2), d(Mo-Br) = 2.582(1), 2.571(1) Å) and *trans*-$[MoCl_2\{Me_8[16]aneS_4\}]BF_4$ (d(Mo-S) = 2.502(5), d(Mo-Br) = 2.550(1) Å) show that increasing the oxidation state results in shortening of the Mo-Br and lengthening of the Mo-S bonds.[47] The macrocycle conformation differs in the two structures being the "all-up" form in the Mo(II) and the "up-up-down-down" in the Mo(III).

The dimolybdenum(III) dimer $[Mo_2Cl_4(\mu\text{-}SEt)_2\{EtS(CH_2)_2SEt\}_2]$ was originally identified as a minor product of the reaction of $[Mo_2Cl_8]^{4-}$ and $EtS(CH_2)_2SEt$ in methanol, the μ-SEt groups coming from fragmentation of the 3,6-dithiaoctane.[48] Better yields are obtained from $[NH_4]_5[Mo_2Cl_9]$, 3,6-dithiaoctane and Et_2S_2,[48,49] and related reactions with $PrS(CH_2)_2SPr$ and Pr_2S_2 have been reported.[50] The structure of $[Mo_2Cl_4(\mu\text{-}SEt)_2\{EtS(CH_2)_2SEt\}_2]$ (Fig. 10) shows an edge-linked bioctahedron with d(Mo-Mo) = 2.682(1) Å, and with markedly shorter Mo-μ-SR (2.400(1), 2.403(1) Å) than $Mo\text{-}SR_2$ (2.579(1) Å) bonds.[49] The magnetic properties and UV-visible spectra of these d^3-d^3 systems have been interpreted in terms of a bond order of approximately two ($\sigma^2\pi^2$) with the two other electrons in closely spaced δ,δ^* orbitals.[49,50]

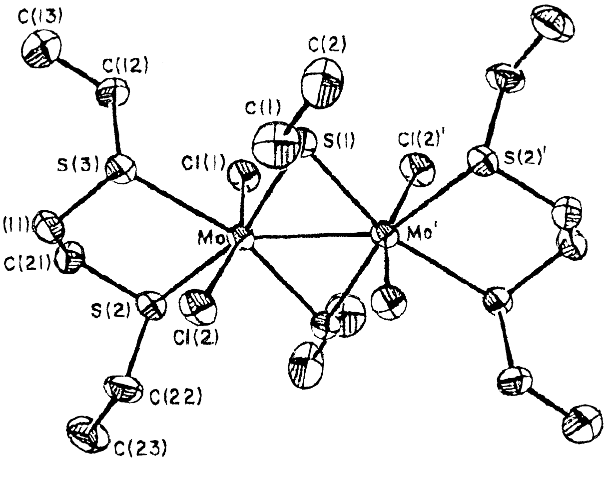

Fig. 10 The structure of $[Mo_2Cl_4(\mu\text{-}SEt)_2\{EtS(CH_2)_2SEt\}_2]$ from ref. 49 by permission of the American Chemical Society.

Conclusions

This short review has described recent work with selected thio- and selenoether polydentates containing Group 3-6 metals in medium or high oxidation states. One result of such a compilation is to identify areas which warrant further work – among many possibilities we suggest the following:

a) the recent demonstration[8] that La and U(III) form complexes with $[9]aneS_3$ should open up a new area in Group III and f-block chemistry;

b) the structural authentication of 6-, 7- and 8-coordination in Zr and Hf thio- and seleno-ethers[14] should prompt further studies of their reaction chemistry *e.g.* with ligands which promote better solubility in non-polar solvents;

c) the Group 5 chemistry of these ligands remains poorly explored and mononuclear M(V), M(IV) and M(III) complexes of Nb and Ta merit detailed studies;

d) although telluroethers are both softer and weaker donors towards hard metals than the S or Se analogues and are stronger reducing agents,[5] it is likely that some early transition metal complexes will be obtained by suitable synthetic strategies;

e) fragmentation of ligands in the presence of these reactive metals may also be relatively common – the C-Se cleavage in $PhSe(CH_2)_2SePh$ by Ti(IV) and Zr(IV),[14] and the abstraction of S^{2-} from dithioethers in some Nb and Ta systems,[29] or SR^- in some Mo dimers are likely to have many analogues. Careful spectroscopic and structural work will be needed to elucidate these reactions;

f) finally, as noted in several places, reinvestigation of many compounds reported pre-1980, especially by X-ray crystallographic methods would be very valuable. Recent advances in X-ray crystallography, especially the ability to handle much smaller crystals and fast data collection on unstable materials routinely at low temperatures,(obviously supplemented by speed of data solution) means that structural work which would have been extremely difficult or impossible 20–30 years ago, is now routine. Whilst such work will no doubt confirm the structures of many compounds are as originally proposed especially for those of CN = 6 (in the process, good quality data on M-S(Se) bonds which should inform our understanding of such bonds will be obtained), structures of compounds of the 4d and 5d elements with CN's of >6 are not readily established spectroscopically and detailed geometries can only come from X-ray crystallography.

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