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Synthesis, properties and structural features of molybdenum(v) oxide trichloride complexes with neutral chalcogenoether ligands†

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Complexes of oxotrichloromolybdenum(v) with neutral group 16 donor ligands, $[MoOCl_3(L{-}L)]$ (L–L = RS$(CH_2)_2$SR, R = ^{i}Pr, Ph; MeS$(CH_2)_3$SMe; MeSe$(CH_2)_2$SeMe; MeSe$(CH_2)_3$SeMe), $[\{MoOCl_2(EMe_2)\}_2(\mu\text{-}Cl)_2]$ (E = S, Se, Te), $[(MoOCl_3)_2\{o\text{-}C_6H_4(EMe)_2\}]_n$ (E = Se or Te) and $[(MoOCl_3)_2\{MeTe(CH_2)_3TeMe\}]_n$, have been obtained by reaction of the ligands with $[MoOCl_3(thf)_2]$ or $MoOCl_3$ in either CH_2Cl_2 or toluene, and characterised by microanalysis, IR and UV-visible spectroscopy and magnetic measurements. The telluroethers are the first examples containing Mo in a positive oxidation state. X-ray crystal structures are reported for the six-coordinate *fac*-$[MoOCl_3\{MeS(CH_2)_3SMe\}]$, *mer*-$[MoOCl_3\{^iPrS(CH_2)_2S^iPr\}]$ and *mer*-$[MoOCl_3\{MeSe(CH_2)_2SeMe\}]$, as well as the six-coordinate chloride-bridged dimers, $[\{MoOCl_2(SMe_2)\}_2(\mu\text{-}Cl)_2]$ and $[\{MoOCl_2(SeMe_2)\}_2(\mu\text{-}Cl)_2]$. The structure of the mixed-valence decomposition product, $[Mo^{IV}Cl\{o\text{-}C_6H_4(TeMe)_2\}_2(\mu\text{-}O)Mo^{V}OCl_4]$, was also determined. In toluene solution $MoOCl_4$ is reduced by MeS$(CH_2)_3$SMe to produce the Mo(v) complex, $[MoOCl_3\{MeS(CH_2)_3SMe\}]$. Crystal structures of the previously unknown diphosphine analogue, $[MoOCl_3\{Me_2P(CH_2)_2PMe_2\}]$, and the mixed-valence derivative $[Mo^{IV}Cl\{Me_2P(CH_2)_2PMe_2\}_2(\mu\text{-}O)Mo^{V}OCl_4]$ are also reported for comparison and help to clarify earlier contradictory literature reports. In contrast to the dimeric EMe_2 complexes, $[\{MoOCl_2(EMe_2)\}_2(\mu\text{-}Cl)_2]$, PMe_3 forms the monomeric complex, *fac*-$[MoOCl_3(PMe_3)_2]$.

Introduction

The coordination chemistry of high oxidation state molybdenum halides and oxide halides was first explored in some detail in the 1970's, with the emphasis on neutral N- and O-donor ligands[1–4] and with much of the impetus coming from modelling of the metal sites in molybdenum enzymes and applications in catalysis.[4–6] Interest in high oxidation molybdenum complexes bearing sulfur donor ligands stems in part from the presence of Mo–S coordination in the molybdenum-containing enzymes, nitrate reductase, sulfite oxidase and Fe–Mo nitrogenases which involve (anionic) cysteine or sulfide ligands.[4–6] The chemistry with neutral P- and As-donor ligands with Mo(v) has also been investigated,[7–11] but sulfur-based ligands were mostly represented by charged thiolate and dithiocarbamate ligands.[2–4] More recent work has reported a series of extremely moisture sensitive Mo(vi) complexes $[MoO_2X_2(dithioether)]$ (X = Cl or Br; dithioether = RS$(CH_2)_2$SR, R = Me, Et, ^{i}Pr), which have distorted octahedral structures with the sulfur donor atoms *trans* to Mo=O;[12,13] there are also some thia-macrocyclic analogues.[14,15] Complexes of the type $[MoOCl_3(dithioether)]$ were briefly described in the 1970's, characterised only by microanalysis and IR spectroscopy, but the structures and isomer(s) present were not established.[15,16] There is a single preliminary report of a selenoether complex of $MoOCl_3$,[17] but no known telluroether complexes.

We have recently examined the complexes of $WOCl_4$, $WOCl_3$, $WSCl_4$ and $WSCl_3$ with mono- and di-thio- and -seleno-ethers, and found that W(vi) or W(v) complexes could be isolated depending upon the reaction conditions. We also showed that selected dithioether complexes, for example $[(WSCl_4)_2(\mu\text{-}^iPrSCH_2CH_2S^iPr)]$, can function as single source LPCVD (low pressure chemical vapour deposition) reagents for the growth of thin films of WS_2, an important semiconducting material.[18] In contrast, very little data on the molybdenum chalcogenide halides or their coordination complexes exists.[19] The crystal structures of two forms of $MoSCl_3$ obtained from crystals grown at high temperature found that both contain

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†Electronic supplementary information (ESI) available: Crystallographic parameters (Table S1), IR and UV/visible spectra for the new complexes. CCDC 2050667: $[\{MoOCl_2(SeMe_2)\}(\mu\text{-}Cl)_2]$, 2050668: $[MoOCl_3(Me_2P(CH_2)_2PMe_2)]$, 2050669: $[MoOCl_3(PhS(CH_2)_2SPh)]$, 2050670: $[MoOCl_3(MeSe(CH_2)_2SeMe)]$, 2050671: $[MoOCl_3(^iPrS(CH_2)_2S^iPr)]$, 2050672: $[\{MoOCl_2(SMe_2)\}(\mu\text{-}Cl)_2]$, 2050673: $[MoCl\{Me_2P(CH_2)_2PMe_2\}_2(\mu\text{-}O)(MoOCl_4)]$, 2050674: $[MoOCl_3(MeS(CH_2)_3SMe)]$ 2050891: $[MoCl\{o\text{-}C_6H_4(TeMe)_2\}_2(\mu\text{-}O)MoOCl_4]\cdot CH_2Cl_2$. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1dt00038a

Mo(IV) as Mo_2 units and disulfide groups, and not Mo(V).[20] It is unclear if $MoSCl_3$ prepared at low temperatures from $MoCl_5$ and $S(SiMe_3)_2$ or Sb_2S_3 contains Mo(V),[21,22] while $MoSCl_4$ is unknown.[19]

In order to allow comparisons with the $WOCl_4$, $WOCl_3$, $WSCl_4$ and $WSCl_3$ chemistry, we have examined the chemistry of $MoOCl_3$ with neutral chalcogenoethers and report here complexes of mono- and bi-dentate thio-, seleno- and telluroethers. Data on diphosphine analogues, which clarifies some of the (inconsistent) earlier studies,[7–9] is also presented.

Results and discussion

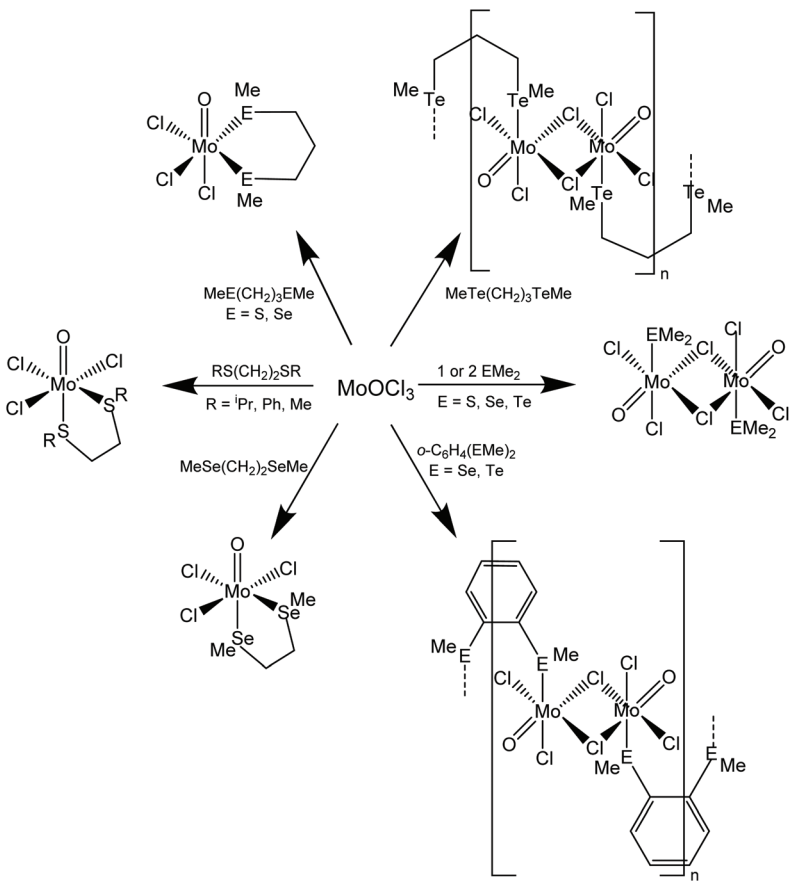
Scheme 1 shows the range of chalcogenoether complexes of Mo(V) prepared in this study and the different structure types observed.

Dithio- and diseleno-ether complexes

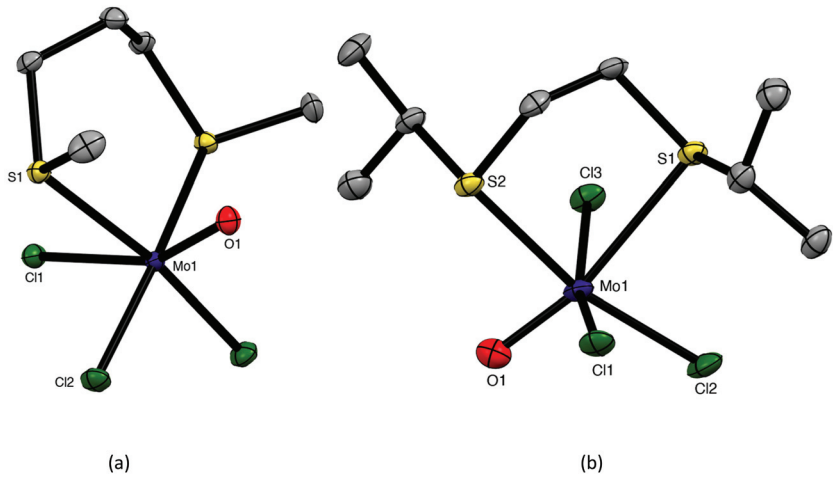
The reaction of $[MoOCl_3(thf)_2]$ with $MeS(CH_2)_3SMe$ or $^iPrS(CH_2)_2S^iPr$ in dry CH_2Cl_2 produced moisture sensitive. green $[MoOCl_3(dithioether)]$ complexes. Structures of both species were determined and revealed that $[MoOCl_3\{MeS(CH_2)_3SMe\}]$ (six-membered chelate ring) was the *fac* isomer, whilst $[MoOCl_3\{^iPrS(CH_2)_2S^iPr\}]$ (five-membered chelate ring) was the *mer*-isomer (Fig. 1). The reason for the different isomers with the five- and six-membered rings is uncertain, although the difference in the S–Mo–S chelate angles of ~20° is notable. The behaviour replicates that found with the tungsten(V) analogues, *fac*-$[WOCl_3\{MeS(CH_2)_3SMe\}]$ and *mer*-$[WOCl_3\{MeS(CH_2)_2SMe\}]$.[18] The bond lengths within the two structures show the expected short Mo=O of ~1.67 Å and that the Mo–Cl and Mo–S *trans* to Mo=O are longer than the other bonds of each type, indicating the high *trans*-influence of the Mo=O bond.

The reaction of $MoOCl_4$ with $MeS(CH_2)_3SMe$ in dry toluene gave a green product with an identical IR spectrum to that of *mer*-$[MoOCl_3\{MeS(CH_2)_3SMe\}]$ and the X-ray structure determination of a crystal obtained from the $MoOCl_4$ synthesis route (Method 2) indeed confirmed it to be the Mo(V) complex. The structural data were identical to that in Table S1,† and hence are not reported, but confirm that thioether ligands reduce $MoOCl_4$ to $MoOCl_3$ complexes, similar to the behaviour reported with some O- and N-donor ligands.[23]

The weaker σ-donor $PhS(CH_2)_2SPh$ failed to displace the thf from $[MoOCl_3(thf)_2]$, but it reacted with a suspension of $MoOCl_3$ in CH_2Cl_2 to form brown $[MoOCl_3\{PhS(CH_2)_2SPh\}]$. The crystal structure of this complex showed it to be the *mer*-



Scheme 1 Methods for the synthesis of the Mo(V) chalcogenoether complexes obtained from $MoOCl_3$. Note that for some of the alkyl-substituted dithioether and diselenoether complexes $[MoOCl_3(thf)_2]$ was used as the Mo(V) source – see discussion below and Experimental.



(a) (b)

Fig. 1 Crystal structures of *fac*-[$MoOCl_3${$MeS(CH_2)_3SMe$}] (a) and *mer*-[$MoOCl_3${$^iPrS(CH_2)_2S^iPr$}] (b) showing the atom numbering scheme. Ellipsoids are shown at 50% probability, hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): (a) Mo1–Cl1 = 2.4540(2), Mo1–Cl2 = 2.3451(2), Mo1–Cl3 = 2.3451(4), Mo1–O1 = 1.674(1), Mo1–S1 = 2.5388(3), Cl1–Mo1–Cl2 = 94.52(2), Cl2–Mo1–Cl3 = 92.55(3), Cl2–Mo1–O1 = 101.87(4), Cl3–Mo1–O1 = 101.87(4), S1–Mo1–S1 = 97.95(2); (b) Mo1–Cl1 = 2.3578(8), Mo1–Cl2 = 2.3378(8), Mo1–Cl3 = 2.3618(7), Mo1–O1 = 1.671(2), Mo1–S1 = 2.8298(8), Mo1–S2 = 2.5665(7), Cl1–Mo1–Cl2 = 91.25(3), Cl1–Mo1–O1 = 98.99(8), Cl1–Mo1–Cl3 = 89.69(3), Cl2–Mo1–O1 = 98.99(8), S1–Mo1–S2 = 78.83(2).

isomer (Fig. 2), which suggests that the ability to form a five-membered chelate ring with a smaller chelate angle (S1–Mo1–S2 = 78.55(3)°) may be an important factor influencing the isomer formed. The structure also reveals a very markedly longer Mo–$S_{trans O}$ = 2.911(1) Å, which compares with Mo–$S_{trans Cl}$ = 2.531(1) Å, showing the high *trans*-influence of the Mo=O bond on the weaker aryl thioether donor ligand.

Brownish diselenoether complexes, [$MoOCl_3$(diselenoether)] (diselenoether = $MeSe(CH_2)_2SeMe$, $MeSe(CH_2)_3SeMe$), were obtained from reaction of the ligands with $MoOCl_3$ or [$MoOCl_3(thf)_2$] in a 1 : 1 molar ratio, but *o*-$C_6H_4(SeMe)_2$ did not displace thf from [$MoOCl_3(thf)_2$]. The reaction of $MeSeCH_2SeMe$ with $MoOCl_3$ produced a black oily decomposition product. However, the 1 : 1 reaction of *o*-$C_6H_4(SeMe)_2$ with $MoOCl_3$ in CH_2Cl_2 gave a brown product for which the microanalytical data indicated a 2 : 1 $MoOCl_3$: diselenoether stoichiometry. This is discussed along with the similar ditelluroether complexes below. The X-ray crystal structure of *mer*-[$MoOCl_3${$MeSe(CH_2)_2SeMe$}] was obtained (Fig. 3).

The five complexes described have room temperature magnetic moments of ~1.7 B.M., similar to other $MoOCl_3$ complexes,[1,2,8,9] and close to the spin-only value expected for a

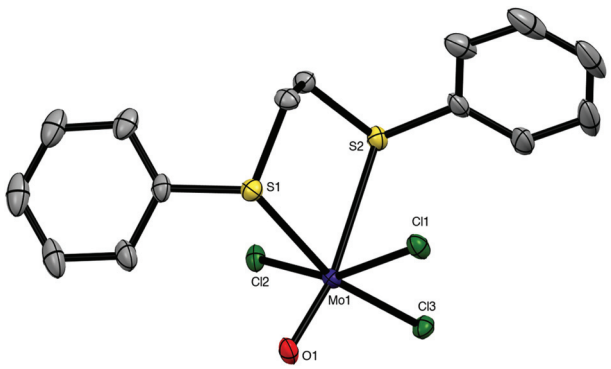


Fig. 2 Crystal structure of *mer*-[$MoOCl_3${$PhS(CH_2)_2SPh$}] showing the atom numbering scheme. Ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Note that the O/Cl exhibited disorder, which was modelled with split atom sites, refined to occupancies of 0.53 : 0.47. Only the major form is shown. Selected bond lengths (Å) and angles (°): Mo1–Cl1 = 2.324(1), Mo1–Cl2 = 2.394(1), Mo1–Cl3 = 2.311(3), Mo1–O1 = 1.706(2), Mo1–S1 = 2.531(1), Mo1–S2 = 2.911(1), Cl1–Mo1–Cl3 = 89.93(7), Cl1–Mo1–O1 = 102.2(5), O1–Mo1–Cl2 = 101.1(5), O1–Mo1–Cl3 = 106.6(3), Cl2–Mo1–Cl3 = 91.28(7), Cl2–Mo1–S1 = 88.39(4), Cl1–Mo1–S2 = 81.49(4), S1–Mo1–S2 = 78.55(3).

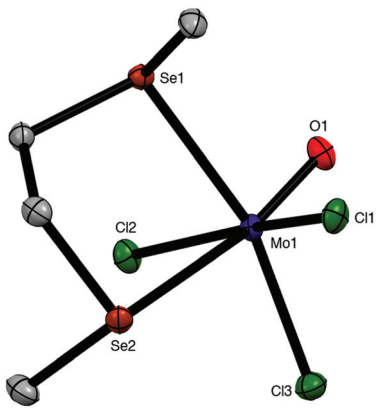


Fig. 3 Crystal structure of *mer*-[$MoOCl_3${$MeSe(CH_2)_2SeMe$}] showing the atom numbering scheme. Ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1–Cl1 = 2.3553(5), Mo1–Cl2 = 2.3517(5), Mo1–Cl3 = 2.3453(5), Mo1–O1 = 1.673(1), Mo1–Se1 = 2.6564(2), Mo1–Se2 = 2.8937(3), Cl1–Mo1–Cl3 = 90.35(2), Cl1––Mo1–O1 = 98.98(5), Cl2–Mo1–Cl3 = 90.65(2), Cl3–Mo1–O1 = 107.36(5), Se1–Mo1–Se2 = 79.76(1).

d^1 complex. This indicates that any orbital contribution is quenched by the very asymmetric field of the molybdenum environment.[24] The IR spectra show very strong single bands due to ν(Mo=O) in the range 950–980 cm^{-1}, as well as strong overlapping bands at 355–300 cm^{-1} assigned as Mo–Cl modes, but do not appear to readily distinguish the isomer present. The UV/visible spectra of the solids show a clear band at 13 000–14 000 cm^{-1} and a second band or shoulder at ~19 000–21 000 cm^{-1}. Assuming C_{4v} symmetry (the actual metal centre symmetry is lower) and placing Mo=O as the dominant contribution along the four-fold axis, leads to the assignment as the d–d bands as $^2B_2 \rightarrow {}^2E$ and $^2B_2 \rightarrow {}^2B_1$, respectively.[25] The intense absorptions >20 000 cm^{-1}, assigned as charge transfer bands, are less clearly resolved, but based upon the usual ligand electronegativities,[25] we assign the first intense feature (~21 000–22 000 cm^{-1}) as S/Se(π) → Mo(d) and the broad overlapping features at ~25 000–30 000 cm^{-1} as Cl(π) → Mo(d). The complexity of the electronic spectra in compounds of this type is shown by a combined UV/visible absorption, MCD and DFT study of $[MoOCl_3\{Ph_2P(CH_2)_2PPh_2\}]$;[26] here we are using the spectra to confirm the presence of Mo(v) in the isolated complexes.

Dimethylchalcogenides (EMe_2, E = S, Se, Te)

Neither SMe_2 or $SeMe_2$ was found to displace thf from $[MoOCl_3(thf)_2]$. However, reaction of a suspension of $MoOCl_3$ in dry CH_2Cl_2 with 2 equivalents of EMe_2 produced complexes with a 1 : 1 Mo : EMe_2 empirical composition, $MoOCl_3(EMe_2)$ (E = S, Se). There was no evidence for the formation of the 1 : 2 $[MoOCl_3(EMe_2)_2]$ complexes. Crystals of both $MoOCl_3(EMe_2)$ (E = S, Se) complexes were obtained and the structures, which are isomorphous (Fig. 4), showed them to be chloride-bridged dimers, with six-coordinate Mo(v) centres, *i.e.* $[\{MoOCl_2(EMe_2)\}_2(\mu\text{-}Cl_2)]$ (E = S, Se).

The Mo=O bonds (~1.65 Å) are trans to asymmetrically bound (by ~0.4 Å) bridging chlorides, with the EMe_2 groups arranged anti and perpendicular to the $Mo_2Cl_4O_2$ plane. The geometries are very similar to those found in $[(MoOCl_2L)_2(\mu\text{-}Cl)_2]$ (L = O=C(H)OMe, thf, O = CEt_2).[27–29]

The reaction of $MoOCl_3$ with $TeMe_2$ in toluene produced brown $[\{MoOCl_2(TeMe_2)\}_2(\mu\text{-}Cl)_2]$, which is the first Mo(v) complex with a neutral tellurium donor ligand. Crystals were not obtained from this complex due to poor solubility and limited stability in solution, but spectroscopically it is very similar to the other EMe_2 complexes. The failure to produce the six-coordinate monomers, $[MoOCl_3(EMe_2)_2]$, even in the presence of excess EMe_2, shows that the molybdenum(v) prefers to bind a chloride from another molecule, creating the bridged dimer structure, and is consistent with the weak donor properties of the EMe_2. The dimers are clearly distinguished from the $[MoOCl_3$(dichalcogenoether)] monomers by their IR spectra, with the dimers showing a strong ν(Mo=O) vibration in the range at 985–1005 cm^{-1} (higher frequency than in the monomeric $[MoOCl_3$(dichalcogenoether)] type) and terminal Mo–Cl modes 360–310 cm^{-1}; weaker bands in the region ~270–250 cm^{-1} and absent in the spectra of the $[MoOCl_3$(dichalcogenoether)] monomers, may be due to the chloride bridges. The magnetic moments of ~1.7 B.M./Mo confirm the Mo(v) assignment and the absence of any magnetic interactions between the molybdenum centres.

Ditelluroethers

The reaction of *o*-$C_6H_4(SeMe)_2$, *o*-$C_6H_4(TeMe)_2$ and MeTe$(CH_2)_3$TeMe (L–L) with $MoOCl_3$ in a 1 : 1 molar ratio in CH_2Cl_2 failed to produce the expected $[MoOCl_3$(L–L)] type complexes. Instead, dark brown complexes, identified by microanalysis as $[(MoOCl_3)_2$(L–L)], were obtained. Once isolated the compounds are very poorly soluble in CH_2Cl_2 and many attempts to

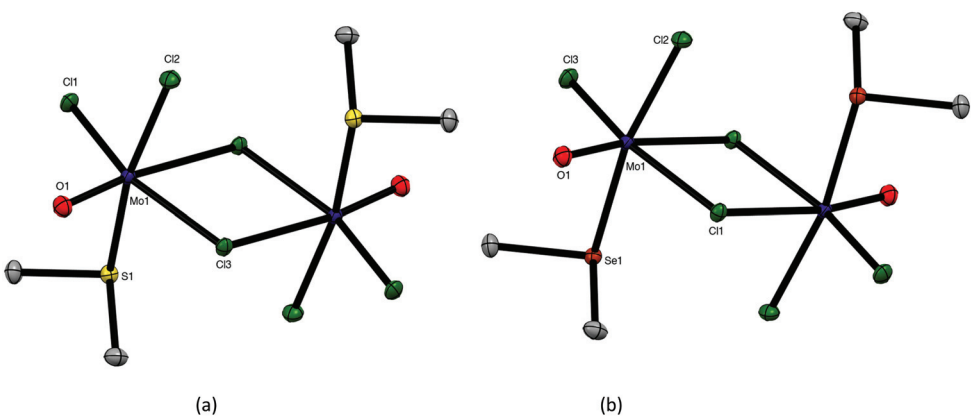


Fig. 4 Crystal structures of $[\{MoOCl_2(SMe_2)\}_2(\mu\text{-}Cl)_2]$ (a) and $[\{MoOCl_2(SeMe_2)\}_2(\mu\text{-}Cl)_2]$ (b) showing the atom numbering scheme. Ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): (a) Mo1–Cl1 = 2.3264(2), Mo1–Cl2 = 2.3341(3), Mo1–Cl3 = 2.3953(3), Mo1–Cl3′ = 2.7942(2), Mo1–O1 = 1.6515(8), Mo1–S1 = 2.5537(3), Cl1–Mo1–O1 = 102.48(1), Cl2–Mo1–O1 = 102.08(3), Cl3–Mo1–O1 = 99.55(3), Cl2–Mo1–Cl3 = 85.77(1), Cl1–Mo1–Cl3 = 92.340(9), Cl1–Mo1–S1 = 85.233(9), O1–Mo1–S1 = 92.67(3), Cl3–Mo1–Cl3 = 77.520(8); (b) Mo1–Cl1 = 2.4024(4), Mo1–Cl2 = 2.3385(4), Mo1–Cl3 = 2.3299(4), Mo1–Cl1′ = 2.7927(4), Mo1–O1 = 1.653(1), Mo1–Se1 = 2.6647(3), Cl1–Mo1–O1 = 98.89(4), Cl2–Mo1–O1 = 103.10(4), Cl3–Mo1–O1 = 102.38(4), Cl2–Mo1–Cl3 = 92.32(2), Se1–Mo1–Cl1 = 78.76(1), Se1–Mo1–Cl1 = 87.438(10), O1–Mo1–Se1 = 92.89(4).

produce crystals for an X-ray structure determination have been unsuccessful. However, the magnetic moments of ~1.7 B.M./Mo and the UV-visible spectra of these solids are consistent with their formulation as six-coordinate oxo-molybdenum(v) complexes.

The UV-visible spectra of the ditelluroether complexes show a d–d band at ~14 000 cm^{-1} ($^2B_2 \rightarrow {}^2E$); a second more intense feature 18 000–20 000 cm^{-1} may be the second d–d band ($^2B_2 \rightarrow {}^2B_1$), but given the lower electronegativity of Te[24] is probably the Te(π) → Mo(d) charge transfer transition, which obscures the d–d band.

The IR spectra are significantly different to those of $[MoOCl_3(L–L)]$ (L–L = dithioether or diphosphine),[8,9] but are similar to those of $[\{MoOCl_2(EMe_2)\}_2(\mu\text{-}Cl)_2]$. In particular, the ν(Mo=O) vibrations are at higher frequency (985–1000 cm^{-1}), and in addition to several terminal ν(Mo–Cl) modes ~320–300 cm^{-1}, also show a peak ~250 cm^{-1}, probably due to a chloride bridge. In the absence of a crystal structure, the geometries cannot be established unequivocally, but the spectroscopic data (and insolubility) are consistent with a structure type similar to those in $[\{MoOCl_2(EMe_2)\}_2(\mu\text{-}Cl)_2]$, with the EMe_2 ligands replaced by bridging ditelluroethers, leading to the formulation as an oligomer, $[(MoOCl_2)_2(\mu\text{-}Cl)_2(\mu\text{-ditelluroether})]_n$. There are several literature examples of Group 16 ligands with *o*-phenylene backbones adopting a bridging mode, authenticated by X-ray crystal structures.[30–32]

The brown solution from the preparation of $[\{MoOCl_3\}_2\{o\text{-}C_6H_4(TeMe)_2\}]_n$ also deposited a few dark green crystals, which were shown by X-ray crystallographic analysis to be the mixed valence complex, $[Mo^{IV}Cl\{o\text{-}C_6H_4(TeMe)_2\}_2(\mu\text{-}O)Mo^{V}OCl_4]$ (Fig. 5). This complex contains a Mo(IV) centre coordinated to two chelating ditelluroethers, a terminal chloride and an Mo=O group, which forms a very asymmetric bridge to a square pyramidal $MoOCl_4^-$ anion, with Mo1–O1 = 1.705(4) Å and Mo2–O1 = 2.368(4) Å. These bond distances may be compared with the terminal Mo=O bond distance (Mo2–O2 = 1.659(5) Å) in the latter. This complex appears to be the first structurally characterised molybdenum-ditelluroether complex in a positive formal oxidation state of the metal; all previously reported complexes are substituted carbonyls.[33,34] Analogous complexes with some diphosphine and diarsine ligands have been reported,[8,9] and the structure of (the previously unknown) $[MoCl\{Me_2P(CH_2)_2PMe_2\}_2(\mu\text{-}O)(MoOCl_4)]$ is discussed below. The crystals of $[Mo^{IV}Cl\{o\text{-}C_6H_4(TeMe)_2\}_2(\mu\text{-}O)Mo^{V}OCl_4]$ result from a redox reaction, and its structure is not consistent with the spectroscopic data on the bulk $[\{MoOCl_3\}_2\{o\text{-}C_6H_4(TeMe)_2\}]_n$. The failure to isolate mononuclear $[MoOCl_3(L–L)]$ complexes with chelating $o\text{-}C_6H_4(SeMe)_2$, $o\text{-}C_6H_4(TeMe)_2$ and $MeTe(CH_2)_3TeMe$, seems analogous to the case of $[\{MoOCl_2(EMe_2)\}_2(\mu\text{-}Cl)_2]$, where the Mo(v) centre prefers to form chloride bridges rather than coordinate to a second, weakly donating chalcogenenoether.

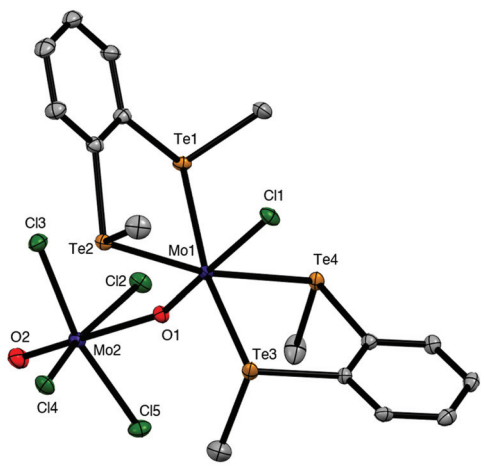


Fig. 5 Crystal structure of $[MoCl\{o\text{-}C_6H_4(TeMe)_2\}_2(\mu\text{-}O)MoOCl_4]\cdot CH_2Cl_2$ showing the atom numbering scheme. Ellipsoids are shown at 50% probability and hydrogen atoms and solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1–Cl1 = 2.4486(7), Mo2–Cl2 – 5 = 2.3640(7) – 2.3930(7), Mo1–Te1 – 4 = 2.7432(3) – 2.7822(3), Mo1–O1 = 1.704(2), Mo2–O1 = 2.370(2), Mo2–O2 = 1.655(2), O2–Mo2–Cl2 – 5 = 78.4(1) – 82.2(1), Te–Mo1–$Te_{(chelate)}$ = 85.316(8), 86.185(8), Te1 – 4–Mo1–Cl1 = 79.647(18)–89.939(18), Cl1–Mo1–O1 = 177.91(7), Mo1–O1–Mo2 = 159.63.1(11).

Phosphine complexes

The coordination behaviour of the chalcogenoether ligands to $MoOCl_3$ has both significant analogies and differences to that of some phosphine ligands, making for informative comparisons. Pink or red complexes $[MoOCl_3(diphosphine)]$ (diphosphine = $Ph_2P(CH_2)_2PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, $o\text{-}C_6H_4(PPh_2)_2$,) were reported in the 1970s and confirmed by IR, UV/visible spectroscopy and magnetic measurements as Mo(v) compounds.[7–9] No structures were obtained, but EPR spectra supported *fac* octahedral isomers.[8,9] A second (brown) form with $Ph_2P(CH_2)_2PPh_2$ and *cis*-$Ph_2PCH = CHPPh_2$ obtained by refluxing the red form in alcohol for several hours, had similar, but not identical, spectroscopic properties; Isovitsch *et al.*,[10] confirmed the crystal structure of the red form of the $Ph_2P(CH_2)_2PPh_2$ complex as the *fac* isomer. In the present work we prepared the new complex $[MoOCl_3\{Me_2P(CH_2)_2PMe_2\}]$ from $[MoOCl_3(thf)_2]$ and confirmed the *fac* geometry by a crystal structure (Fig. 6). The spectroscopic data on this complex (Experimental section) are in good agreement with that of the red isomers with other diphosphines.[7–9] Notably, the five-membered chelate ring diphosphine complexes are *fac* isomers, contrasting with the *mer*-$[MoOCl_3(dichalcogenoether)]$ described above.

The nature of the brown "isomers" is not entirely clear, but the original study[8] of the red and brown forms of $[MoOCl_3\{cis\text{-}Ph_2PCH{=}CHPPh_2\}]$ showed they had identical EPR spectra with coupling to equivalent phosphorus donors, *i.e.* were both *fac* forms. Hence the brown form seems likely to be the red isomer co-crystallised with a second complex, probably an EPR silent Mo(IV) species. The presence of varying amounts of a co-crystallised second species would account for the various (small) differences reported by other workers.[7,8,10] Similar problems, including X-ray structures with a variety of bond lengths for apparently the same complex, led to the proposal

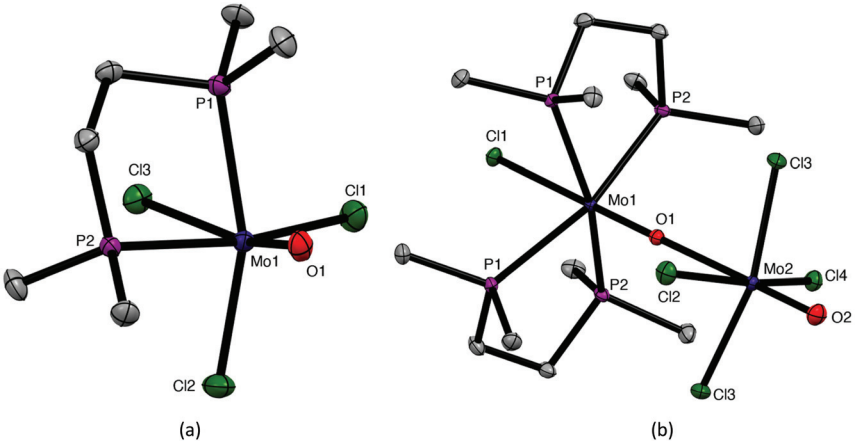


Fig. 6 Crystal structures of $[MoOCl_3(Me_2PCH_2CH_2PMe_2)]$ (a) and $[MoCl(Me_2PCH_2CH_2PMe_2)_2(\mu\text{-}O)MoOCl_4]$ (b) showing the atom numbering scheme. Ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): (a) Mo1–Cl1 = 2.3824(9), Mo1–Cl2 = 2.383(1), Mo1–Cl3 = 2.5011(8), Mo1–O1 = 1.680(2), Mo1–P1 = 2.5260(2), Mo1–P2 = 2.5250(8), Cl1–Mo1–Cl2 = 96.98(3), Cl1–Mo1–O1 = 100.19(8), Cl2–Mo1–Cl3 = 88.76(3), Cl2–Mo1–O1 = 104.66(8), P1–Mo1–P2 = 78.84(3); (b) Mo1–Cl1 = 2.5186(2), Mo1–O1 = 1.703(4), Mo1–P1 = 2.5131(2), Mo1–P2 = 2.5139(3), Mo2–O1 = 2.394(2), Mo2–O2 = 1.657(8), Mo2–Cl2 – 5 = 2.3573(4) – 2.3824(3), Cl1–Mo1–P1 = 78.92(2), Cl1–Mo1–P2 = 83.26(4), O2–Mo2–Cl2 – 5 = 97.57(2) – 98.89(4), P1–Mo1–P2 = 80.16(4), Mo1–O1–Mo2 = 178.05(8).

of *bond-stretch or distortional isomerism* in some other early d-block complexes, a concept subsequently considered to be erroneous.[35]

Pink or purple complexes with microanalyses indicating a $[MoCl_{2.5}O(diphosphine)]$ were isolated in some systems[7–9] and were formulated as the ionic Mo(IV)–Mo(V) species $[Mo^{IV}OCl(diphosphine)_2][Mo^{V}OCl_4]$, based upon spectroscopic data, and the observation that metathesis with $NaBPh_4$ gave $[Mo^{IV}OCl(diphosphine)_2][BPh_4]$.

During attempts to grow crystals of orange-yellow $[MoOCl_3\{Me_2P(CH_2)_2PMe_2\}]$, a few deep purple crystals were also isolated that were confirmed by an X-ray structure (Fig. 6) to be $[MoCl\{Me_2P(CH_2)_2PMe_2\}_2(\mu\text{-}O)(MoOCl_4)]$, analogous to $[MoCl\{o\text{-}C_6H_4(TeMe)_2\}_2(\mu\text{-}O)(MoOCl_4)]$ described above. Both molybdenum centres are in a distorted octahedral geometry and linked by a very asymmetric oxide bridge, Mo1–O1 = 1.703(4), Mo2–O1 = 2.394(2) Å, which may be compared with Mo2–O2 = 1.657(8) Å for the terminal Mo=O unit. The original formulation[7,8] was as ionic salts, $[Mo^{IV}OCl(diphosphine)_2][Mo^{V}OCl_4]$. The reformulation as neutral μ-oxido dimers in the solid state is likely to apply to all the reported examples, with the long Mo–O bond easily cleaved to give ions in solution.

Red *fac*-$[MoOCl_3(PMe_3)_2]$ was obtained by Limberg *et al.*[11] as one product from reaction of the alkoxide complex, $[Cl_2OMo(\mu\text{-}OEt)_2(\mu\text{-}EtOH)MoOCl_2]$ with PMe_3; we obtained the same complex directly from $[MoOCl_3(thf)_2]$ and PMe_3 in CH_2Cl_2. Our X-ray structure and the spectroscopy (Experimental section) are in good agreement with published data,[7] and are not discussed further here. The interest lies in the formation of a discrete *pseudo*-octahedral 1 : 2 Mo : PMe_3 monomer with the strong σ-donor alkyl phosphine, which contrasts with the formation of chloride-bridged dimers, $[\{MoOCl_2(EMe_2)\}_2(\mu\text{-}Cl)_2]$ (E = S, Se, Te), with the weaker donor chalcogenoethers discussed above.

Experimental

Syntheses were performed using standard Schlenk and glove-box techniques under a dry N_2 atmosphere. Solvents were dried by distillation from CaH_2 (CH_2Cl_2) or Na/benzophenone ketyl (toluene, n-hexane, diethyl ether). $MoCl_5$ and $O(SiMe_3)_2$ were obtained from Sigma-Aldrich. The monodentate ligands (SMe_2, PMe_3, $SeMe_2$) were obtained from Sigma-Aldrich or Strem and dried over molecular sieves. $TeMe_2$ was made by the method of Kuhn *et al.*[36] The dithioethers,[37] diselenoethers[38,39] and ditelluroethers[40,41] were prepared as described or by minor modifications thereof. $MoOCl_3$ was prepared from $MoCl_5$ and $O(SiMe_3)_2$.[42] and $MoOCl_4$ obtained from Climax Molybdenum.

Infrared spectra were recorded on a PerkinElmer Spectrum 100 spectrometer in the range 4000–200 cm^{-1}, with samples prepared as Nujol mulls between CsI plates. UV/visible spectra were recorded on powdered solids using the diffuse reflectance attachment of a PerkinElmer 750S spectrometer. Magnetic measurements were made using a Johnson Matthey magnetic balance. Microanalyses on new compounds were undertaken by London Metropolitan University or Medac Ltd.

mer-$[MoOCl_3(thf)_2]$

Prepared following the literature method.[43] Yield: 87%. IR spectrum (Nujol, ν/cm^{-1}): 982 s Mo=O, 1117 s, 833 s br thf, 342 s, 315 m Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 32 550, 26 200, 22 000, 13 250. μ_{eff}: 1.71 B.M.

fac-[MoOCl$_3${MeS(CH$_2$)$_3$SMe}]

Method 1. [MoOCl$_3$(thf)$_2$] (0.150 g, 0.41 mmol) was suspended in CH_2Cl_2 (3 mL) and a solution of MeS(CH$_2$)$_3$SMe (0.056 g, 0.41 mmol) in CH_2Cl_2 (2 mL) was added slowly and the solution left to stir for 1 h. The brown solution formed was then concentrated to 3 mL *in vacuo* and the green solid which precipitated, was filtered off and dried *in vacuo.* Yield: 0.070 g, 40%. Required for $C_5H_{12}Cl_3MoOS_2$ (354.58): C, 16.94; H, 3.41. Found: C, 17.02; H, 3.39%. IR spectrum (Nujol, ν/cm^{-1}): 955 s Mo═O, 348 s, 327 s, 306 m Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 27 400, 26 000, 21 150, 18 350, 13 700. μ_{eff}: 1.71 B.M.

Method 2. $MoOCl_4$ (0.150 g, 0.59 mmol) was suspended in toluene (5 mL) and a solution of MeS(CH$_2$)$_3$SMe (0.081 g, 0.59 mmol) in toluene (2 mL) was slowly added and the green solution left to stir for 1 h. The green solution was concentrated to 3 mL *in vacuo* to produce a green precipitate that was filtered off and dried *in vacuo.* The green solid was washed in hexane (3 × 5 mL) and dried. Yield: 0.153 g, 70%. Required for $C_5H_{12}Cl_3MoOS_2{\cdot}0.2C_7H_8$ (373.00): C, 20.61; H, 3.67. Found: C, 20.82; H, 3.77%. The complex was spectroscopically identical to that made by Method 1. Green crystals suitable for X-ray crystallography were grown from CH_2Cl_2.

mer-[MoOCl$_3${^{i}PrS(CH$_2$)$_2$S^{i}Pr}]

[MoOCl$_3${^{i}PrS(CH$_2$)$_2$S^{i}Pr}] was prepared similarly to Method 1 above, and isolated as a pale green solid. Yield: 62%. Required for $C_8H_{18}Cl_3MoOS_2$ (396.66): C, 24.22; H, 4.57. Found: C: 24.45; H, 4.15%. IR spectrum (Nujol, ν/cm^{-1}): 979 s Mo═O, 349 s, 312 m Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 32 300, 30 400, 27 700, 23 000 sh, 21 500 sh, 13 600. μ_{eff}: 1.69 B.M.

mer-[MoOCl$_3${PhS(CH$_2$)$_2$SPh}]

$MoOCl_3$ (0.150 g, 0.69 mmol) was suspended in CH_2Cl_2 (3 mL) and a solution of PhS(CH$_2$)$_2$SPh (0.170 g, 0.69 mmol) in CH_2Cl_2 (2 mL) was added slowly and the resulting green solution left to stir for 1 h. The resulting brown solution was concentrated to 3 mL *in vacuo* and filtered, and the orange-brown solid dried *in vacuo.* Yield: 0.244 g, 76%. Required for $C_{14}H_{14}Cl_3MoOS_2$ (464.69): C, 36.19; H, 3.04. Found: C, 35.97; H, 3.18%. IR spectrum (Nujol, ν/cm^{-1}): 966 s Mo═O, 354 s, 319 m Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 32 200, 26 900, 22 600, 21 300, 18 500 sh, 13 000. μ_{eff}: 1.71 B.M.

[{MoOCl$_2$(SMe$_2$)}$_2$(μ-Cl)$_2$]

$MoOCl_3$ (0.150 g, 0.69 mmol) was suspended in CH_2Cl_2 (3 mL) and a solution of SMe_2 (0.085 g, 1.38 mmol) in CH_2Cl_2 (2 mL) was added slowly and the green solution left to stir for 1 h. The clear green solution was then concentrated to 3 mL *in vacuo* and layered with hexane (3 mL). The green crystals formed were isolated *via* filtration and dried *in vacuo.* Yield: 0.73 g, 38%. Required for $C_4H_{12}Cl_6Mo_2O_2S_2$ (560.86): C, 8.57; H, 2.16. Found: C, 8.98; H, 2.37%. IR spectrum (Nujol, ν/cm^{-1}): 1004 s Mo═O, 356 s, 319 s, 268 m Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 26 000, 22 300, 19 600 sh, 13 800. μ_{eff}: 1.72 B.M./Mo.

[{MoOCl$_2$(SeMe$_2$)}$_2$(μ-Cl)$_2$]

$MoOCl_3$ (0.150 g, 0.69 mmol) was suspended in CH_2Cl_2 (3 mL) and a solution of $SeMe_2$ (0.150 g, 1.38 mmol) in CH_2Cl_2 (2 mL) was slowly added and the green solution left to stir for 1 h. The red solution formed was concentrated to 3 mL *in vacuo* and layered with hexane (3 mL). The dark brown crystals were isolated *via* filtration, and dried *in vacuo.* Yield: 0.154 g, 68%. Required for $C_4H_{12}Cl_6Mo_2O_2Se_2$ (654.65): C, 7.34; H, 1.85%. Found: C, 7.43; H, 1.93%. IR spectrum (Nujol, ν/cm^{-1}): 1004 s Mo═O, 368 sh, 351 s, 313 m Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 32 500, 26 500, 20 700, 14 100. μ_{eff}: 1.68 B.M./Mo.

mer-[MoOCl$_3${MeSe(CH$_2$)$_2$SeMe}]

[MoOCl$_3$(thf)$_2$] (0.150 g, 0.41 mmol) was suspended in CH_2Cl_2 (3 mL) and a solution of MeSe(CH$_2$)$_3$SeMe (0.089 g, 0.41 mmol) in CH_2Cl_2 (2 mL) was added slowly and the green solution left to stir for 1 h. The resulting brown solution was concentrated to 3 mL *in vacuo* and filtered, then the solid dried *in vacuo*, isolating a dark brown solid. Crystals grown from CH_2Cl_2 were dark green. Yield: 0.160 g, 90%. Required for $C_4H_{10}Cl_3MoOSe_2$ (434.34): C, 11.06; H, 2.32. Found: C, 11.60; H, 2.50%. IR spectrum (Nujol, ν/cm^{-1}): 960 s Mo═O, 342 s, 310 m Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 25 800, 21 500, 19 300, 14 600. μ_{eff}: 1.71 B.M.

[MoOCl$_3${MeSe(CH$_2$)$_3$SeMe}]

$MoOCl_3$ (0.150 g, 0.69 mmol) was suspended in CH_2Cl_2 (3 mL) and a solution of MeSe(CH$_2$)$_3$SeMe (0.158 g, 0.69 mmol) in CH_2Cl_2 (2 mL) was slowly added and the red/brown solution left to stir for 1 h. The brown solution was concentrated to 3 mL *in vacuo* and filtered and the dark brown solid isolated was dried *in vacuo*. A deep orange-brown crystalline solid was obtained from CH_2Cl_2 solution. Yield: 0.178 g, 58%. Required for $C_5H_{12}Cl_3MoOSe_2{\cdot}CH_2Cl_2$ (533.30): C, 13.51; H, 2.65. Found: C, 13.96; H, 2.95%. IR spectrum (Nujol ν/cm^{-1}): 954 s Mo═O, 346 s vbr, Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 32 000 sh, 2700 br, 21 400, 19 500, 14 000. μ_{eff}: 1.70 B.M.

[(MoOCl$_3$)$_2${*o*-C$_6$H$_4$(SeMe)$_2$}]$_n$

$MoOCl_3$ (0.150 g, 0.69 mmol) was suspended in dichloromethane (3 mL) and a solution of *o*-C$_6$H$_4$(SeMe)$_2$ (0.226 g, 0.69 mmol) in dichloromethane (2 mL) was added slowly and the dark red/brown solution left to stir for 1 h. The brown solution was then concentrated to 3 mL *in vacuo*, producing a brown precipitate, which was washed with OEt_2 (3 × 5 mL), then the brown-pink solid was dried *in vacuo.* Yield: 0.170 g, 53%. Required for $C_8H_{10}Cl_6Mo_2O_2Se_2$ (700.68): C, 13.71; H, 1.44. Found: C, 13.43; H, 1.53%. IR spectrum (Nujol, ν/cm^{-1}): 999 s br Mo═O, 351 w, 302 s, 292 sh, 256 m Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 29 500 sh, 24 900, 20 900, 14 300. μ_{eff}: 1.69 B.M./Mo.

[{MoOCl$_2$(TeMe$_2$)}$_2$(μ-Cl)$_2$]

$MoOCl_3$ (0.150 g, 0.69 mmol) was suspended in toluene (3 mL) and a solution of $TeMe_2$ (0.217 g, 1.38 mmol) in toluene (2 mL) was added slowly and the purple solution left to stir for 1 h. The deep purple solution was concentrated to 3 mL *in vacuo* and filtered, then the dark brown solid was dried *in vacuo.* Yield: 0.203 g, 78%. Required for $C_4H_{12}Cl_6Mo_2O_2Te_2$ (751.93): C, 6.39; H, 1.61. Found: C, 6.76; H, 2.06%. IR spectrum (Nujol, ν/cm^{-1}): 985 s br Mo=O, 327, 302 s br, 256 m Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 34 500, 29 700 sh, 27 150, 26 100, 20 900, 19 500, 14 400. μ_{eff}: 1.68 B.M./Mo.

[(MoOCl$_3$)$_2${MeTe(CH$_2$)$_3$TeMe}]$_n$

$MoOCl_3$ (0.150 g, 0.69 mmol) was suspended in dichloromethane (3 mL) and a solution of $MeTe(CH_2)_3TeMe$ (0.217 g, 0.69 mmol) in dichloromethane (2 mL) was added slowly and the brown solution left to stir for 1 h. The brown solution was concentrated to 3 mL *in vacuo*, producing a brown precipitate which was washed with OEt_2 (3 × 5 mL), then the dark brown solid was dried *in vacuo.* Yield: 0.322 g, 61%. Required for $C_5H_{12}Cl_6Mo_2O_2Te_2$ (763.95): C, 7.86; H, 1.58. Found: C, 7.20; H, 1.38%. IR spectrum (Nujol, ν/cm^{-1}): 988 m Mo=O, 303 s, 292 m, 249 m Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 26 500, 21 700, 18 600, ~13 000. μ_{eff}: 1.68 B.M./Mo.

[(MoOCl$_3$)$_2${*o*-C$_6$H$_4$(TeMe)$_2$}]$_n$

$MoOCl_3$ (0.150 g, 0.69 mmol) was suspended in dichloromethane (3 mL) and a solution of *o*-$C_6H_4(TeMe)_2$ (0.249 g, 0.69 mmol) in dichloromethane (2 mL) was added slowly and the dark brown solution left to stir for 1 h. The brown solution was concentrated to 3 mL *in vacuo*, producing a brown precipitate which was washed with OEt_2 (3 × 5 mL), and dried *in vacuo.* Yield: 0.285 g, 52%. Required for $C_8H_{10}Cl_6Mo_2O_2Te_2$ (797.96): C, 12.04; H, 1.26. Found: C, 12.27; H, 1.43%. IR spectrum (Nujol, ν/cm^{-1}): 992 s br Mo=O, 343 m, 328 m, 302 s, 254 m Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 32 500, 25 000 sh, 21 000, 19 200, 14 500. μ_{eff}: 1.70 B.M./Mo.

***fac*-[MoOCl$_3$(PMe$_3$)$_2$]**

[MoOCl$_3$(thf)$_2$] (0.150 g, 0.41 mmol) was suspended in CH_2Cl_2 (3 mL) and a solution of PMe_3 (0.063 g, 0.82 mmol) in CH_2Cl_2 (3 mL) was added slowly and the dark green solution left to stir for 1 h. The red solution produced was then concentrated to 3 mL *in vacuo* and filtered, and the red solid dried *in vacuo*. Yield: 0.047 g, 31%. Required for $C_6H_{18}Cl_3MoOP_2$ (370.45): C, 19.45; H, 4.90. Found: C, 19.28; H, 4.74%. IR spectrum (Nujol, ν/cm^{-1}): 957 s Mo=O, 352 sh, 324 s, 305 m Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 29 600, 26 500, 21 600, 20 500 sh, 15 500.

***fac*-[MoOCl$_3${Me$_2$P(CH$_2$)$_2$PMe$_2$}]**

[MoOCl$_3$(thf)$_2$] (0.150 g, 0.41 mmol) was suspended in CH_2Cl_2 (3 mL) and a solution of $Me_2PCH_2CH_2PMe_2$ (0.165 g, 0.41 mmol) in CH_2Cl_2 (3 mL) was added slowly and the solution left to stir for 1 h. The was concentrated to 3 mL *in vacuo*, filtered and then the solid was dried *in vacuo.* Yield: 0.131 g, 81%. Required for $C_6H_{16}Cl_3MoOP_2$ (368.44): C, 19.56; H, 4.38. Found: C, 19.83; H, 4.26%. IR spectrum (Nujol, ν/cm^{-1}): 951 s Mo=O, 362 m, 325 s, 306 s Mo–Cl. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1}: 29 600, 26 500 sh, 21 600, 20 000, 15 500. μ_{eff}: 1.72 B.M.

X-ray experimental

Crystals were grown from slow evaporation of saturated solutions in CH_2Cl_2 or by liquid–liquid diffusion using CH_2Cl_2 and hexane. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum (λ = 0.71073 Å) rotating anode generator with VHF Varimax optics (70 micron focus) with the crystal held at 100 K (N_2 cryostream). Crystallographic parameters are presented in Table S1.† Structure solution and refinement were performed using SHELX(T)-2018/2, SHELX-2018/3 through Olex2[44] and were mostly straightforward. H atoms were added and refined with a riding model. Where additional restraints were required, details are provided in the cif file for each structure found on CCDC.

Conclusions

A range of $MoOCl_3$ complexes with thio- and seleno-ethers have been prepared from [MoOCl$_3$(thf)$_2$] and the ligands in anhydrous CH_2Cl_2 solution. The more weakly coordinating $PhS(CH_2)_2SPh$, SMe_2 and $SeMe_2$ fail to displace the thf, but complexes of these can be obtained using a suspension of $MoOCl_3$ in CH_2Cl_2. The reaction of $MoOCl_4$ with dithioethers results in reduction to Mo(v) as [MoOCl$_3$(dithioether)], behaviour which contrasts with that of $WOCl_4$ or $WSCl_4$, where either W(vi) or W(v) complexes can be obtained depending upon the reaction conditions.[18] The stabilising effect of two oxido-groups on molybdenum(vi) is shown by the successful isolation of [MoO_2X_2(dithioether)] (X = Cl or Br).[12,13] The limited affinity of the hard $MoOCl_3$ for the weaker donor monochalcogenoethers is reflected in the formation of 1 : 1 adducts, which achieve six-coordination by forming chloride bridges, as in [{MoOCl$_2$(E'Me$_2$)}$_2$(μ-Cl)$_2$] (E' = S, Se), rather than by coordinating a second neutral donor ligand. The same explanation accounts for the formation of oligomeric complexes, [(MoOCl$_3$)$_2$(L–L)]$_n$ with *o*-$C_6H_4(SeMe)_2$, *o*-$C_6H_4(TeMe)_2$ and $MeTe(CH_2)_3TeMe$, postulated to have a structure with only one chalcogen donor atom on each molybdenum, and where six-coordination is achieved *via* bridging chlorides and bridging dichalcogenoethers (Scheme 1). Although bridging behaviour might seem unexpected for chelates with *o*-C_6H_4-backbones, the presence of aryl groups makes these ligands weaker donors to hard metal centres – compare $PhS(CH_2)_2SPh$ and $^iPrS(CH_2)_2S^iPr$. There are several literature examples of *o*-phe-

nylene-based dichalcogenoethers adopting a bridging coordination mode.[30–32] The behaviour contrasts with that of *o*-C_6H_4-based group 15 ligands, where *o*-$C_6H_4(PMe_2)_2$ or *o*-$C_6H_4(AsMe_2)_2$ can produce seven- or eight-coordination in tungsten(VI) complexes, such as $[WOCl_4\{o\text{-}C_6H_4(PMe_2)_2\}]$ or $[WF_4\{o\text{-}C_6H_4(PMe_2)_2\}_2]^{2+}$.[45,46] The present work has also reported the first examples of Mo(V) telluroether complexes. Although the large soft tellurium centres are not usually thought to be good ligands for high valent d-block metals, a range of compounds has been reported in the last few years, including examples with $NbCl_4$,[47] $NbCl_5$[48] and $TaCl_5$,[48] although the complexes reported here are the first examples in Group 6. Also notable is the X-ray structural characterisation of the mixed valence $[Mo^{IV}Cl\{o\text{-}C_6H_4(TeMe)_2\}_2(\mu\text{-}O)Mo^{V}OCl_4]$ and of the diphosphine analogue $[Mo^{IV}Cl\{Me_2P(CH_2)_2PMe_2\}_2(\mu\text{-}O)(Mo^{V}OCl_4)]$; complexes of the latter type were reported in the 1970s [7,8] but this is the first structural authentication.

The work has provided detailed characterisation of $MoOCl_3$-chalocogenoether complexes, and comparison with the W(VI) and W(V) analogues, and lays the basis for exploration of corresponding molybdenum sulfide chloride complexes,[19] which may provide single source LPCVD reagents for deposition of MoS_2 thin films. The sulfide chloride systems will form the basis of future work.

Conflicts of interest

The authors have no conflicts to declare.

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