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

Danielle E. Smith, William Levason,  James Powell  and Gillian Reid *

Complexes of oxotrichloromolybdenum(v) with neutral group 16 donor ligands, $[\text{MoOCl}_3(\text{L-L})]$ ($\text{L-L} = \text{RS}(\text{CH}_2)_2\text{SR}$, $\text{R} = {}^i\text{Pr}$, Ph ; $\text{MeS}(\text{CH}_2)_3\text{SMe}$; $\text{MeSe}(\text{CH}_2)_2\text{SeMe}$; $\text{MeSe}(\text{CH}_2)_3\text{SeMe}$), $\{[\text{MoOCl}_2(\text{EMe}_2)]_2(\mu\text{-Cl})_2\}$ ($\text{E} = \text{S}$, Se , Te), $\{[\text{MoOCl}_3]_2[\text{o-C}_6\text{H}_4(\text{EMe}_2)_2]_n\}$ ($\text{E} = \text{Se}$ or Te) and $\{[\text{MoOCl}_3]_2(\text{MeTe}(\text{CH}_2)_3\text{TeMe})_n\}$, have been obtained by reaction of the ligands with $[\text{MoOCl}_3(\text{thf})_2]$ 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*- $[\text{MoOCl}_3(\text{MeS}(\text{CH}_2)_3\text{SMe})]$, *mer*- $[\text{MoOCl}_3({}^i\text{PrS}(\text{CH}_2)_2\text{S}^i\text{Pr})]$ and *mer*- $[\text{MoOCl}_3(\text{MeSe}(\text{CH}_2)_2\text{SeMe})]$, as well as the six-coordinate chloride-bridged dimers, $\{[\text{MoOCl}_2(\text{SMe}_2)]_2(\mu\text{-Cl})_2\}$ and $\{[\text{MoOCl}_2(\text{SeMe}_2)]_2(\mu\text{-Cl})_2\}$. The structure of the mixed-valence decomposition product, $[\text{Mo}^{\text{IV}}\text{Cl}\{\text{o-C}_6\text{H}_4(\text{TeMe})_2(\mu\text{-O})\text{Mo}^{\text{VO}}\text{OCl}_4\}]$, was also determined. In toluene solution MoOCl_4 is reduced by $\text{MeS}(\text{CH}_2)_3\text{SMe}$ to produce the Mo(v) complex, $[\text{MoOCl}_3(\text{MeS}(\text{CH}_2)_3\text{SMe})]$. Crystal structures of the previously unknown diphosphine analogue, $[\text{MoOCl}_3(\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2)]$, and the mixed-valence derivative $[\text{Mo}^{\text{IV}}\text{Cl}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2(\mu\text{-O})\text{Mo}^{\text{VO}}\text{OCl}_4]$ are also reported for comparison and help to clarify earlier contradictory literature reports. In contrast to the dimeric EMe_2 complexes, $\{[\text{MoOCl}_2(\text{EMe}_2)]_2(\mu\text{-Cl})_2\}$, PMe_3 forms the monomeric complex, *fac*- $[\text{MoOCl}_3(\text{PMe}_3)_2]$.

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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 $[\text{MoO}_2\text{X}_2(\text{dithioether})]$ ($\text{X} = \text{Cl}$ or Br ; dithioether = $\text{RS}(\text{CH}_2)_2\text{SR}$, $\text{R} = \text{Me}$, Et , ${}^i\text{Pr}$), which have distorted octahedral structures with the sulfur donor atoms *trans* to $\text{Mo}=\text{O}$;^{12,13} there are also some thia-macrocyclic analogues.^{14,15} Complexes of the type $[\text{MoOCl}_3(\text{dithioether})]$ 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 $[(\text{WSCl}_4)_2(\mu\text{-}^i\text{PrSCH}_2\text{CH}_2\text{S}^i\text{Pr})]$, 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

School of Chemistry, University of Southampton, Southampton SO17 1BJ, UK.

E-mail: G.Reid@soton.ac.uk

† Electronic supplementary information (ESI) available: Crystallographic parameters (Table S1), IR and UV/visible spectra for the new complexes. CCDC 2050667: $\{[\text{MoOCl}_2(\text{SeMe}_2)]_2(\mu\text{-Cl})_2\}$, 2050668: $[\text{MoOCl}_3(\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2)]$, 2050669: $[\text{MoOCl}_3(\text{PhS}(\text{CH}_2)_2\text{SPh})]$, 2050670: $[\text{MoOCl}_3(\text{MeSe}(\text{CH}_2)_2\text{SeMe})]$, 2050671: $[\text{MoOCl}_3({}^i\text{PrS}(\text{CH}_2)_2\text{S}^i\text{Pr})]$, 2050672: $\{[\text{MoOCl}_2(\text{SMe}_2)]_2(\mu\text{-Cl})_2\}$, 2050673: $[\text{MoCl}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2(\mu\text{-O})(\text{MoOCl}_4)]$, 2050674: $[\text{MoOCl}_3(\text{MeS}(\text{CH}_2)_3\text{SMe})]$, 2050891: $[\text{MoCl}\{\text{o-C}_6\text{H}_4(\text{TeMe})_2(\mu\text{-O})\text{MoOCl}_4\} \cdot \text{CH}_2\text{Cl}_2]$. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1dt00038a

In order to allow comparisons with the WOCl_4 , WOCl_3 , WSl_4 and WSl_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.

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

The reaction of $[\text{MoOCl}_3(\text{thf})_2]$ with $\text{MeS}(\text{CH}_2)_3\text{SMe}$ or $^i\text{PrS}(\text{CH}_2)_2\text{S}^i\text{Pr}$ in dry CH_2Cl_2 produced moisture sensitive, green $[\text{MoOCl}_3(\text{dithioether})]$ complexes. Structures of both species were determined and revealed that $[\text{MoOCl}_3\{\text{MeS}(\text{CH}_2)_3\text{SMe}\}]$ (six-membered chelate ring) was the *fac* isomer, whilst

The reaction of MoOCl_4 with $\text{MeS}(\text{CH}_2)_3\text{SMe}$ in dry toluene gave a green product with an identical IR spectrum to that of *mer*- $[\text{MoOCl}_3\{\text{MeS}(\text{CH}_2)_3\text{SMe}\}]$ 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 $\text{PhS}(\text{CH}_2)_2\text{SPh}$ failed to displace the thf from $[\text{MoOCl}_3(\text{thf})_2]$, but it reacted with a suspension of MoOCl_3 in CH_2Cl_2 to form brown $[\text{MoOCl}_3\{\text{PhS}(\text{CH}_2)_2\text{SPh}\}]$. The crystal structure of this complex showed it to be the *mer*-



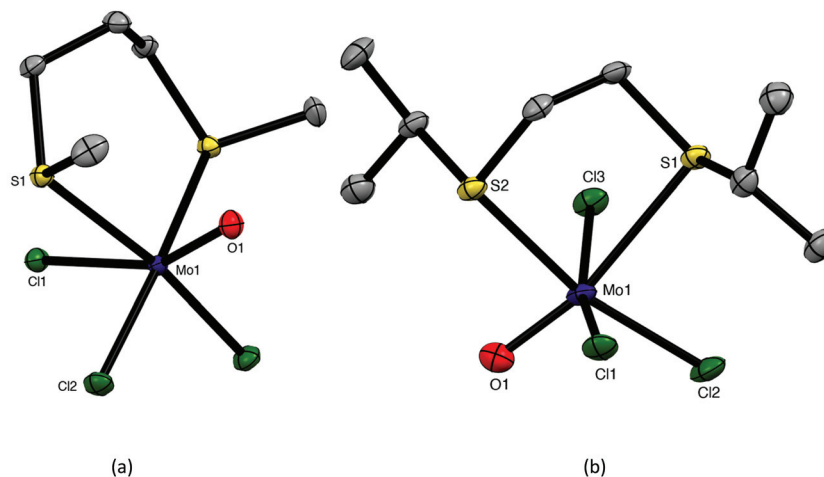


Fig. 1 Crystal structures of *fac*-[MoOCl₃{MeS(CH₂)₃SMe}] (a) and *mer*-[MoOCl₃{*t*PrS(CH₂)₂S^{*i*}Pr}] (b) showing the atom numbering scheme. Ellipsoids are shown at 50% probability, hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): (a) Mo1–Cl1 = 2.4540(2), Mo1–Cl2 = 2.3451(2), 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_{transO} = 2.911(1) Å, which compares with Mo–S_{transCl} = 2.531(1) Å, showing the high *trans*-influence of the Mo=O bond on the weaker aryl thioether donor ligand.

Brownish diselenoether complexes, [MoOCl₃{diselenoether}] (diselenoether = MeSe(CH₂)₂SeMe, MeSe(CH₂)₃SeMe), were obtained from reaction of the ligands with MoOCl₃ or

[MoOCl₃(thf)₂] in a 1 : 1 molar ratio, but *o*-C₆H₄(SeMe)₂ did not displace thf from [MoOCl₃(thf)₂]. The reaction of MeSeCH₂SeMe with MoOCl₃ produced a black oily decomposition product. However, the 1 : 1 reaction of *o*-C₆H₄(SeMe)₂ with MoOCl₃ in CH₂Cl₂ gave a brown product for which the microanalytical data indicated a 2 : 1 MoOCl₃ : diselenoether stoichiometry. This is discussed along with the similar ditelluroether complexes below. The X-ray crystal structure of *mer*-[MoOCl₃{MeSe(CH₂)₂SeMe}] was obtained (Fig. 3).

The five complexes described have room temperature magnetic moments of ~1.7 B.M., similar to other MoOCl₃ complexes,^{1,2,8,9} and close to the spin-only value expected for a

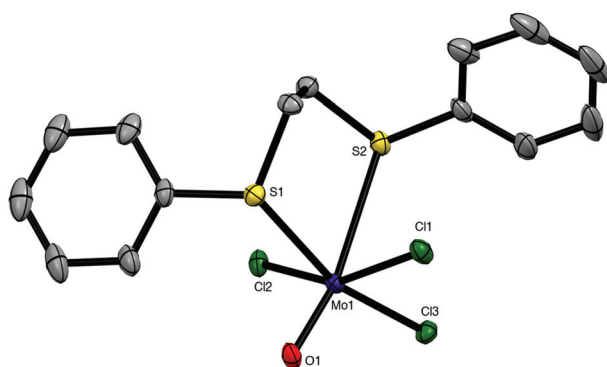


Fig. 2 Crystal structure of *mer*-[MoOCl₃{PhS(CH₂)₂SPh}] showing the atom numbering scheme. Ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Note that the O/Cl exhibited disorder, which was modelled with split atom sites, refined to occupancies of 0.53 : 0.47. Only 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).

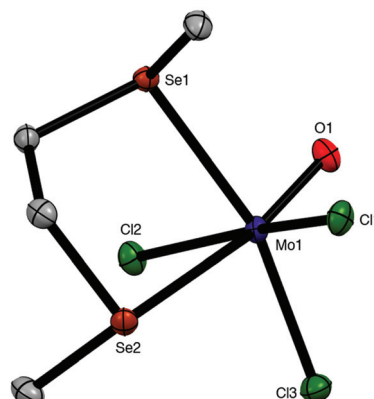


Fig. 3 Crystal structure of *mer*-[MoOCl₃{MeSe(CH₂)₂SeMe}] showing the atom numbering scheme. Ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Mo1–Cl1 = 2.3553(5), Mo1–Cl2 = 2.3517(5), Mo1–Cl3 = 2.3453(5), Mo1–O1 = 1.673(1), 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 $\nu(\text{Mo}=\text{O})$ in the range $950\text{--}980\text{ cm}^{-1}$, as well as strong overlapping bands at $355\text{--}300\text{ cm}^{-1}$ 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 $13\,000\text{--}14\,000\text{ cm}^{-1}$ and a second band or shoulder at $\sim 19\,000\text{--}21\,000\text{ cm}^{-1}$. 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 $>20\,000\text{ cm}^{-1}$, assigned as charge transfer bands, are less clearly resolved, but based upon the usual ligand electronegativities,²⁵ we assign the first intense feature ($\sim 21\,000\text{--}22\,000\text{ cm}^{-1}$) as $S/\text{Se}(\pi) \rightarrow \text{Mo}(\text{d})$ and the broad overlapping features at $\sim 25\,000\text{--}30\,000\text{ cm}^{-1}$ as $\text{Cl}(\pi) \rightarrow \text{Mo}(\text{d})$. The complexity of the electronic spectra in compounds of this type is shown by a combined UV/visible absorption, MCD and DFT study of $[\text{MoOCl}_3\{\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2\}]$;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 $[\text{MoOCl}_3(\text{thf})_2]$. 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, $\text{MoOCl}_3(\text{EMe}_2)$ (E = S, Se). There was no evidence for the formation of the 1 : 2 $[\text{MoOCl}_3(\text{EMe}_2)_2]$ complexes. Crystals of both $\text{MoOCl}_3(\text{EMe}_2)$ (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.* $[\{\text{MoOCl}_2(\text{EMe}_2)\}_2(\mu\text{-Cl}_2)]$ (E = S, Se).

The Mo=O bonds ($\sim 1.65\text{ \AA}$) are trans to asymmetrically bound (by $\sim 0.4\text{ \AA}$) bridging chlorides, with the EMe_2 groups arranged anti and perpendicular to the $\text{Mo}_2\text{Cl}_4\text{O}_2$ plane. The geometries are very similar to those found in $[\{\text{MoOCl}_2\text{L}\}_2(\mu\text{-Cl})_2]$ (L = $\text{O}=\text{C}(\text{H})\text{OME}$, thf, $\text{O}=\text{CET}_2$).^{27–29}

The reaction of MoOCl_3 with TeMe_2 in toluene produced brown $[\{\text{MoOCl}_2(\text{TeMe}_2)\}_2(\mu\text{-Cl})_2]$, 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, $[\text{MoOCl}_3(\text{EMe}_2)_2]$, 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 $[\text{MoOCl}_3(\text{dichalcogenoether})]$ monomers by their IR spectra, with the dimers showing a strong $\nu(\text{Mo}=\text{O})$ vibration in the range at $985\text{--}1005\text{ cm}^{-1}$ (higher frequency than in the monomeric $[\text{MoOCl}_3(\text{dichalcogenoether})]$ type) and terminal Mo–Cl modes $360\text{--}310\text{ cm}^{-1}$; weaker bands in the region $\sim 270\text{--}250\text{ cm}^{-1}$ and absent in the spectra of the $[\text{MoOCl}_3(\text{dichalcogenoether})]$ monomers, may be due to the chloride bridges. The magnetic moments of $\sim 1.7\text{ B.M./Mo}$ confirm the Mo(v) assignment and the absence of any magnetic interactions between the molybdenum centres.

Ditelluroethers

The reaction of $o\text{-C}_6\text{H}_4(\text{SeMe})_2$, $o\text{-C}_6\text{H}_4(\text{TeMe})_2$ and $\text{MeTe}(\text{CH}_2)_3\text{TeMe}$ (L–L) with MoOCl_3 in a 1 : 1 molar ratio in CH_2Cl_2 failed to produce the expected $[\text{MoOCl}_3(\text{L-L})]$ type complexes. Instead, dark brown complexes, identified by microanalysis as $[\{\text{MoOCl}_2\}_2(\text{L-L})]$, were obtained. Once isolated the compounds are very poorly soluble in CH_2Cl_2 and many attempts to

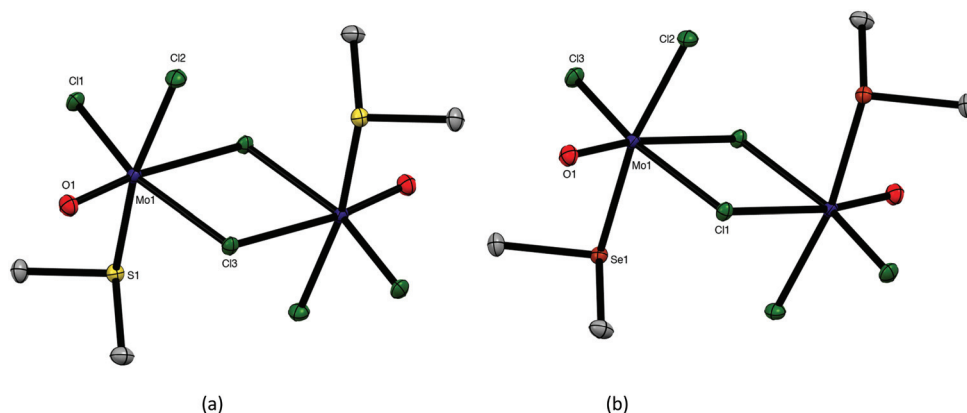


Fig. 4 Crystal structures of $[\{\text{MoOCl}_2(\text{SMe}_2)\}_2(\mu\text{-Cl})_2]$ (a) and $[\{\text{MoOCl}_2(\text{SeMe}_2)\}_2(\mu\text{-Cl})_2]$ (b) showing the atom numbering scheme. Ellipsoids are shown at 50% probability and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and 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 $\sim 14\,000\text{ cm}^{-1}$ ($^2\text{B}_2 \rightarrow ^2\text{E}$); a second more intense feature $18\,000\text{--}20\,000\text{ cm}^{-1}$ may be the second d-d band ($^2\text{B}_2 \rightarrow ^2\text{B}_1$), but given the lower electronegativity of Te²⁴ is probably the Te(π) \rightarrow Mo(d) charge transfer transition, which obscures the d-d band.

The IR spectra are significantly different to those of $[\text{MoOCl}_3(\text{L-L})]$ (L-L = dithioether or diphosphine),^{8,9} but are similar to those of $[\{\text{MoOCl}_2(\text{EMe}_2)\}_2(\mu\text{-Cl})_2]$. In particular, the $\nu(\text{Mo=O})$ vibrations are at higher frequency ($985\text{--}1000\text{ cm}^{-1}$), and in addition to several terminal $\nu(\text{Mo-Cl})$ modes $\sim 320\text{--}300\text{ cm}^{-1}$, also show a peak $\sim 250\text{ cm}^{-1}$, 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 $[\{\text{MoOCl}_2(\text{EMe}_2)\}_2(\mu\text{-Cl})_2]$, with the EMe_2 ligands replaced by bridging ditelluroethers, leading to the formulation as an oligomer, $[(\text{MoOCl}_2)_2(\mu\text{-Cl})_2(\mu\text{-ditelluroether})]_n$. 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 $[\{\text{MoOCl}_3\}_2\{o\text{-C}_6\text{H}_4(\text{TeMe})_2\}_n]$ also deposited a few dark green crystals, which were shown by X-ray crystallographic analysis to be the mixed valence complex, $[\text{Mo}^{\text{IV}}\text{Cl}\{o\text{-C}_6\text{H}_4(\text{TeMe})_2\}_2(\mu\text{-O})\text{Mo}^{\text{V}}\text{OCl}_4]$ (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 = $1.705(4)\text{ \AA}$ and Mo2–O1 = $2.368(4)\text{ \AA}$. These bond distances may be compared with the terminal Mo=O bond distance (Mo2–O2 = $1.659(5)\text{ \AA}$) 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) $[\text{MoCl}\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}_2(\mu\text{-O})(\text{MoOCl}_4)]$ is discussed below. The crystals of $[\text{Mo}^{\text{IV}}\text{Cl}\{o\text{-C}_6\text{H}_4(\text{TeMe})_2\}_2(\mu\text{-O})\text{Mo}^{\text{V}}\text{OCl}_4]$ result from a redox reaction, and its structure is not consistent with the spectroscopic data on the bulk $[\{\text{MoOCl}_3\}_2\{o\text{-C}_6\text{H}_4(\text{TeMe})_2\}_n]$. The failure to isolate mononuclear $[\text{MoOCl}_3(\text{L-L})]$ complexes with chelating *o*- $\text{C}_6\text{H}_4(\text{SeMe})_2$, *o*- $\text{C}_6\text{H}_4(\text{TeMe})_2$ and $\text{MeTe}(\text{CH}_2)_3\text{TeMe}$, seems analogous to the case of $[\{\text{MoOCl}_2(\text{EMe}_2)\}_2(\mu\text{-Cl})_2]$, where the Mo(v) centre prefers to form chloride bridges rather than coordinate to a second, weakly donating chalcogenoether.

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 $[\text{MoOCl}_3(\text{diphosphine})]$ (diphosphine = $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$, *cis*- $\text{Ph}_2\text{PCH=CHPPh}_2$, *o*- $\text{C}_6\text{H}_4(\text{PPh}_2)_2$) 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 $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ and *cis*- $\text{Ph}_2\text{PCH=CHPPh}_2$ 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 $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2$ complex as the *fac* isomer. In the present work we prepared the new complex $[\text{MoOCl}_3\{\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2\}]$ from $[\text{MoOCl}_3(\text{thf})_2]$ 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*- $[\text{MoOCl}_3(\text{dichalcogenoether})]$ described above.

The nature of the brown “isomers” is not entirely clear, but the original study⁸ of the red and brown forms of $[\text{MoOCl}_3\{\text{cis-Ph}_2\text{PCH=CHPPh}_2\}]$ 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

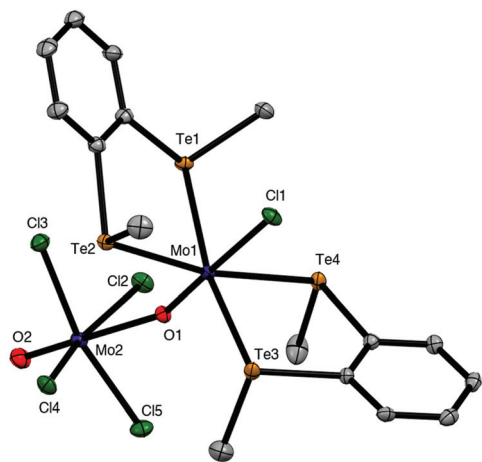


Fig. 5 Crystal structure of $[\text{MoCl}\{o\text{-C}_6\text{H}_4(\text{TeMe})_2\}_2(\mu\text{-O})\text{MoOCl}_4]\cdot\text{CH}_2\text{Cl}_2$ showing the atom numbering scheme. Ellipsoids are shown at 50% probability and hydrogen atoms and solvent are omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Mo1–Cl1 = $2.4486(7)$, Mo2–Cl2 = $2.3640(7)$ – $2.3930(7)$, Mo1–Te1 = $2.7432(3)$ – $2.7822(3)$, Mo1–O1 = $1.704(2)$, Mo2–O1 = $2.370(2)$, Mo2–O2 = $1.655(2)$, O2–Mo2–Cl2 = $78.4(1)$ – $82.2(1)$, 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 = $159.63.1(11)$.



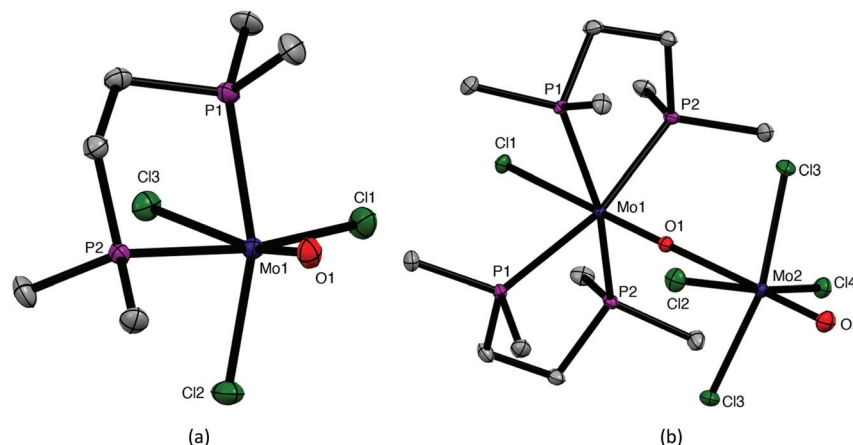


Fig. 6 Crystal structures of $[\text{MoOCl}_3(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)]$ (a) and $[\text{MoCl}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2(\mu\text{-O})\text{MoOCl}_4]$ (b) showing the atom numbering scheme. Ellipsoids are shown at 50% probability and hydrogen atoms are omitted 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 = 2.3573(4) – 2.3824(3), Cl1–Mo1–P1 = 78.92(2), Cl1–Mo1–P2 = 83.26(4), O2–Mo2–Cl2 = 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 $[\text{MoCl}_{2.5}\text{O}(\text{diphosphine})]$ were isolated in some systems^{7–9} and were formulated as the ionic Mo(IV)–Mo(V) species $[\text{Mo}^{\text{IV}}\text{OCl}(\text{diphosphine})_2][\text{Mo}^{\text{V}}\text{OCl}_4]$, based upon spectroscopic data, and the observation that metathesis with NaBPh_4 gave $[\text{Mo}^{\text{IV}}\text{OCl}(\text{diphosphine})_2][\text{BPh}_4]$.

During attempts to grow crystals of orange-yellow $[\text{MoOCl}_3(\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2)]$, a few deep purple crystals were also isolated that were confirmed by an X-ray structure (Fig. 6) to be $[\text{MoCl}(\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2)_2(\mu\text{-O})(\text{MoOCl}_4)]$, analogous to $[\text{MoCl}(\text{o-C}_6\text{H}_4(\text{TeMe})_2)_2(\mu\text{-O})(\text{MoOCl}_4)]$ 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, $[\text{Mo}^{\text{IV}}\text{OCl}(\text{diphosphine})_2][\text{Mo}^{\text{V}}\text{OCl}_4]$. 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*- $[\text{MoOCl}_3(\text{PMe}_3)_2]$ was obtained by Limberg *et al.*¹¹ as one product from reaction of the alkoxide complex, $[\text{Cl}_2\text{OMo}(\mu\text{-OEt})_2(\mu\text{-EtOH})\text{MoOCl}_2]$ with PMe_3 ; we obtained the same complex directly from $[\text{MoOCl}_3(\text{thf})_2]$ 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,

$[\{\text{MoOCl}_2(\text{EMe}_2)_2\}_2(\mu\text{-Cl})_2]$ (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 $\text{O}(\text{SiMe}_3)_2$ 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 $\text{O}(\text{SiMe}_3)_2$,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- $[\text{MoOCl}_3(\text{thf})_2]$

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*-[MoOCl₃{MeS(CH₂)₃SMe}]**

Method 1. [MoOCl₃(thf)₂] (0.150 g, 0.41 mmol) was suspended in CH₂Cl₂ (3 mL) and a solution of MeS(CH₂)₃SMe (0.056 g, 0.41 mmol) in CH₂Cl₂ (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 then precipitated, was filtered off and dried *in vacuo*. Yield: 0.070 g, 40%. Required for C₅H₁₂Cl₃MoOS₂ (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. MoOCl₄ (0.150 g, 0.59 mmol) was suspended in toluene (5 mL) and a solution of MeS(CH₂)₃SMe (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 C₅H₁₂Cl₃MoOS₂·0.2C₇H₈ (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 CH₂Cl₂.

***mer*-[MoOCl₃{ⁱPrS(CH₂)₂SⁱPr}]**

[MoOCl₃{ⁱPrS(CH₂)₂SⁱPr}] was prepared similarly to Method 1 above, and isolated as a pale green solid. Yield: 62%. Required for C₈H₁₈Cl₃MoOS₂ (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*-[MoOCl₃{PhS(CH₂)₂SPh}]**

MoOCl₃ (0.150 g, 0.69 mmol) was suspended in CH₂Cl₂ (3 mL) and a solution of PhS(CH₂)₂SPh (0.170 g, 0.69 mmol) in CH₂Cl₂ (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 C₁₄H₁₄Cl₃MoOS₂ (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.

[{MoOCl₂(SMe₂)₂}(μ-Cl)₂]

MoOCl₃ (0.150 g, 0.69 mmol) was suspended in CH₂Cl₂ (3 mL) and a solution of SMe₂ (0.085 g, 1.38 mmol) in CH₂Cl₂ (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 C₄H₁₂Cl₆Mo₂O₂S₂ (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 spec-

trum (diffuse reflectance) ν/cm^{-1} : 26 000, 22 300, 19 600 sh, 13 800. μ_{eff} : 1.72 B.M./Mo.

[{MoOCl₂(SeMe₂)₂}(μ-Cl)₂]

MoOCl₃ (0.150 g, 0.69 mmol) was suspended in CH₂Cl₂ (3 mL) and a solution of SeMe₂ (0.150 g, 1.38 mmol) in CH₂Cl₂ (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 C₄H₁₂Cl₆Mo₂O₂Se₂ (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*-[MoOCl₃{MeSe(CH₂)₂SeMe}]**

[MoOCl₃(thf)₂] (0.150 g, 0.41 mmol) was suspended in CH₂Cl₂ (3 mL) and a solution of MeSe(CH₂)₃SeMe (0.089 g, 0.41 mmol) in CH₂Cl₂ (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 CH₂Cl₂ were dark green. Yield: 0.160 g, 90%. Required for C₄H₁₀Cl₃MoOSe₂ (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.

[MoOCl₃{MeSe(CH₂)₃SeMe}]

MoOCl₃ (0.150 g, 0.69 mmol) was suspended in CH₂Cl₂ (3 mL) and a solution of MeSe(CH₂)₃SeMe (0.158 g, 0.69 mmol) in CH₂Cl₂ (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 CH₂Cl₂ solution. Yield: 0.178 g, 58%. Required for C₅H₁₂Cl₃MoOSe₂·CH₂Cl₂ (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.

[(MoOCl₃)₂{*o*-C₆H₄(SeMe)₂}]_n

MoOCl₃ (0.150 g, 0.69 mmol) was suspended in dichloromethane (3 mL) and a solution of *o*-C₆H₄(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 OEt₂ (3 × 5 mL), then the brown-pink solid was dried *in vacuo*. Yield: 0.170 g, 53%. Required for C₈H₁₀Cl₆Mo₂O₂Se₂ (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.



$[\{\text{MoOCl}_2(\text{TeMe}_2)\}_2(\mu\text{-Cl})_2]$

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 $\text{C}_4\text{H}_{12}\text{Cl}_6\text{Mo}_2\text{O}_2\text{Te}_2$ (751.93): C, 6.39; H, 1.61. Found: C, 6.76; H, 2.06%. IR spectrum (Nujol, ν/cm^{-1}): 985 s br $\text{Mo}=\text{O}$, 327, 302 s br, 256 m $\text{Mo}-\text{Cl}$. 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.

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

MoOCl_3 (0.150 g, 0.69 mmol) was suspended in dichloromethane (3 mL) and a solution of $\text{MeTe}(\text{CH}_2)_3\text{TeMe}$ (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 $\text{C}_5\text{H}_{12}\text{Cl}_6\text{Mo}_2\text{O}_2\text{Te}_2$ (763.95): C, 7.86; H, 1.58. Found: C, 7.20; H, 1.38%. IR spectrum (Nujol, ν/cm^{-1}): 988 m $\text{Mo}=\text{O}$, 303 s, 292 m, 249 m $\text{Mo}-\text{Cl}$. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1} : 26 500, 21 700, 18 600, ~ 13 000. μ_{eff} : 1.68 B.M./Mo.

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

MoOCl_3 (0.150 g, 0.69 mmol) was suspended in dichloromethane (3 mL) and a solution of $o\text{-C}_6\text{H}_4(\text{TeMe})_2$ (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 $\text{C}_8\text{H}_{10}\text{Cl}_6\text{Mo}_2\text{O}_2\text{Te}_2$ (797.96): C, 12.04; H, 1.26. Found: C, 12.27; H, 1.43%. IR spectrum (Nujol, ν/cm^{-1}): 992 s br $\text{Mo}=\text{O}$, 343 m, 328 m, 302 s, 254 m $\text{Mo}-\text{Cl}$. 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- $[\text{MoOCl}_3(\text{PMe}_3)_2]$

$[\text{MoOCl}_3(\text{thf})_2]$ (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 $\text{C}_6\text{H}_{18}\text{Cl}_3\text{MoOP}_2$ (370.45): C, 19.45; H, 4.90. Found: C, 19.28; H, 4.74%. IR spectrum (Nujol, ν/cm^{-1}): 957 s $\text{Mo}=\text{O}$, 352 sh, 324 s, 305 m $\text{Mo}-\text{Cl}$. UV/Vis spectrum (diffuse reflectance) ν/cm^{-1} : 29 600, 26 500, 21 600, 20 500 sh, 15 500.

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

$[\text{MoOCl}_3(\text{thf})_2]$ (0.150 g, 0.41 mmol) was suspended in CH_2Cl_2 (3 mL) and a solution of $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (0.165 g, 0.41 mmol) in CH_2Cl_2 (3 mL) was added slowly and the solu-

tion 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 $\text{C}_6\text{H}_{16}\text{Cl}_3\text{MoOP}_2$ (368.44): C, 19.56; H, 4.38. Found: C, 19.83; H, 4.26%. IR spectrum (Nujol, ν/cm^{-1}): 951 s $\text{Mo}=\text{O}$, 362 m, 325 s, 306 s $\text{Mo}-\text{Cl}$. 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 ($\lambda = 0.71073$ 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 Olex2⁴⁴ 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 $[\text{MoOCl}_3(\text{thf})_2]$ and the ligands in anhydrous CH_2Cl_2 solution. The more weakly coordinating $\text{PhS}(\text{CH}_2)_2\text{SPh}$, 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 $[\text{MoOCl}_3(\text{dithioether})]$, 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 $[\text{MoO}_2\text{X}_2(\text{dithioether})]$ ($\text{X} = \text{Cl}$ 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 $[\{\text{MoOCl}_2(\text{E}'\text{Me}_2)\}_2(\mu\text{-Cl})_2]$ ($\text{E}' = \text{S}, \text{Se}$), rather than by coordinating a second neutral donor ligand. The same explanation accounts for the formation of oligomeric complexes, $[(\text{MoOCl}_3)_2(\text{L}-\text{L})]_n$ with $o\text{-C}_6\text{H}_4(\text{SeMe})_2$, $o\text{-C}_6\text{H}_4(\text{TeMe})_2$ and $\text{MeTe}(\text{CH}_2)_3\text{TeMe}$, 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 $o\text{-C}_6\text{H}_4$ -backbones, the presence of aryl groups makes these ligands weaker donors to hard metal centres – compare $\text{PhS}(\text{CH}_2)_2\text{SPh}$ and $^i\text{PrS}(\text{CH}_2)_2\text{S}^i\text{Pr}$. 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*-C₆H₄-based group 15 ligands, where *o*-C₆H₄(PMe₂)₂ or *o*-C₆H₄(AsMe₂)₂ can produce seven- or eight-coordination in tungsten(vi) complexes, such as [WOCl₄{*o*-C₆H₄(PMe₂)₂}] or [WF₄{*o*-C₆H₄(PMe₂)₂}]₂²⁺.^{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 NbCl₄,⁴⁷ NbCl₅⁴⁸ and TaCl₅,⁴⁸ 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-C₆H₄(TeMe)₂}₂(μ-O)Mo^VOCl₄] and of the diphosphine analogue [Mo^{IV}Cl{Me₂P(CH₂)₂PMe₂}₂(μ-O)(Mo^VOCl₄)]; 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 MoOCl₃-chalcogenoether 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 MoS₂ 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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