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# Tungsten(VI) and Molybdenum(VI) Complexes with Soft Thioether Ligand Coordination – Synthesis, Spectroscopic and Structural Studies

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Reaction of $WX_6$ (X = Cl or Br) with $O(SiMe_3)_2$ in $CH_2Cl_2$, followed by addition of MeCN and a further equivalent of $O(SiMe_3)_2$ in $CH_2Cl_2$ gives $[WO_2X_2(MeCN)_2]$ in situ, which subsequently react with the dithioethers $MeS(CH_2)_2SMe$, $iPrS(CH_2)_2SiPr$ or 1,4-dithiane to afford the first series of $W^{VI}$ thioether complexes, $[WO_2X_2(\text{dithioether})]$. The very moisture-sensitive yellow complexes have been characterised by microanalysis, IR, $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopy, which indicate *cis*-dioxido and *trans*-dihalide arrangements in the monomers with two thioether donor atoms completing the very distorted octahedral geometry (confirmed by a crystal structure of $[WO_2Cl_2\{iPrS(CH_2)_2SiPr\}]$). The strongly polymerised $WO_2X_2$ compounds themselves are not useful synthons for the preparation of the $W^{VI}$ thioether complexes and substitution of the dimethoxyethane ligand in $[WO_2Cl_2\{MeO(CH_2)_2OMe\}]$ by dithioethers is also incomplete. Molybdenum(VI) dioxidodichloride thioether complexes of the form $[MoO_2Cl_2(L)]$ (L = $iPrS(CH_2)_2SiPr$, 1,4-dithiane, $\kappa^2$-[15]ane$S_2O_3$, $\kappa^2$-[14]ane$S_4$ and $\kappa^2$-[12]ane$S_4$) ([15]ane$S_2O_3$ = 1,4-dithia-7,10,13-trioxacyclopentadecane, [14]ane$S_4$ = 1,4,8,11-tetrathiacyclotetradecane, [12]ane$S_4$ = 1,4,7,10-tetrathiacyclododecane) and the unusual dinuclear $[Mo_2O_4Cl_4\{o\text{-}C_6H_4(CH_2SMe)_2\}_2]$ are obtained by direct treatment of $MoO_2Cl_2$ with the appropriate ligand. The $[Mo_2O_4Cl_4\{o\text{-}C_6H_4(CH_2SMe)_2\}_2]$ adopts an unexpected metallocyclic structure with *cis*-$MoCl_2$ units and bridging bidentate dithioether (confirmed crystallographically). The structure of a new polymorph of $[WO_2Cl_2\{MeO(CH_2)_2OMe\}]$ is also described.

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## Introduction

While thioether coordination chemistry is dominated by complexes involving late transition metals in medium oxidation states, we and others have shown that under appropriate experimental conditions these soft and modest σ-donor ligands can also form complexes with hard, medium and high oxidation state early transition metal ions,[1] including for example $Sc^{III}$,[2] $La^{III}$ and $U^{III}$ [3] complexes with the trithioether macrocycle [9]ane$S_3$, and $Ti^{IV}$, $Zr^{IV}$, $Hf^{IV}$, $V^{III,IV}$ and $Cr^{III}$ complexes with both acyclic and macrocyclic thioethers.[4–7] We have also established that the choice of chalcogenoether ligand architecture plays a very important role in facilitating the stabilisation of these hard/soft metal/ligand combinations, with dimethylene-linkages between the S atoms leading to increased stability, and macrocyclic frameworks further stabilising the complexes. Further, we have shown that reaction of $Ti^{IV}$, $Cr^{III}$ and $V^{III}$ precursors with mixed thia-oxa macrocyclic ligands involving $C_2$-linkages between adjacent heteroatoms results in preferential coordination via the softer S-donor groups – an observation we have attributed to destabilisation of the M–O(ether) coordination due to ring strain in the five-membered chelate rings.[8,9]

The coordination chemistry of molybdenum and tungsten continues to attract considerable interest owing to the roles that these elements play in biologically important species, the molybdo- and tungsto-enzymes,[10] and also due to the use of high oxidation state Mo and W species in ring-opening metathesis catalysis.[11] The chemistry of medium and high oxidation state Mo centres with neutral sulfur donor ligands remains little studied, with some examples of $Mo^{III,IV,V}$ thioether complexes.[12–19] In 2004 we reported the preparations and spectroscopic characterisation of the first examples of $Mo^{VI}$ complexes involving thioether and selenoether coordination, including crystal structure determinations of representative examples of the form $[MoO_2X_2\{RS(CH_2)_2SR\}]$ (X = Cl or Br; R = Me or Et) which confirmed *cis*-oxido ligands, *trans*-halides and bidentate chelating dithioether.[20] We found that these species form only for a very limited range of dichalcogenoether ligands – $Me_2S$, $MeS(CH_2)_3SMe$, MeSCH=CHSMe and even the $PhS(CH_2)_2SPh$ all lead to reduction of the metal and give no evidence for $Mo^{VI}$ thioether complexes. Medium and high oxidation state tungsten thioether complexes

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are even less explored than with molybdenum and, whereas direct reaction of $MoO_2X_2$ with the $RS(CH_2)_2SR$ (R = alkyl) in $CH_2Cl_2$ gives the requisite complexes, $WO_2X_2$ (X = Cl or Br) do not provide viable entries to this chemistry because they are unreactive and strongly polymerised.[21] We were interested in trying to extend the range of thioether and selenoether complexes of the hard, oxophilic $Mo^{VI}$ ion, to understand how the ligand donor properties and architecture influence the stability of the complexes, and also in developing synthetic routes to $W^{VI}$ analogues.

In order to investigate the chemistry of dioxidotungsten(VI) with thioether ligands and to widen the presently very limited range of thioether ligand types capable of coordinating to dioxidomolybdenum(VI), we report here the results of our studies on the preparations and properties of the first series of $W^{VI}$ dihalidedioxido complexes involving dithioether ligands and several new $Mo^{VI}$ dihalidedioxido complexes incorporating a range of ligand architectures and both thioether and mixed thia/oxa-macrocyclic ligands. The crystal structures of $[Mo_2O_4Cl_4\{o\text{-}C_6H_4(CH_2SMe)_2\}_2]$, $[WO_2Cl_2\{i\text{Pr}S(CH_2)_2Si\text{Pr}\}]$ and a new polymorph of $[WO_2Cl_2\{MeO(CH_2)_2OMe\}]$ are reported and discussed.

## Results and Discussion

### Tungsten Thioether Complexes

Development of a synthetic route to give $W^{VI}$ complexes in respectable yields is much more difficult than for $Mo^{VI}$. The strongly polymerised nature of $WO_2Cl_2$[21] means that this is usually not a useful synthon for coordination complexes of $WO_2Cl_2$, hence alternative precursor compounds were sought. We have shown very recently that $WCl_6$ or $WBr_6$ react with two mol. equivs. of $O(SiMe_3)_2$ in $CH_2Cl_2$, followed by addition of two mol. equivs. of $OPR_3$ (R = Pr or Me) or one molar equivalent of $Ph_2P(O)(CH_2)_nP(O)Ph_2$ (n = 1 or 2) or $o\text{-}C_6H_4(P(O)Ph_2)_2$, to give the distorted octahedral $[WO_2X_2(OPR_3)_2]$, $[WO_2X_2\{Ph_2P(O)(CH_2)_nP(O)Ph_2\}]$ or $[WO_2X_2\{o\text{-}C_6H_4(P(O)Ph_2)_2\}]$ respectively in good yields.[22] However, using this approach with $MeS(CH_2)_2SMe$ in place of the $OPR_3$ ligand gave mostly insoluble, polymeric $WO_2Cl_2$ (IR evidence) with only very weak bands in the IR spectrum corresponding to $[WO_2Cl_2(\text{dithioether})]$. We conclude from this that soft thioether ligands have less affinity for the hard $W^{VI}$ and are more dissociated in solution than the phosphane oxide complexes of $W^{VI}$, hence while the phosphane oxide "traps" the $WO_2Cl_2$ as a molecular complex, in the thioether ligand systems $(WO_2Cl_2)_n$ precipitates from the solution, removing it from the reaction.

Schulzke et al. have described the preparation of the only known thioether adduct of $W^{VI}$, $[WO_2Cl_2\{MeS(CH_2)_2SMe\}]$ by a closely related route, involving reaction of $WOCl_4$ with one molar equivalent of $O(SiMe_3)_2$ in $CH_2Cl_2$ solution, followed by addition of the dithioether. While the crystal structure of the distorted octahedral species was reported, no solution spectroscopic data were presented.[23] We have also investigated this reaction and in our hands it reproducibly leads to formation of a white solid which was very poorly soluble. While weak ν(W=O) and ν(W-Cl) bands consistent with the literature data were evident in the IR spectra of these products, strong, broad absorptions around 600–700 $cm^{-1}$ were also evident, which are indicative of polymeric $WO_2Cl_2$. The $^1H$ NMR spectra of the $CDCl_3$ soluble component of our reaction products from repeated attempts at this reaction consistently showed significant amounts of uncoordinated dithioether, and only very minor resonances for $[WO_2Cl_2\{MeS(CH_2)_2SMe\}]$ (ca. 10–15% by integration). Using $i\text{Pr}S(CH_2)_2Si\text{Pr}$ gave similar results, although we were able to grow light yellow crystals of $[WO_2Cl_2\{i\text{Pr}S(CH_2)_2Si\text{Pr}\}]$ by filtering the reaction mixture and cooling a $CH_2Cl_2$ solution of the complex in the freezer, however the yield based on tungsten was still very low. The crystal structure confirms the formation of the distorted octahedral $[WO_2Cl_2\{i\text{Pr}S(CH_2)_2Si\text{Pr}\}]$ (Figure 1, Table 1) in which the W atom is bound to *cis*-oxido groups, *trans*-Cl ligands and the two S donor atoms of a chelating dithioether. An alternative description of the core geometry would be a distorted tetrahedral primary $O_2Cl_2$ coordination with additional weak $S_2$ coordination completing a very distorted six-coordination. The W–S bond lengths are 2.759(2) and 2.768(2) Å and compare with $d$(W–S) = 2.748 and 2.752 Å in $[WO_2Cl_2\{MeS(CH_2)_2SMe\}]$.[23] The complex adopts a DL configuration with the isopropyl substituents lying on opposite sides of the $WO_2S_2$ plane. The S–W–S chelate bite angle is 77.34(5)°, very similar to that in $[WO_2Cl_2\{MeS(CH_2)_2SMe\}]$ (77.4°) and $[MoO_2Cl_2\{RS(CH_2)_2SR\}]$; R = Me: 77.29(3)°; R = Et: 78.01(2)°.[20]

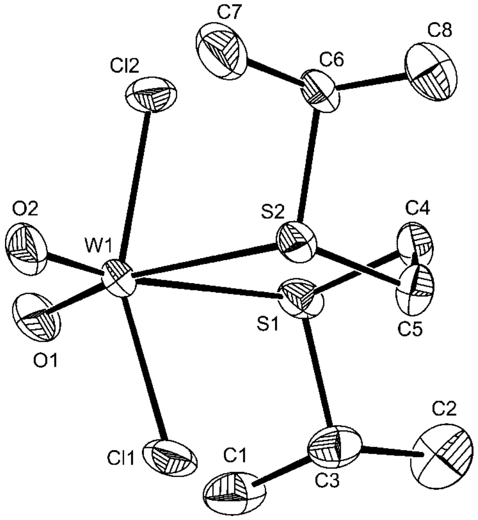

Figure 1. View of the structure of the $[WO_2Cl_2\{i\text{Pr}S(CH_2)_2Si\text{Pr}\}]$ with numbering scheme adopted. Ellipsoids are drawn at 50% probability level and H atoms are omitted for clarity.

Small pale yellow crystals of the $Mo^{VI}$ analogue (below), $[MoO_2Cl_2\{i\text{Pr}S(CH_2)_2Si\text{Pr}\}]$, were also obtained from $CH_2Cl_2$ solution. The structure determination shows that this compound is isostructural with the tungsten species ($C_8H_{18}Cl_2MoO_2S_2$, $MW$ = 377.18, $a$ = 11.838(2), $b$ = 13.034(2), $c$ = 18.951(3) Å, $\alpha = \beta = \gamma$ = 90°, $V$ =

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Table 1. Selected bond lengths [Å] and angles [°] for [$WO_2Cl_2\{i PrS(CH_2)_2S i Pr\}$].

| | | | |
|---|---|---|---|
| W1–O1 | 1.726(6) | W1–O2 | 1.741(6) |
| W1–Cl1 | 2.345(2) | W1–Cl2 | 2.334(2) |
| W1–S1 | 2.768(2) | W1–S2 | 2.759(2) |
| O1–W1–O2 | 105.9(3) | O1–W1–Cl2 | 96.9(2) |
| O2–W1–Cl2 | 97.9(2) | O1–W1–Cl1 | 97.8(2) |
| O2–W1–Cl1 | 97.2(2) | Cl2–W1–Cl1 | 155.17(8) |
| O1–W1–S2 | 163.7(2) | O2–W1–S2 | 89.9(2) |
| Cl2–W1–S2 | 84.51(6) | Cl1–W1–S2 | 75.94(7) |
| O1–W1–S1 | 87.2(2) | O2–W1–S1 | 166.6(2) |
| Cl2–W1–S1 | 76.78(8) | Cl1–W1–S1 | 84.03(6) |
| S2–W1–S1 | 77.34(5) | | |

2924.3(8) Å$^3$, $Z = 8$), although the crystal quality was poorer, giving rather high $R_1$ and $wR_2$ values ($R_1$ [$I_o > 2\sigma(I_o)$] = 0.0921, $wR_2$ [$I_o > 2\sigma(I_o)$] = 0.1814), with $d$(Mo–S) = 2.764(3), 2.783(4), $d$(Mo–O) = 1.673(12), 1.705(11), $d$(Mo–Cl) = 2.341(4), 2.345(4) Å and S1–Mo–S2 = 77.31(9)°.

The very poor yields from these tungsten reactions prompted further efforts to avoid formation of the insoluble by-products. We explored using the soluble and well-defined [$WO_2Cl_2\{MeO(CH_2)_2OMe\}$],[24] however addition of the dithioether to a $CH_2Cl_2$ solution of this compound resulted in incomplete substitution of the dimethoxyethane, while treatment of [$WOCl_4$] with one molar equivalent of $O(SiMe_3)_2$ in refluxing octane solution, followed by addition of dithioether gave light yellow insoluble, polymeric products with no evidence for thioether coordination. One route to [$WO_2X_2$(dithioether)] (X = Cl or Br) was via reaction of [$WOX_4$] with $O(SiMe_3)_2$ in MeCN solution,[25] to give a colourless solution of [$WO_2X_2(MeCN)_2$] in situ, followed by concentration of the solvent by ca. 50% in vacuo and addition of a solution of one molar equivalent of $RS(CH_2)_2SR$ (R = Me or *i*Pr) in anhydrous $CH_2Cl_2$. These reactions gave the desired compounds in good yields as yellow solids following removal of the solvent in vacuo and washing with hexane, with minimal polymer formation (and this could be removed by careful recrystallisation of the thioether complex from anhydrous $CH_2Cl_2$). The key to the success of this route is the clean formation of the molecular [$WO_2X_2(MeCN)_2$] intermediates which seem to prevent the generation of the insoluble polymers. Using a similar approach we have found that the complexes may also be made in good yield from $WX_6$. Thus, reaction of $WX_6$ with one molar equivalent of $O(SiMe_3)_2$ in $CH_2Cl_2$ solution (to form $WOX_4$ in situ), followed by addition of ca. 0.5 mL MeCN, then another molar equivalent of $O(SiMe_3)_2$, and finally one equivalent of the dithioether gives yellow/brown solutions. Concentration of the solution in vacuo and cooling to ca. –15 °C (freezer) leads to deposition of the complexes as yellow (Cl) or yellow/brown (Br) precipitates. This approach was also used to obtain the 1,4-dithiane complexes, [$WO_2X_2$(1,4-dithiane)]. We note that the dithiane complexes are relatively stable when stored as solids under a dry atmosphere, whereas the acyclic dithioether complexes are extremely moisture-sensitive and they also darken, turning blue-green over a few days, even when stored as powdered solids in the glove-box. The most sensitive is the light yellow [$WO_2Cl_2\{i PrS(CH_2)_2S i Pr\}$] which develops an intense blue/green colour instantly on exposure to air and solutions of which become dark blue with trace water.

The IR spectra of the six W$^{VI}$ dithioether complexes show two strong ν(W=O) and one strong ν(W–X) bands, consistent with mutually *cis*-O and *trans*-X ligands. These are ca. 20–30 cm$^{-1}$ to high frequency of the corresponding Mo species.[20] This is typical of other series of $MO_2X_2$ compounds, e.g. [$MO_2X_2(OPR_3)_2$] M = Mo or W,[23] although the difference is less in the phosphane oxide complexes. The higher frequency ν(M=O] for W is consistent with stronger metal-oxido bonds. The $^1$H and $^{13}$C{$^1$H} NMR spectra show small high frequency coordination shifts, although the patterns are indicative of fast pyramidal inversion. This was proven by obtaining spectra of representative examples at low temperature, whereupon resonances attributable to individual invertomers were observed. Samples containing added free ligand show resolved resonances for both coordinated and "free" ligand, demonstrating that intermolecular ligand exchange is slow on the NMR time scales at ambient temperatures.

In the course of our attempts to utilise [$WO_2Cl_2\{MeO(CH_2)_2OMe\}$] as a molecular synthon for W$^{VI}$ thioether complexes we obtained colourless crystals. A structure analysis (120 K) revealed that these were in fact the [$WO_2Cl_2\{MeO(CH_2)_2OMe\}$] precursor. A crystal structure of this species has been reported previously,[24] and while our cell is related to the published cell, we were unable to refine the structure using the published cell. Hence we conclude that this is a second polymorph. The new data refined very well, revealing (Figure 2, Table 2) a very similar distorted octahedral geometry based upon a W atom coordinated to *cis*-oxido groups, *trans*-Cl atoms and a chelating dimethoxyethane, giving a DL configuration. The bond lengths and angles are similar to those in the published structure.[24]

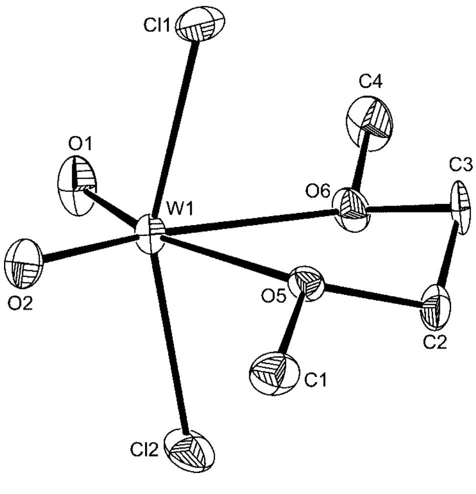

Figure 2. View of the structure of one of the two crystallographically independent [$WO_2Cl_2\{MeO(CH_2)_2OMe\}$] molecules in the asymmetric unit with numbering scheme adopted. Ellipsoids are drawn at 50% probability level and H atoms are omitted for clarity. The second molecule is very similar.

Table 2. Selected bond lengths [Å] and angles [°] for $[WO_2Cl_2\{MeO(CH_2)_2OMe\}]$.

| | | | |
|---|---|---|---|
| W1–O2 | 1.705(3) | W1–O1 | 1.706(4) |
| W1–O5 | 2.274(3) | W1–O6 | 2.288(3) |
| W1–Cl2 | 2.3375(14) | W1–Cl1 | 2.3563(13) |
| W2–O4 | 1.707(4) | W2–O3 | 1.708(4) |
| W2–O7 | 2.260(3) | W2–O8 | 2.286(3) |
| W2–Cl3 | 2.3513(13) | W2–Cl4 | 2.3556(14) |
| O2–W1–O1 | 104.23(17) | O2–W1–O5 | 94.49(14) |
| O1–W1–O5 | 161.26(14) | O2–W1–O6 | 165.17(15) |
| O1–W1–O6 | 90.60(14) | O5–W1–O6 | 70.67(12) |
| O2–W1–Cl2 | 96.87(12) | O1–W1–Cl2 | 97.74(13) |
| O5–W1–Cl2 | 80.60(9) | O6–W1–Cl2 | 80.93(9) |
| O2–W1–Cl1 | 96.81(12) | O1–W1–Cl1 | 96.69(13) |
| O5–W1–Cl1 | 79.98(9) | O6–W1–Cl1 | 81.12(9) |
| Cl2–W1–Cl1 | 157.01(5) | O4–W2–O3 | 104.78(18) |
| O4–W2–O7 | 92.71(15) | O3–W2–O7 | 162.52(15) |
| O4–W2–O8 | 163.50(15) | O3–W2–O8 | 91.72(15) |
| O7–W2–O8 | 70.80(12) | O4–W2–Cl3 | 96.63(13) |
| O3–W2–Cl3 | 96.94(13) | O7–W2–Cl3 | 80.65(9) |
| O8–W2–Cl3 | 80.67(9) | O4–W2–Cl4 | 96.25(13) |
| O3–W2–Cl4 | 96.37(13) | O7–W2–Cl4 | 81.57(9) |
| O8–W2–Cl4 | 82.08(9) | Cl3–W2–Cl4 | 158.46(5) |

## Molybdenum Thioether Complexes

The very unusual and highly sensitive metallocyclic compound $[Mo_2O_4Cl_4\{o\text{-}C_6H_4(CH_2SMe)_2\}_2]$ was prepared by treatment of $MoO_2Cl_2$ with one molar equivalent of $o\text{-}C_6H_4(CH_2SMe)_2$ in anhydrous $CH_2Cl_2$ or $Et_2O$. The formulation as a dinuclear complex follows from the spectroscopic and structural data. Two distinct ν(Mo–Cl) bands at 389 and 355 $cm^{-1}$ are evident, consistent with *cis*-Cl atoms, contrasting with the structures previously determined for $[MoO_2X_2\{RS(CH_2)_2SR\}]$ (X = Cl or Br; R = Me or Et) which have *trans*-halides and *cis*-oxido ligands.[20] The room temperature $^1H$ NMR spectrum of the $MoO_2Cl_2\text{-}o\text{-}C_6H_4(CH_2SMe)_2$ system is simple and little different from the thioether ligand itself. Upon cooling to 183 K the spectrum becomes more complex with high frequency coordination shifts with three $\delta$(Me) resonances evident at low temperature, consistent with the presence of stereoisomers, indicating that the compound is undergoing reversible ligand dissociation and fast pyramidal inversion under ambient conditions. In order to identify unambiguously the structure of this complex, light yellow crystals which were extremely air and moisture-sensitive, were obtained by cooling a solution containing the complex dissolved in $CH_2Cl_2$. The structure shows (Figure 3, Table 3) an unusual centrosymmetric dinuclear metallocyclic species in which each formally $Mo^{VI}$ is in a distorted octahedral geometry, coordinated to *cis*-oxido, *cis*-chlorido and *cis*-thioether groups. The $o\text{-}C_6H_4(CH_2SMe)_2$ ligands are not chelating, but instead function as bridging bidentates, with one S atom *trans* to O and one *trans* to Cl. This represents the first metallocyclic species incorporating the *o*-xylyl dithioether ligand. The different *trans* influences of these ligands are very clearly reflected in the disparate bond lengths within pairs of ligands, e.g. Mo–Cl 2.278(3), 2.423(3) Å, the longer bond being associated with the Cl *trans* to O. Even the Mo=O bond lengths are disparate due to the *trans* ligands; Mo–O 1.726(7), 1.777(7) Å. The Mo–S distances are *d*(Mo–S) = 2.604(3), 2.826(3) Å, with the exceptionally long Mo–S bond lying *trans* to the oxido ligand. These compare with *d*(Mo–S) = 2.73–2.77 Å in the other structurally characterised $Mo^{VI}$ thioether complexes.[20] The angles involving the mutually *cis* pairs of ligands also show considerable variation, O1–Mo–O2 105.3(4), Cl1–Mo–Cl2 91.21(12), S1–Mo–S2a 82.52(9)°, and the S–Mo–S angle is some 4–5° larger than in the chelate complexes $[MoO_2Cl_2\{RS(CH_2)_2SR\}]$ (R = Me or Et). This is the first $Mo^{VI}$ complex incorporating other than a dimethylene-linked dithioether ligand and follows from our earlier work which has shown that the $o\text{-}C_6H_4(CH_2EMe)_2$ (E = S, Se, Te) are remarkably effective ligands for a range of late transition metal ions.[26] The occurrence of a metallocyclic structure with bridging bidentate $o\text{-}C_6H_4(CH_2SMe)_2$ ligands in the case of the $Mo^{VI}$ species, may be a consequence of the sterically demanding *o*-xylyl linkage and the small radius of $Mo^{VI}$. We have shown previously that the E–M–E chelate angle in transition metal complexes involving the $o\text{-}C_6H_4(CH_2EMe)_2$ (E = S, Se or Te) ligands is invariably close to 100°.[26] In the dinuclear $[Mo_2O_4Cl_4\{o\text{-}C_6H_4(CH_2SMe)_2\}_2]$ the Me groups within a single dithioether ligand are *anti* (the SMe group coordinated to one Mo atom lies on the opposite side of the $MoO_2S_2$ coordination plane to that on the other Mo atom), while the coordinated SMe groups on each individual Mo atom are *syn* (Me substituents on a single Mo atom lie on the same side of the $MoO_2S_2$ plane) – Figure 3. A similar reaction using $MoO_2Cl_2$ with $o\text{-}C_6H_4(CH_2SeMe)_2$ led to reduction of the metal centre.

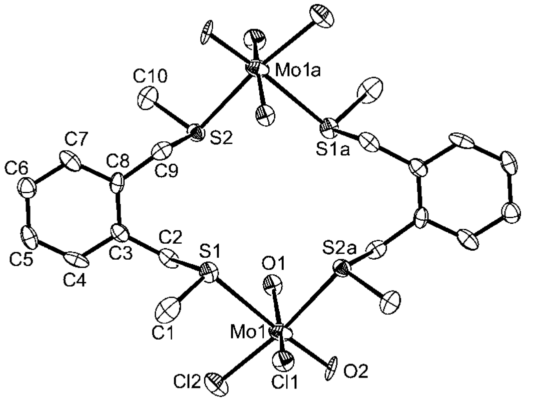

Figure 3. View of the structure of $[Mo_2O_4Cl_4\{o\text{-}C_6H_4(CH_2SMe)_2\}_2]$ with numbering scheme adopted. Ellipsoids are drawn at 50% probability level and H atoms are omitted for clarity. Symmetry operation *a* = 1 – *x*, 2 – *y*, –*z*.

The moisture-sensitive (macro)cyclic complexes of $Mo^{VI}$, $[MoO_2Cl_2(L)]$ (L = 1,4-dithiane, [15]ane$S_2O_3$, [12]ane$S_4$, [14]ane$S_4$), as well as $[MoO_2Cl_2\{iPrS(CH_2)_2SiPr\}]$ have been obtained similarly as light yellow solids in good yield. The isolated solids were stored in the glove box (<5 ppm $H_2O$) to prevent decomposition and have been characterised by microanalysis, IR, $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopy. The IR spectra of these Mo species show evidence

Table 3. Selected bond lengths [Å] and angles [°] for $[Mo_2O_4Cl_4\{o\text{-}C_6H_4(CH_2SMe)_2\}_2]$.[a]

| | | | |
|---|---|---|---|
| Mo1–O1 | 1.726(7) | Mo1–O2 | 1.777(7) |
| Mo1–Cl1 | 2.423(3) | Mo1–Cl2 | 2.278(3) |
| Mo1–S1 | 2.826(3) | Mo1–S2a | 2.604(3) |
| O1–Mo1–O2 | 105.3(4) | O1–Mo1–Cl2 | 102.7(3) |
| O2–Mo1–Cl2 | 99.8(3) | O1–Mo1–Cl1 | 150.5(3) |
| O2–Mo1–Cl1 | 97.6(2) | Cl2–Mo1–Cl1 | 91.21(12) |
| O1–Mo1–S2a | 81.9(3) | O2–Mo1–S2a | 91.1(3) |
| Cl2–Mo1–S2a | 166.45(13) | Cl1–Mo1–S2a | 79.32(10) |
| O1–Mo1–S1 | 78.6(3) | O2–Mo1–S1 | 172.1(3) |
| Cl2–Mo1–S1 | 85.89(12) | Cl1–Mo1–S1 | 76.64(10) |
| S2a–Mo1–S1 | 82.52(9) | | |

[a] Symmetry operation: $a = 1 - x, 2 - y, -z$.

for coordinated thioether ligand, and two strong bands in the region 900–950 $cm^{-1}$ indicative is the *cis*-dioxido unit. For the mononuclear species one strong absorption at ca. 350–360 $cm^{-1}$, suggesting mutually *trans* Cl ligands (and confirmed crystallographically for $[MoO_2Cl_2\{i\text{Pr}S(CH_2)_2S i\text{Pr}\}]$ – above). The $^1H$ NMR spectrum of $[MoO_2Cl_2\{i\text{Pr}S(CH_2)_2S i\text{Pr}\}]$ is simple, with resonances to high frequency of $i\text{Pr}S(CH_2)_2S i\text{Pr}$, consistent with coordination of the dithioether ligand to Mo, and fast pyramidal inversion – similar to the behaviour observed previously for $[MoO_2X_2\{RS(CH_2)_2SR\}]$.[20] Molybdenum-95 NMR spectroscopy reveals a resonance at $\delta = 225$ ppm, also in the same range as for $[MoO_2Cl_2\{RS(CH_2)_2SR\}]$ (R = Me or Et) described previously, and an X-ray structure determination showed that $[MoO_2Cl_2\{i\text{Pr}S(CH_2)_2S i\text{Pr}\}]$ is isostructural with its W analogue (above), based upon distorted octahedral Mo with *cis*-oxido and *trans*-Cl ligands and a chelating dithioether ligand. The dithiane complex $[MoO_2Cl_2(\text{dithiane})]$ exhibits a singlet methylene resonance in the $^1H$ NMR spectrum at ambient temperatures, indicating either bridging dithiane or reversible chelate ring opening. However, this broadens and splits into complex multiplets at low temperature (183 K), consistent with chelation for which an AA′BB′ pattern is expected.[27]

For the complex $[MoO_2Cl_2([15]aneS_2O_3)]$, assuming six-coordination, the possible macrocycle coordination modes are $S_2$, SO or $O_2$. The former would give rise to a symmetrical pattern, and hence five distinct $CH_2$ resonances, whereas SO or $O_2$ coordination would lead to a less symmetrical species and hence a more complicated $^1H$ NMR pattern. In fact, the $^1H$ NMR spectrum of $[MoO_2Cl_2([15]aneS_2O_3)]$ clearly reveals five resonances, and comparison with the spectrum of the parent macrocycle is also consistent with $S_2$ coordination to molybdenum. The $^{95}Mo$ NMR spectrum of $[MoO_2Cl_2([15]aneS_2O_3)]$ shows a single resonance at $\delta = 194$ ppm, slightly to low frequency of $[MoO_2Cl_2\{MeS(CH_2)_2SMe\}]$ ($\delta = 210$ ppm) and $[MoO_2Cl_2\{EtS(CH_2)_2SEt\}]$ ($\delta = 225$ ppm).[20]

The poor solubilities of the yellow $[MoO_2Cl_2([n]aneS_4)]$ ($n$ = 12 or 14) in solvents which would not react with the complex hindered attempts to obtain solution spectroscopic data for these species. However, the IR spectra are consistent with a $Cl_2O_2S_2$ coordination sphere at $Mo^{VI}$ in $[MoO_2Cl_2([n]aneS_4)]$ ($n$ = 12 or 14), with *cis*-oxido ligands and *trans*-chlorines; microanalyses confirm the formulation. The reaction of $MoO_2Cl_2$ with $[14]aneS_4$ has been mentioned previously.[19]

## Conclusions

The first series of dioxidotungsten(VI) complexes with soft dithioethers has been prepared in good yield and characterised structurally and spectroscopically. Successful formation of these compounds is very sensitive to the precise reaction conditions, and they appear to be much more reactive than their $Mo^{VI}$ analogues, consistent with dioxidotungsten(VI) being harder than dioxidomolybdenum(VI). Several new examples of dioxidomolybdenum(VI) thioether complexes, including the unique dinuclear metallocyclic $[Mo_2O_4Cl_4\{o\text{-}C_6H_4(CH_2SMe)_2\}_2]$ which involves the rare *cis*-$MoCl_2$ unit, and examples containing the small cyclic 1,4-dithiane ligand and several macrocyclic thia- and mixed S/O-ligands have also been prepared and characterised. Work involving other $W^{VI}$ species with neutral sulfur ligands and related $M^{IV}$ and $M^{V}$ (M = Mo or W) complexes which may be relevant as redox models for the molybdo- and tungsto-enzymes, is underway.

## Experimental Section

Infrared spectra were recorded as Nujol mulls between CsI discs using a Perkin–Elmer 983G spectrometer over the range 4000–200 $cm^{-1}$. $^1H$ NMR spectra were recorded using a Bruker AV300 spectrometer. $^{13}C\{^1H\}$ and $^{95}Mo$ NMR spectra were recorded using a Bruker DPX400 spectrometer operating at 100.6 and 26.1 MHz, respectively, and are referenced to TMS and 1 mol $dm^{-3}$ $Na_2[MoO_4]$ respectively. Microanalyses were undertaken by the University of Strathclyde microanalytical service.

Solvents were dried prior to use and all preparations were undertaken using standard Schlenk techniques under a $N_2$ atmosphere. $MoO_2Cl_2$, $WCl_6$ and $W(CO)_6$ were obtained from Aldrich and used as received. $WBr_6$ was prepared by treating $W(CO)_6$ with $Br_2$.[28] The ligands $MeS(CH_2)_2SMe$, $i\text{Pr}S(CH_2)_2S i\text{Pr}$, $o\text{-}C_6H_4(CH_2SMe)_2$, $MeSe(CH_2)_2SeMe$, $[12]aneS_2O_2$ and $[15]aneS_2O_3$ were prepared as described previously,[26,29,30] while 1,4-dithiane, $[12]aneS_4$ and $[14]aneS_4$ were obtained from Aldrich and the solids dried by heating in vacuo for ca. 1 h before use.

**$[WO_2Cl_2\{MeS(CH_2)_2SMe\}]$. Method 1:** An acetonitrile solution of $(Me_3Si)_2O$ (0.049 g, 0.3 mmol in 5 mL of $CH_3CN$) was added dropwise at room temperature to a stirred suspension of $WOCl_4$ (0.103 g, 0.3 mmol) in acetonitrile (5 mL) over a period of 10 min. The $WOCl_4$ was consumed to give a clear, colourless solution, which was stirred for a further 10 min. The solution was then concentrated to half volume in vacuo and a $CH_2Cl_2$ solution of $MeS(CH_2)_2SMe$ (0.037 g, 0.3 mmol) was added dropwise. After stirring for ca. 30 min the solvent was removed in vacuo, leaving a yellow precipitate, which was washed with $n$-hexane and dried in vacuo. Yield 0.094 g, 76%.

**Method 2:** A suspension of $WCl_6$ (0.50 g, 1.25 mmol) in dry $CH_2Cl_2$ (10 mL) was treated dropwise with $(Me_3Si)_2O$ (0.20 g, 1.25 mmol) in $CH_2Cl_2$ (5 mL) and the mixture stirred for 10 min during which orange $WOCl_4$ deposited from the solution. Dry MeCN (0.5 mL) was added, followed by dropwise addition of $(Me_3Si)_2O$ (0.20 g, 1.25 mmol) and the solution stirred for 30 min when it became colourless (or sometimes very faintly blue). $MeS(CH_2)_2SMe$ (0.16 g, 1.3 mmol) in $CH_2Cl_2$ solution (2 mL) was added producing a pale yellowish solution. The solution was stirred for 10 min and then concentrated in vacuo to ca. 2 mL, and refrigerated overnight. The yellow powder deposited was separated by decantation of the solvent and dried in vacuo. Yield 0.30 g, 58%.

Both methods gave the same product as confirmed by spectroscopic studies. $C_4H_{10}Cl_2O_2S_2W$ (409.0): calcd. C 11.7, H 2.5; found C 11.0, H 2.9. IR (Nujol): $\tilde{\nu}$ = 956, 918 (W=O), 343 (W–Cl) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 300 K): $\delta$ = 3.24 (br. s, $CH_2S$, 4 H), 2.51 (br. s, Me, 6 H); (223 K): $\delta$ = 3.40–3.05 (m, $CH_2S$), 2.52 (s, Me, minor), 2.44 (s, Me, major). $^{13}C\{^1H\}$ ($CD_2Cl_2$, 300 K): br., ill-defined; (223 K): $\delta$ = 33.65 ($CH_2$), 18.1 (Me).

**$[WO_2Cl_2\{iPrS(CH_2)_2SiPr\}]$:** An acetonitrile solution of $(Me_3Si)_2O$ (0.048 g, 0.2 mmol in 5 mL of MeCN) was added dropwise at room temperature to a stirred suspension of $WOCl_4$ (0.102 g, 0.2 mmol) in acetonitrile (5 mL) over a period of 10 min to give a clear, colourless solution. After stirring for a further 10 min the solution was concentrated to half volume in vacuo and a $CH_2Cl_2$ solution of *i*PrS$(CH_2)_2$S*i*Pr (0.053 g, 0.2 mmol) was added dropwise at room temperature. The reaction mixture was stirred for ca. 30 min and then the solvent was evaporated to dryness in vacuo, leaving a yellow solid, which was washed with *n*-hexane and dried in vacuo. Yield 0.104 g, 75%. The compound was also prepared by method 2 used for $[WO_2Cl_2\{MeS(CH_2)_2SMe\}]$ above. Yield 55%. $C_8H_{18}Cl_2O_2S_2W\cdot CH_2Cl_2$ (550.0): calcd. C 19.6, H 3.7; found C 18.9, H 4.7. IR (Nujol): $\tilde{\nu}$ = 963, 923 (W=O), 338 (W–Cl) $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 300 K): $\delta$ = 3.30 (br., CH, 2 H), 3.18 (br., $CH_2$, 4 H), 1.38 (br., $CHMe_2$, 12 H). $^{13}C\{^1H\}$ ($CDCl_3$, 300 K): $\delta$ = 36.6 (CH), 28.1($CH_2$), 23.2(Me).

**$[WO_2Cl_2(1,4\text{-dithiane})]$:** A suspension of $WCl_6$ (0.50 g, 1.25 mmol) in dry $CH_2Cl_2$ (10 mL) was treated dropwise with $(Me_3Si)_2O$ (0.20 g, 1.25 mmol) in $CH_2Cl_2$ (5 mL) and the mixture stirred for 10 min. Dry MeCN (0.5 mL) was added to the orange suspension, followed by dropwise addition of $(Me_3Si)_2O$ (0.20 g, 1.25 mmol) and the solution stirred for 30 min when it became colourless. 1,4-Dithiane, which had been freshly sublimed in vacuo, (0.145 g, 1.2 mmol) in $CH_2Cl_2$ solution (5 mL) was added producing a pale yellowish solution. The solution was stirred for 10 min and then concentrated in vacuo to ca. 4 mL, and refrigerated for 48 h. The very fine yellow powder deposited was separated by decantation of the solvent and dried in vacuo. Yield 0.28 g, 55%. $C_4H_8Cl_2O_2S_2W$ (407.0): calcd. C 11.8, H 2.0; found C 11.5, H 2.9. IR (Nujol): $\tilde{\nu}$ = 940, 903 (W=O), 338 (W–Cl) $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 300 K): $\delta$ = 2.91 (s, $CH_2$). $^{13}C\{^1H\}$ ($CDCl_3$, 300 K): $\delta$ = 29.3 ($CH_2$).

**$[WO_2Br_2\{MeS(CH_2)_2SMe\}]$:** A suspension of $WBr_6$ (0.66 g, 1.0 mmol) in dry $CH_2Cl_2$ (10 mL) was treated dropwise with $(Me_3Si)_2O$ (0.16 g, 1.0 mmol) in $CH_2Cl_2$ (5 mL) and the mixture stirred for 10 min. Dry MeCN (0.5 mL) was added to the yellow-green suspension, followed by dropwise addition of $(Me_3Si)_2O$ (0.16 g, 1.0 mmol) and the solution stirred for 30 min when it became pale yellow-brown. $MeS(CH_2)_2SMe$ (0.12 g, 1.0 mmol) in $CH_2Cl_2$ solution (5 mL) was added producing a brown-yellow solution. The solution was stirred for 10 min and then concentrated in vacuo to ca. 5 mL, and refrigerated for 48 h. Only a small quantity of yellow-brown precipitate formed, so the solvent was removed in vacuo, and the residue stirred with hexane (10 mL). The powder deposited was separated by decantation of the solvent and dried in vacuo. Yield 0.3 g, 60%. $C_4H_{10}Br_2O_2S_2W$ (497.9): calcd. C 9.6, H 2.0; found C 10.2, H 1.3. IR (Nujol): $\tilde{\nu}$ = 965, 917 (W=O), 228 (W–Br) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 300 K): $\delta$ = 2.90 (s, $CH_2S$, 4 H), 2.43 (s, Me, 6 H). $^{13}C\{^1H\}$ ($CDCl_3$, 300 K): $\delta$ = 33.4 ($CH_2$), 18.4 (Me).

**$[WO_2Br_2\{iPrS(CH_2)_2SiPr\}]$:** An acetonitrile solution of $(Me_3Si)_2O$ (0.038 g, 0.2 mmol in 5 mL of MeCN) was added dropwise at room temperature to a stirred suspension of $WOBr_4$ (0.123 g, 0.2 mmol) in MeCN (5 mL) over a period of 10 min. The reaction mixture changed to a green coloured solution which was stirred for a further 10 min. The solution was concentrated to half volume in vacuo and a $CH_2Cl_2$ solution of *i*PrS$(CH_2)_2$S*i*Pr (0.042 g, 0.2 mmol) was added dropwise and the mixture was stirred for ca. 30 min. At this point the solvent was removed in vacuo, leaving a yellow-brown solid which was stirred with *n*-hexane (10 mL), separated by decantation and dried in vacuo. Yield 0.093 g, 71%. The compound was also prepared by method 2 used for $[WO_2Cl_2\{MeS(CH_2)_2SMe\}]$ above. $C_8H_{18}Br_2O_2S_2W\cdot 1/4C_6H_{14}$ (575.7): calcd. C 19.8, H 3.8; found C 19.9, H 4.0. IR (Nujol): $\tilde{\nu}$ = 962, 920 (W=O), 230 (W–Br) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 300 K): $\delta$ = 3.48 (br. s, CH, 2 H) 3.30 (br. s, $CH_2$, 4 H), 1.46 (br. s, CH*Me*$_2$, 6 H); (223 K): $\delta$ = 3.01–3.53 (overlapping m, CH and $CH_2$), 1.43, 1.38 (s, Me). $^{13}C\{^1H\}$ ($CDCl_3$, 300 K): $\delta$ = 34.9 (CH), 30.7 ($CH_2$), 23.3 (Me).

**$[WO_2Br_2(1,4\text{-dithiane})]$:** A suspension of $WBr_6$ (0.66 g, 1.0 mmol) in dry $CH_2Cl_2$ (10 mL) was treated dropwise with $(Me_3Si)_2O$ (0.16 g, 1.0 mmol) in $CH_2Cl_2$ (5 mL) and the mixture stirred for 10 min. Dry MeCN (0.5 mL) was added to the blue-green suspension, followed by dropwise addition of $(Me_3Si)_2O$ (0.16 g, 1.0 mmol) and the solution stirred for 30 min when it became pale yellow-brown. 1,4-Dithiane, which had been freshly sublimed in vacuo, (0.12 g, 1.0 mmol) in $CH_2Cl_2$ solution (5 mL) was added producing a brown-yellow solution. The solution was stirred for 10 min and then concentrated in vacuo to ca. 4 mL, and refrigerated for 48 h. The yellow-brown powder deposited was separated by decantation of the solvent, rinsed with dry hexane (5 mL) and dried in vacuo. Yield 0.35 g, 70%. $C_4H_8Br_2O_2S_2W$ (495.9): calcd. C 9.7, H 1.6; found C 9.0, H 1.7. IR (Nujol): $\tilde{\nu}$ = 961, 902 (W=O), 238 (W–Br) $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 300 K): $\delta$ = 2.85 ($CH_2$). $^{13}C\{^1H\}$ ($CDCl_3$, 300 K): $\delta$ = 29.2 ($CH_2$).

**$[Mo_2O_4Cl_4\{o\text{-}C_6H_4(CH_2SMe)_2\}_2]$:** A degassed ether solution of *o*-$C_6H_4(CH_2SMe)_2$ (0.104 g, 0.52 mmol) in 5 mL of $Et_2O$ was added dropwise at room temperature to a stirred solution of $MoO_2Cl_2$ (0.104 g, 0.52 mmol) in diethyl ether (10 mL) over a period of 5 min, giving a light yellow solution. The solution was stirred at room temperature for a further 30 min. The solution was then concentrated in vacuo by ca. 50% and placed in the freezer. This produced a yellow precipitate, which was collected by filtration and dried in vacuo. Yield 0.153 g, 74%. $C_{20}H_{28}Cl_4Mo_2O_4S_4$ (794.4): calcd. C 30.2, H 3.6; found C 29.2, H 3.8. IR (Nujol): $\tilde{\nu}$ = 933, 895 (Mo=O), 387, 355 (Mo–Cl) $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 298 K): $\delta$ = 7.29 (br. s, *o*-$C_6H_4$, 4 H), 3.95 (br., $CH_2$, 4 H), 2.29 (br., Me, 6 H); (183 K): $\delta$ = 7.33–7.11 (m, *o*-$C_6H_4$, 4 H), 4.15, 3.74 (br., $CH_2$, 4 H), 2.64, 2.26, 1.94 (s, Me, 6 H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K): no spectrum; (223 K): $\delta$ = 133.00 (*ipso*-C, *o*-$C_6H_4$), 132.67, 129.28 (*o*-$C_6H_4$), 37.21 ($CH_2$), 20.99 (Me).

**$[MoO_2Cl_2\{iPrS(CH_2)_2SiPr\}]$:** To a suspension of $MoO_2Cl_2$ (0.103 g, 0.52 mmol) in $CH_2Cl_2$ (20 mL) was added a $CH_2Cl_2$ solution (5 mL) of *i*PrS$(CH_2)_2$S*i*Pr (0.093 g, 0.52 mmol). Stirring the reaction mixture for ca. 15 min afforded a pale yellow solution which was reduced in vacuo to ca. 3 mL. Layering with anhydrous diethyl ether and storing the resulting mixture overnight at ca. –18 °C gave pale yellow crystals which were filtered, washed with diethyl ether and dried in vacuo. Yield 85%. $C_8H_{18}Cl_2MoO_2S_2$

(377.2): calcd. C 25.5, H 4.8; found C 25.3, H 5.1. IR (Nujol): ṽ = 944, 913 (Mo=O), 348 (Mo–Cl) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 300 K): $\delta$ = 3.30 (sept, CH, 2 H), 3.08 (s, $CH_2$, 4 H), 1.47 (d, CH*Me₂*, 12 H). $^{13}C\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$, 300 K): $\delta$ = 38.25 (CH), 31.01 ($CH_2$), 21.99 ($CHMe_2$) ppm. $^{95}Mo$ NMR ($CH_2Cl_2/CDCl_3$): $\delta$ = 225.

**[$MoO_2Cl_2$(1,4-dithiane)]:** A degassed diethyl ether (5 mL) solution of 1,4-dithiane (0.072 g, 0.6 mmol) was added dropwise at room temperature to a stirred solution of $MoO_2Cl_2$ (0.120 g, 0.6 mmol) in diethyl ether (10 mL) over a period of 5 min, giving a light yellow precipitate. The reaction mixture was stirred at room temperature for a further 1 h. The yellow precipitate was collected by filtration and dried in vacuo. Yield 0.128 g, 67%. $C_4H_8Cl_2MoO_2S_2$ (319.1): calcd. C 15.1, H 2.5; found C 15.4, H 2.4. IR (Nujol): ṽ = 946, 916 (Mo=O), 362 (Mo–Cl) $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 298 K): $\delta$ = 2.98 (s, $CH_2$); (183 K): $\delta$ = 3.53–2.69 (br. m, $CH_2$).

**[$MoO_2Cl_2$([15]ane$S_2O_3$)]:** A dry, degassed $CH_2Cl_2$ solution (5 mL) of [15]ane$S_2O_3$ (0.010 g, 0.4 mmol) was added dropwise at room temperature to a stirred solution of $MoO_2Cl_2$ (0.080 g, 0.4 mmol) in degassed diethyl ether (10 mL) over a period of 5 min, giving a light yellow precipitate. The reaction mixture was stirred at room temperature for a further 3 h. The yellow precipitate was collected by filtration and dried in vacuo. Yield 0.124 g, 68%. $C_{10}H_{20}Cl_2MoO_5S_2$ (451.2): calcd. C 26.6, H 4.5; found C 26.6, H 4.5. IR (Nujol): ṽ = 939, 908 (Mo=O), 355 (Mo–Cl) $cm^{-1}$. $^1H$ NMR ($CDCl_3$, 300 K): $\delta$ = 3.97 (br. s, $CH_2O$, 4 H), 3.84 (s, $CH_2O$, 4 H), 3.77 (s, $CH_2O$, 4 H), 3.15 (s, $CH_2S$, 4 H), 3.02 (s, $CH_2S$, 4 H). $^{95}Mo$ NMR ($CH_2Cl_2/CDCl_3$, 300 K): $\delta$ = 194.

**[$MoO_2Cl_2$([14]ane$S_4$)]:** Addition of a solution of $MoO_2Cl_2$ (0.075 g, 0.38 mmol) in dry diethyl ether (5 mL) dropwise via a bypass funnel at room temperature to a solution of [14]ane$S_4$ (0.102 g, 0.38 mmol) in dry $CH_2Cl_2$ (10 mL) over a period of 5 min, produced a light yellow precipitate. The reaction mixture was stirred at room temperature for a further 60 min, and the yellow precipitate was collected by filtration and dried in vacuo. Yield 0.135 g, 76%. $C_{10}H_{20}Cl_2MoO_2S_4$ (467.4): calcd. C 25.7, H 4.3; found C 25.9, H 4.5. IR (Nujol): ṽ = 939, 913 (Mo=O), 359 (Mo–Cl) $cm^{-1}$. $^1H$ NMR ($CDCl_3$, very poorly soluble, 300 K): $\delta$ = 2.72 (s, $SCH_2CH_2S$, 8 H), 2.61 (t, $SCH_2CH_2CH_2S$, 8 H), 1.88 (q, $SCH_2CH_2CH_2S$, 4 H) ([14]ane$S_4$).

**[$MoO_2Cl_2$([12]ane$S_4$)]:** Addition of a solution of $MoO_2Cl_2$ (0.084 g, 0.42 mmol) in dry diethyl ether (5 mL) dropwise via a bypass funnel at room temperature to a solution of [12]ane$S_4$ (0.102 g, 0.42 mmol) in dry $CH_2Cl_2$ (10 mL) over a period of 5 min, produced a light yellow precipitate. The reaction mixture was stirred at room temperature for a further 60 min. The yellow precipitate was collected by filtration and dried in vacuo. Yield 0.141 g, 76%. $C_8H_{16}Cl_2MoO_2S_4\cdot CH_2Cl_2$ (524.2): calcd. C 20.6, H 3.5; found C 20.6, H 3.5. IR (Nujol): ṽ = 944, 919 (Mo=O), 358 (Mo–Cl) $cm^{-1}$. $^1H$ NMR ($CDCl_3$, very poorly soluble, 300 K): $\delta$ = 2.72 (s, $CH_2$) ([12]ane$S_4$).

**X-ray Crystallography:** Details of the crystallographic data collection and refinement parameters are given in Table 4. Yellow crystals of [$WO_2Cl_2\{i$PrS$(CH_2)_2$S*i*Pr$\}$], [$Mo_2O_4Cl_4\{o$-$C_6H_4(CH_2SMe)_2\}_2$] and a new polymorph of [$WO_2Cl_2\{MeO(CH_2)_2OMe\}$] were obtained by liquid diffusion of diethyl ether into a $CH_2Cl_2$ solution of the complex. The crystals of [$Mo_2O_4Cl_4\{o$-$C_6H_4(CH_2SMe)_2\}_2$] were extremely moisture-sensitive and some degradation occurred during transfer from the Schlenk flask to the diffractometer – the data presented are those from the best crystal from several different crystals examined. Nevertheless the quality was rather poor and hence the residuals are higher than usually expected. Data collection used a Nonius Kappa CCD diffractometer ($T$ = 120 K) and with graphite-monochromated Mo-$K_\alpha$ X-radiation ($\lambda$ = 0.71073 Å). Structure solution and refinement were routine.[31,32] with H atoms being placed in geometrically calculated positions. Selected bond lengths and angles are given in Table 1, Table 2, and Table 3.

CCDC-626755 (for W/S), -626756 (for W/O), -626754 and -626757 (for Mo) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 4. Crystallographic parameters.[a]

| Compound | [$WO_2Cl_2\{i$PrS$(CH_2)_2$S*i*Pr$\}$] | [$WO_2Cl_2\{MeO(CH_2)_2OMe\}$] | [$(MoO_2Cl_2)_2\{o$-$C_6H_4(CH_2SMe)_2\}_2$] |
|---|---|---|---|
| Formula | $C_8H_{18}Cl_2O_2S_2W$ | $C_4H_{10}Cl_2O_4W$ | $C_{20}H_{28}Cl_4Mo_2O_4S_4$ |
| $M$ | 465.09 | 376.87 | 794.34 |
| Crystal system | orthorhombic | monoclinic | monoclinic |
| Space group | *Pbca* (no. 61) | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) |
| $a$ [Å] | 11.7823(16) | 14.248(3) | 7.4251(12) |
| $b$ [Å] | 12.964(2) | 11.216(3) | 23.984(4) |
| $c$ [Å] | 19.111(3) | 13.497(3) | 8.2293(14) |
| $\alpha$ [°] | 90 | 90 | 90 |
| $\beta$ [°] | 90 | 118.213(10) | 94.964(9) |
| $\gamma$ [°] | 90 | 90 | 90 |
| $U$ [Å$^3$] | 2919.2(8) | 1900.5(7) | 1460.0(4) |
| $Z$ | 8 | 8 | 2 |
| $\mu$(Mo-$K_\alpha$) [$mm^{-1}$] | 8.547 | 12.686 | 1.537 |
| Total number of reflections | 29514 | 11475 | 7617 |
| $R_{int}$ | 0.069 | 0.032 | 0.064 |
| Unique reflections | 3341 | 4179 | 2418 |
| Number of parameters | 136 | 203 | 154 |
| $R_1$ [$I_o > 2\sigma(I_o)$] | 0.0489 | 0.0282 | 0.0884 |
| $R_1$ [all data] | 0.0704 | 0.0391 | 0.1110 |
| $wR_2$ [$I_o > 2\sigma(I_o)$] | 0.0880 | 0.0536 | 0.2232 |
| $wR_2$ [all data] | 0.0959 | 0.0580 | 0.2411 |

[a] Common items: temperature = 120 K; wavelength (Mo-$K_\alpha$) = 0.71073 Å; $\theta$(max.) = 27.5°; $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

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[1] W. Levason, G. Reid, *J. Chem. Res. (S)* **2002**, 467–472.

[2] C. S. Tredget, F. Bonnet, A. R. Cowley, P. Mountford, *Chem. Commun.* **2005**, 3301–3303.

[3] L. Karmazin, M. Mazzanti, J. Pécaut, *Chem. Commun.* **2002**, 654–655.

[4] a) W. Levason, B. Patel, G. Reid, V.-A. Tolhurst, M. Webster, *J. Chem. Soc., Dalton Trans.* **2000**, 3001–3006; b) P. J. McKarns, T. S. Lewkebandara, G. P. A. Yap, L. M. Liable-Sands, A. L. Rheingold, C. H. Winter, *Inorg. Chem.* **1998**, *37*, 418–424; c) P. J. Wilson, A. J. Blake, M. Schröder, *Chem. Commun.* **1998**, 1007–1008; d) W. Levason, B. Patel, G. Reid, *Inorg. Chim. Acta* **2004**, *357*, 2115–2120.

[5] R. Hart, W. Levason, B. Patel, G. Reid, *J. Chem. Soc., Dalton Trans.* **2002**, 3153–3159.

[6] a) H.-J. Küppers, K. Wieghardt, *Polyhedron* **1989**, *8*, 1770–1773; b) N. R. Champness, S. R. Jacob, G. Reid, C. S. Frampton, *Inorg. Chem.* **1995**, *34*, 396–398; c) S. J. A. Pope, N. R. Champness, G. Reid, *J. Chem. Soc., Dalton Trans.* **1997**, 1639–1644; d) G. J. Grant, K. E. Rogers, W. N. Setzer, D. G. VanDerveer, *Inorg. Chim. Acta* **1995**, *234*, 35–45.

[7] a) M. C. Durrant, S. Davies, D. L. Hughes, C. Le Floc'h, R. L. Richards, J. R. Sanders, N. R. Champness, S. J. Pope, G. Reid, *Inorg. Chim. Acta* **1996**, *251*, 13–14; b) S. C. Davies, M. C. Durrant, D. L. Hughes, C. Le Floc'h, S. J. A. Pope, G. Reid, R. L. Richards, J. R. Sanders, *J. Chem. Soc., Dalton Trans.* **1998**, 2191–2198; c) G. R. Willey, M. T. Lakin, N. W. Alcock, *J. Chem. Soc., Chem. Commun.* **1991**, 1414–1416.

[8] W. Levason, M. C. Popham, G. Reid, M. Webster, *Dalton Trans.* **2003**, 291–294.

[9] C. D. Beard, L. Carr, M. F. Davis, J. Evans, W. Levason, L. D. Norman, G. Reid, M. Webster, *Eur. J. Inorg. Chem.* **2006**, 4399–4406.

[10] J. M. Tunney, J. McMaster, C. D. Garner, in *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier, Amsterdam, **2004**, vol. 8, p. 459.

[11] See for example A. H. Hoveyda, R. R. Schrock, in *Comprehensive Asymmetric Catalysis* (Eds.: E. N. Jacobsen, A. Pfaltz, H. Yamamoto), Springer, Heidelberg, **2004**, vol. 1, p. 207 and references cited therein.

[12] D. Sevdić, L. Fekete, *Polyhedron* **1985**, *4*, 1371–1378.

[13] W. Levason, C. A. McAuliffe, F. P. McCullough, S. G. Murray, C. A. Rice, *Inorg. Chim. Acta* **1977**, *22*, 227–231.

[14] D. Sellmann, L. Zapf, *J. Organomet. Chem.* **1985**, *289*, 57–59.

[15] T. Yoshida, T. Adachi, T. Ueda, M. Watanabe, M. Kaminaka, T. Higuchi, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1171–1172.

[16] T. Adachi, M. D. Durrant, D. L. Hughes, C. J. Pickett, R. L. Richards, J. Talarmin, T. Yoshida, *J. Chem. Soc., Chem. Commun.* **1992**, 1464–1467.

[17] F. A. Cotton, G. L. Powell, *J. Am. Chem. Soc.* **1984**, *106*, 3371–3372.

[18] F. A. Cotton, M. P. Diebold, C. J. O'Connor, G. L. Powell, *J. Am. Chem. Soc.* **1985**, *107*, 7438–7445.

[19] D. Sevdić, L. Fekete, *Inorg. Chim. Acta* **1982**, *57*, 111–117.

[20] M. D. Brown, M. B. Hursthouse, W. Levason, R. Ratnani, G. Reid, *Dalton Trans.* **2004**, 2487–2491.

[21] a) O. Jarchow, F. Schröder, H. Schulz, *Z. Anorg. Allgem. Chem.* **1968**, *363*, 58–71; b) I. Abrahams, J. L. Nowinski, P. G. Bruce, V. C. Gibson, *J. Sol. State Chem.* **1993**, *102*, 140–145.

[22] a) M. F. Davis, W. Levason, R. Ratnani, G. Reid, T. Rose, M. Webster, *Eur. J. Inorg. Chem.* **2007**, 306–313; b) M. B. Hursthouse, W. Levason, R. Ratnani, G. Reid, *Polyhedron* **2004**, *23*, 1915–1921.

[23] X. Ma, K. Starke, C. Schulzke, H.-G. Schmidt, M. Noltemeyer, *Eur. J. Inorg. Chem.* **2006**, 628–637.

[24] K. Dreisch, C. Andersson, C. Stalhandske, *Polyhedron* **1991**, *10*, 2417–2421.

[25] V. C. Gibson, T. P. Kee, A. Shaw, *Polyhedron* **1990**, *9*, 2293–2298.

[26] a) W. Levason, B. Patel, G. Reid, A. J. Ward, *J. Organomet. Chem.* **2001**, *619*, 218–225; b) W. Levason, M. Nirwan, R. Ratnani, G. Reid, N. Tsoureas, M. Webster, *Dalton Trans.* **2007**, 439–448.

[27] Y. Yamamoto, S. Sakamoto, Y. Ohki, A. Usuzawa, M. Fujita, T. Mochida, *Dalton Trans.* **2003**, 3534–3540.

[28] a) A. K. Brisdon, E. G. Hope, W. Levason, J. S. Ogden, *J. Chem. Soc., Dalton Trans.* **1989**, 313–316; b) P. C. Crouch, G. W. A. Fowles, R. A. Walton, *J. Inorg. Nucl. Chem.* **1970**, *32*, 329–333.

[29] F. R. Hartley, S. G. Murray, W. Levason, H. E. Soutter, C. A. McAuliffe, *Inorg. Chim. Acta* **1979**, *35*, 265–277.

[30] a) J. S. Bradshaw, J. Y. Hui, B. L. Haymore, J. J. Christensen, R. M. Izatt, *J. Heterocycl. Chem.* **1973**, *10*, 1–4; b) J. S. Bradshaw, J. Y. Hui, Y. Chan, B. L. Haymore, R. M. Izatt, J. J. Christensen, *J. Heterocycl. Chem.* **1974**, *11*, 45–49.

[31] G. M. Sheldrick, SHELXS-97, *Program for crystal structure solution*, University of Göttingen, Germany, **1997**.

[32] G. M. Sheldrick, SHELXL-97, *Program for crystal structure refinement*, University of Göttingen, Germany, **1997**.

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