DALTON
FULL PAPER

Molybdenum complexes with tridentate NS_2 ligands. Synthesis, crystal structures and spectroscopic properties

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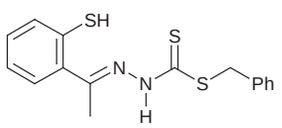
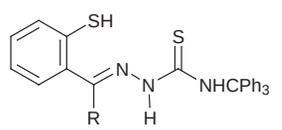
Reaction of the new tridentate NS_2 ligands 2-$HSC_6H_4C(Me)$=NNHC(S)SCH_2Ph (H_2L^1), 2-$HSC_6H_4C(Me)$=NNHC(S)$NHCPh_3$ (H_2L^2), 2-HSC_6H_4CH=NNHC(S)$NHCPh_3$ (H_2L^3) and 1-Ph-3-Me-5-HS-C_3N_2-CH=NNC(SH)-$NHCPh_3$ (H_2L^4) with dioxomolybdenum(VI) precursors yielded mononuclear molybdenum(VI) complexes $[MoO_2(L^1)(pic)]$ **1** (pic = 4-methylpyridine), $[MoO_2L^2(MeOH)]\cdot 2.25$ MeOH **2** and the dinuclear molybdenum(V) complexes $[Mo_2O_3L^3{}_2]\cdot 3CH_2Cl_2$ **3** and $[Mo_2O_3L^4{}_2]$ **4**. The molecular structures of **1**–**3** were determined by single-crystal X-ray analysis. Complexes **1** and **2** each consist of a central *cis*-MoO_2 unit with a *mer* co-ordinating tridentate dianionic ligand and one neutral donor molecule completing the octahedral environment of molybdenum(VI). Complex **3** exhibits an *anti*-Mo_2O_3 group co-ordinated by two *mer* chelating ligands. The symmetry-related molybdenum(V) centres are in a square pyramidal environment. Infrared, NMR and MS studies evidenced a comparable structure for **4**. The reduction of the dioxomolybdenum(VI) compounds **1** and **2**, achieved by addition of phosphines like PPh_3, also leads to dinuclear μ-oxo-bridged complexes. The reverse oxidations of the oxomolybdenum(V) complexes are restricted by the nature of the ligand and the oxidizing agents.

Thiosemicarbazone based ligands have been widely used for the preparation of transition metal complexes.[1] Particularly tridentate ONS-chelating ligands derived from thiosemicarbazones or dithiocarbazates of salicylaldehydes have recently attracted considerable interest.[2] Surprisingly analogous NS_2-chelating ligands have, to our knowledge, not yet been reported. The tautomerism of these ligands as well as the well known tendency of sulfur donors to act as bridging ligands allow various structural possibilities for the corresponding metal complexes. The versatile applications of thiosemicarbazone complexes as well as our general interest in transition metal complexes co-ordinated by sulfur or mixed sulfur–nitrogen donor atoms therefore prompted us to synthesize the tridentate NS_2-Schiff base ligands H_2L^1 to H_2L^4. In this paper we further report the preparation of some corresponding oxomolybdenum complexes. Related complexes with tridentate ONS ligands have been reported to undergo reversible oxo-transfer reactions involving molybdenum-(VI) and -(IV) species.[2c–f] As the oxo-transfer generally increases with the number of sulfur atoms in the ligand environment[2d,3] we thought it worthwhile to check the reactivity of our complexes towards such reactions and to elucidate the structure of the reaction products.

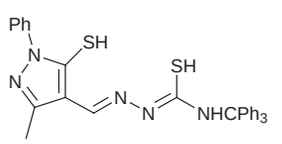


H_2L^1



H_2L^2 R = Me

H_2L^3 R = H



H_2L^4

Results and discussion

Synthesis of the ligands and complexes

The appropriate ligands H_2L^1, H_2L^2 and H_2L^4 were readily prepared by Schiff base condensation of 4-(triphenylmethyl)thiosemicarbazide or *S*-benzyl dithiocarbazate with the respective 2-sulfanyl carbonyl compounds (2-sulfanylacetophenone, 4-formyl-3-methyl-1-phenyl-5-sulfanylpyrazole) in ethanolic solution. Compound H_2L^3 can be prepared in the same manner. However, due to the instability of 2-sulfanylbenzaldehyde, it was more convenient first to condense 2,2′-dithiobenzaldehyde with 2 equivalents of 4-(triphenylmethyl)thiosemicarbazide and then reduce the disulfide bond by treatment with alkaline glucose solution. The ligands H_2L^2–H_2L^4 were generally isolated as slightly coloured solids which are quite stable and can be stored under nitrogen for several weeks without decomposition. Compound H_2L^1 was obtained as an orange oil by evaporating the reaction mixture and used without further purification. In fact H_2L^2 and H_2L^3 present very similar structures and reactivities, and we mainly focused our attention on the synthesis of complexes featuring H_2L^2. However, as X-ray structural information was first obtained for complex $[Mo_2O_3L^3{}_2]\cdot 3CH_2Cl_2$ by the use of H_2L^3 we here report the synthesis of both ligands.

The dioxomolybdenum(VI) complex $[MoO_2L^1(pic)]$ **1** was obtained as an orange-brown solid by the reaction of H_2L^1 with an equimolar amount of $[MoO_2(acac)_2]$ in ethanol in the presence of 4-methylpyridine (pic). Crystalline samples were obtained by vapour diffusion of *n*-hexane into an ethyl acetate solution of **1**. Analogous reactions of $[MoO_2(acac)_2]$ with the ligands H_2L^2, H_2L^3 and H_2L^4 were accompanied by an immediate change of the solutions to purple. Upon evaporation of the solvent dinuclear molybdenum(V) compounds of the general formula $[Mo_2O_3L_2]$ (L = L^2, L^3 or L^4) precipitated as deep red to purple solids. Crystallization of $[Mo_2O_3L^3{}_2]\cdot 3CH_2Cl_2$ **3** was achieved by vapour diffusion of diethyl ether into a dichloromethane solution of the complex. While H_2L^1 reacts in a simple ligand exchange reaction with $[MoO_2(acac)_2]$ to form $[MoO_2L^1(pic)]$ **1**, the ligands based on the (triphenylmethyl)thiosemi-

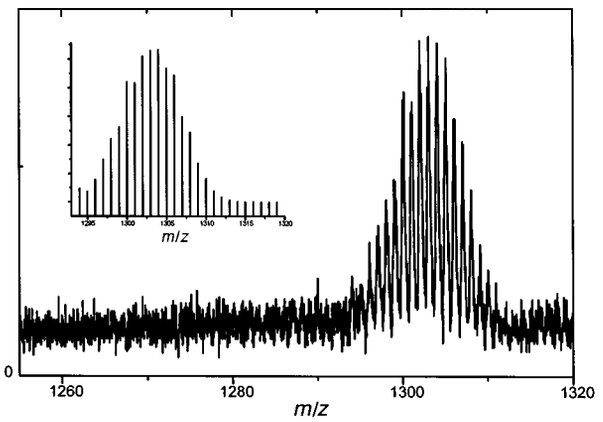


Fig. 1 Isotopic distribution of the M^- peak of $[Mo_2O_3L^4_2]$ **4**. Inset: calculated distribution for $C_{62}H_{50}Mo_2N_{10}O_3S_4$.

carbazide fragment react both as ligands and reducing agents. Such behaviour has been observed previously upon the reaction of thiol ligands with $[MoO_2(acac)_2]$.[4] Dioxomolybdenum(VI) complexes with the ligand H_2L^2 could be more successfully obtained by the use of MoO_2Cl_2 instead of $[MoO_2(acac)_2]$. However the formation of the dinuclear molybdenum(V) complexes could not be completely excluded. The complex $[MoO_2L^2(MeOH)]\cdot 2.25MeOH$ **2** was thus isolated from the methanolic mother-liquor by fractional crystallization on the basis of its better solubility. Attempts to isolate any dioxomolybdenum(VI) complex with the ligand H_2L^3 or H_2L^4 have been unsuccessful up to now.

Spectroscopic studies

The infrared spectra of complexes **1** and **2** (in parentheses) exhibit, beside typical ligand vibrations, two strong absorptions at 927 and 896 (927 and 893) cm^{-1} which are attributed to the symmetric and asymmetric ν(Mo=O) vibrations of the C_{2v} *cis*-MoO_2^{2+} groups, thus confirming the formation of mononuclear molybdenum(VI) complexes. In contrast the IR spectra of **3** and **4** show only one strong absorption at ≈970 cm^{-1} and a medium intensity band at ≈750 cm^{-1} which are readily assigned to ν(Mo=O) and ν(Mo–O–Mo) vibrations of the central Mo_2O_3 unit.[5] The co-ordination of the ligands through the arenethiolate function is confirmed for all complexes by the disappearance of the ν(SH) vibration in comparison to the spectra of free H_2L. Furthermore the red shift (≈10–20 cm^{-1}) of the ν(C=N) vibration is of diagnostic value for the co-ordination of the azomethine nitrogen.[2e–f] The lack of a vibration at ≈1030 cm^{-1} is in accordance with the co-ordination of the thione in the iminothiolate mode. The ^{1}H NMR spectra of all complexes confirm the dianionic co-ordination of the ligands by the loss of the signals for the SH and NH protons. While there is no indication of the formation of a dinuclear compound in the spectrum of $[Mo_2O_3L^3_2]$ **3**, in the spectrum of **4** the resonances for the methyl, azomethine and amine protons are each split into two signals with an intensity ratio of ≈2:1. These results clearly support the formulation of **4** as $[Mo_2O_3L^4_2]$ in two diastereomeric forms.[6] Further evidence was obtained by the TOF-SIMS (time-of-flight secondary ion mass spectroscopy) spectra of **4**. Both the negative and positive SIMS spectra exhibit the ion peak of the dinuclear compound with its characteristic isotope distribution. The relative intensities fit well with the calculated distribution for the formulation as $[Mo_2O_3L^4_2]$ (Fig. 1). A signal pattern corresponding to a MoO_2L^4 or $MoO(L^4)$ ion was not observed.

Molecular structures of complexes 1 and 2

Orange crystals were grown by vapour diffusion of *n*-hexane into an ethyl acetate solution of complex **1** while crystals of **2** were obtained by slow evaporation of a methanolic solution. Both crystal structures (Figs. 2 and 3) consist of well separated mononuclear molecules. The co-ordination spheres of these molecules are severely distorted octahedral exhibiting the typical *cis*-MoO_2 unit of dioxomolybdenum(VI) complexes.[5] The tridentate Schiff base ligands display *mer* co-ordination with the sulfur donor atoms mutually *trans*, and *cis* to the oxide ligands. The neutrality of the complexes requires dianionic ligands in the thiophenolate–azaenethiolate form as confirmed by bond lengths within the ligand chain. Thus the C(9)–S(2) distances of 1.735(4) Å in **1** and 1.767(5) Å in **2** (Tables 1 and 2)

Table 1 Selected interatomic distances (Å) and angles (°) for complex **1**

Mo–O(2)	1.695(2)	S(2)–C(9)	1.735(4)
Mo–O(1)	1.700(2)	S(3)–C(9)	1.763(4)
Mo–N(1)	2.288(2)	N(1)–C(7)	1.294(4)
Mo–S(1)	2.402(1)	N(1)–N(2)	1.415(4)
Mo–N(3)	2.426(2)	N(2)–C(9)	1.288(4)
Mo–S(2)	2.457(1)	N(1)–C(7)	1.294(4)
S(1)–C(1)	1.756(3)		
N(1)–Mo–S(1)	80.37(7)	S(1)–Mo–N(3)	78.3(1)
S(1)–Mo–S(2)	149.58(3)	O(2)–Mo–S(2)	101.7(1)
O(1)–Mo–S(1)	103.8(1)	O(1)–Mo–S(2)	94.2(1)
O(2)–Mo–N(3)	169.3(1)	N(1)–Mo–S(2)	75.62(7)
O(1)–Mo–N(3)	84.5(1)	N(3)–Mo–S(2)	79.3(1)
O(2)–Mo–O(1)	106.0(1)	C(6)–C(7)–N(1)	121.6(3)
O(2)–Mo–N(1)	90.2(1)	C(7)–N(1)–N(2)	113.6(3)
O(1)–Mo–N(1)	162.5(1)	N(1)–N(2)–C(9)	112.8(3)
O(2)–Mo–S(1)	96.69(9)	N(2)–C(9)–S(2)	128.3(3)
N(1)–Mo–N(3)	79.73(8)		112.8(2)

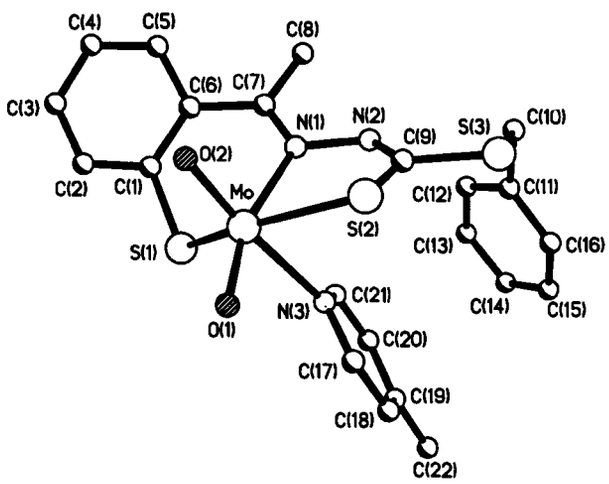


Fig. 2 Molecular structure and atom numbering scheme for complex **1**.

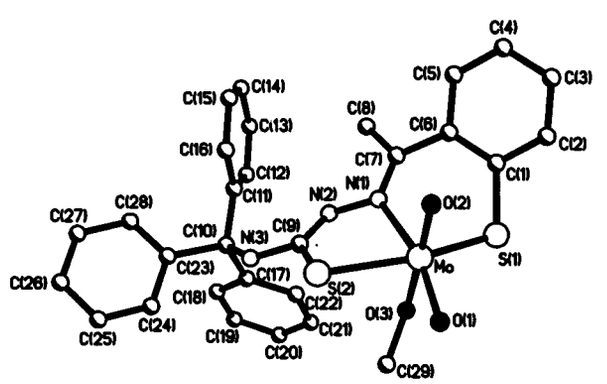


Fig. 3 Molecular structure and atom numbering scheme for complex **2**.

Table 2 Selected interatomic distances (Å) and angles (°) for complex **2**

Mo–O(2)	1.699(3)	S(2)–C(9)	1.767(5)
Mo–O(1)	1.709(4)	N(2)–C(9)	1.287(6)
Mo–N(1)	2.304(4)	N(3)–C(9)	1.355(6)
Mo–O(3)	2.322(4)	N(3)–C(10)	1.477(6)
Mo–S(1)	2.389(1)	N(1)–C(7)	1.285(6)
Mo–S(2)	2.442(1)	N(1)–N(2)	1.412(5)
S(1)–C(1)	1.767(5)		
O(2)–Mo–O(1)	105.7(2)	O(3)–Mo–S(1)	77.5(1)
O(1)–Mo–S(1)	104.4(1)	O(2)–Mo–S(2)	100.8(1)
N(1)–Mo–S(1)	80.3(1)	O(1)–Mo–S(2)	94.3(1)
O(2)–Mo–S(1)	96.2(1)	N(1)–Mo–S(2)	74.6(1)
S(1)–Mo–S(2)	150.3(1)	O(3)–Mo–S(2)	81.7(1)
O(2)–Mo–N(1)	93.4(2)	C(6)–C(7)–N(1)	120.7(5)
O(1)–Mo–N(1)	159.6(2)	C(7)–N(1)–N(2)	112.5(4)
O(2)–Mo–O(3)	169.4(2)	N(1)–N(2)–C(9)	113.1(4)
O(1)–Mo–O(3)	84.3(2)	N(2)–C(9)–S(2)	125.7(4)
N(1)–Mo–O(3)	77.2(1)	N(2)–C(9)–N(3)	121.2(4)

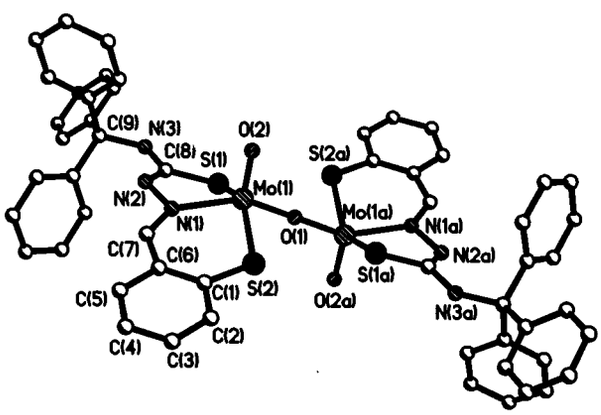


Fig. 4 Molecular structure and atom numbering scheme for complex **3**.

are consistent with the formation of a single bond whereas the C(9)–N(2) bond lengths of 1.288(4) and 1.287(6) Å are typical for C=N double bonds. The sixth positions completing the octahedral co-ordination of the molybdenum framework are occupied by a picoline ligand in **1** and a methanol molecule in **2** respectively. Owing to the *trans* effect of the terminal oxide ligands the corresponding bond lengths Mo(1)–N(3) [2.426(2) Å] in **1** and Mo(1)–O(3) [2.322(4) Å] in **2** are relatively long. However all observed metal–ligand distances are unexceptional and compare closely to those in related molecules.[2c,4–7]

Molecular structure of complex 3

Deep red to purple crystals of complex **3** were grown by vapour diffusion of diethyl ether into a dichloromethane solution of it. The neutral dinuclear complex exhibits an *anti*-Mo_2O_3 group typical for oxo-bridged molybdenum(v) complexes with the bridging oxygen atom located on a crystallographic inversion centre (Fig. 4). Each Mo atom is co-ordinated by one tridentate ligand L^3 in the doubly deprotonated thiophenolate–azaene-thiolate form. In contrast to the molybdenum(vi) compounds **1** and **2** the Mo atoms in **3** are only five-co-ordinated with the terminal oxo groups O(2) and O(2a) in the apical position of a distorted square pyramidal conformation, confirmed by the value of 0.15 determined for the structural index τ.[8] In the absence of any sixth donor the tridentate ligand L^3 is able to encapsulate the metal centres by diminishing repulsions between sulfur atoms and the terminal oxo groups. Hence the S(1)–Mo–O(2) and S(2)–Mo–O(2) bond angles (Table 3) are at least 13° larger than in **1** or **2**. The metal–donor bond lengths are in the normal range for this type of complex,[5] but they are all slightly shorter than their counterparts in **1** and **2**.

Table 3 Selected interatomic distances (Å) and angles (°) for complex **3**

Mo(1)–O(2)	1.658(8)	S(2)–C(1)	1.744(7)
Mo(1)–O(1)	1.860(1)	N(1)–C(7)	1.286(7)
Mo(1)–N(1)	2.157(4)	N(2)–C(8)	1.294(7)
Mo(1)–S(2)	2.357(2)	N(1)–N(2)	1.417(6)
Mo(1)–S(1)	2.375(2)	N(3)–C(8)	1.349(7)
S(1)–C(8)	1.754(5)	N(3)–C(9)	1.486(6)
O(2)–Mo(1)–O(1)	108.7(2)	O(1)–Mo(1)–S(1)	87.4(1)
O(2)–Mo(1)–S(2)	111.6(2)	N(1)–Mo(1)–S(1)	78.0(1)
O(2)–Mo(1)–S(1)	109.8(2)	C(6)–C(7)–N(1)	130.7(6)
S(2)–Mo(1)–S(1)	138.3(1)	C(7)–N(1)–N(2)	111.0(4)
O(2)–Mo(1)–N(1)	103.6(2)	N(1)–N(2)–C(8)	113.3(4)
O(1)–Mo(1)–N(1)	147.4(1)	N(2)–C(8)–S(1)	124.7(4)
O(1)–Mo(1)–S(2)	83.8(1)	N(2)–C(8)–N(3)	120.0(5)
N(1)–Mo(1)–S(2)	88.1(1)		

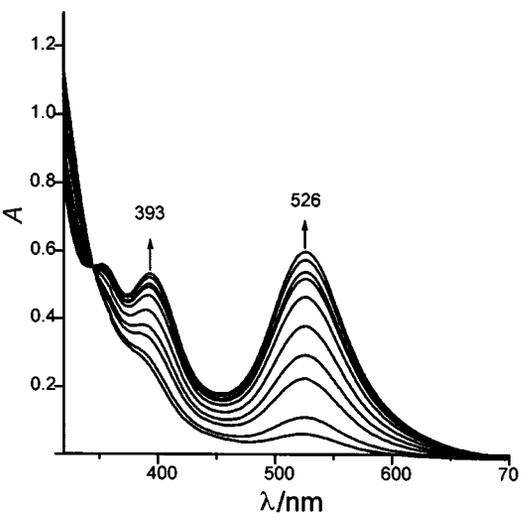


Fig. 5 Reduction of $[MoO_2L^2]$ **2** with PPh_3 in CH_2Cl_2 at 25 °C (spectra taken every 60 s).

Reactivity

Dioxomolybdenum(vi) complexes have attracted considerable interest in catalysing oxo-transfer reactions. A frequently used model reaction is the oxidation of triphenylphosphine by dmso. The formation of μ-oxo-dimers during the reduction of MoO_2 complexes is normally considered to be capable of breaking any catalytic cycle unless there is an equilibrium between the dimer of the $Mo^{VI}O_2$ complexes and a $Mo^{IV}O$ species. The oxo-bridged dimer itself has been considered to be reactive to oxygen atom transfer in some cases.[6,9] As apparent from the formation of dinuclear side products during the synthesis of the $Mo^{VI}O_2$ complexes, a reduction to μ-oxo-bridged complexes should be expected upon reduction of **1** and **2** by phosphines. However the sulfur-richness of the NS_2 ligands as well as the potentially vacant co-ordination site in the reduced dimer, as demonstrated in the crystal structure of **3**, might enable facile oxo-transfer reactions. In fact, the complexes **1** and **2** react readily at room temperature with PPh_3 to form corresponding dinuclear oxomolybdenum(v) compounds of the type $[Mo_2O_3L_2]$. The reactions have been monitored spectrophotometrically under pseudo-first-order conditions (100 fold excess of PPh_3) (see for example Fig. 5). In both cases the reactions are accompanied by the progressive increase of an LMCT band at ≈390 nm and the formation of a new LMCT band at ≈525 nm. The latter is characteristic for sulfur co-ordinated dinuclear $Mo^{V}_2O_3$ compounds and responsible for the red-purple colour of the complexes. Isosbestic points, predicting the involvement of only two components, are observed at ≈340 nm. There is no indication for the presence of an intermediate $Mo^{IV}O$ species.

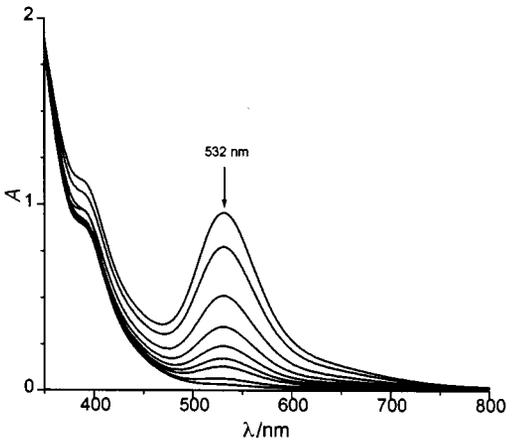


Fig. 6 Oxidation of $[Mo_2O_3L^3_2]$ **3** with pyridine *N*-oxide in dmf at 25 °C (spectra taken every 10 min).

The facile formation of dinuclear oxomolybdenum(V) complexes either as side products during complexation or upon reduction of the molybdenum(VI) complexes is surprising at first when compared with those complexes bearing analogous ONS Schiff base ligands where monomeric or polymeric molybdenum(IV) complexes have been suggested as reduction products.[2e–f] In our cases neither the thiophenolate nor the azaenethiolate functions tend to form μ-sulfur bridges in the molybdenum complexes. On the other hand the results are consistent with the finding that oxo-bridging proceeds easily unless suppressed by effective steric hindrance or added ligands.[10] The fact that we have not been able to isolate any molybdenum(IV) species when adding stabilizing ligands points to a fast and exclusive dimer formation. The reason for the different reduction products of our complexes and those with related ONS ligands remains unclear but is certainly not caused by steric constraints.

Oxidation reactions of the molybdenum(V) compounds **3** and **4** were studied by the use of oxygen, dmso and pyridine *N*-oxide. Complex **3** does not react with molecular oxygen but can be oxidized by dmso or, more rapidly, by pyridine *N*-oxide to the molybdenum(VI) complex (see for example Fig. 6). The oxidation proceeds in CH_2Cl_2 and, albeit slowly, in the potentially co-ordinating solvent dmf. The vacant co-ordination sites at the molybdenum centres in non-co-ordinating solvents enable the direct reaction of the substrate with the molybdenum(V) dimers whereas a displacement of co-ordinated solvent has to precede in dmf solutions. Unfortunately, a large excess of pyridine *N*-oxide finally leads to the decomposition of the molybdenum(VI) products, thus limiting possible catalytic oxo-transfer reactions. Compound **4** remains unchanged upon exposure to oxygen, dmso and pyridine *N*-oxide at room temperature. Hence the reversibility of oxo-transfer reactions involving molybdenum(V) dimers strongly depends on electronic features of the ligands whereas steric effects seem to be negligible here. Further studies to determine the corresponding rate constants are in current progress.

Conclusion

New thiosemicarbazone based NS_2 ligands and oxomolybdenum complexes have been prepared. The ligands are readily accessible in good yields and comparatively stable towards moisture and air. Modifications can easily be achieved by the use of various thiosemicarbazides and 2-sulfanylcarbonyl compounds as shown by representative examples. Considering the significant role of thiosemicarbazone based ONS ligands in co-ordination chemistry and catalytic applications,[1,2] the present class of sulfur ligands is very interesting for the preparation of a larger group of functional complexes with several other transition metals. Towards oxomolybdenum precursors, the ligands act as dianionic tridentate chelating ligands as well as reducing agents, giving the corresponding mononuclear dioxomolybdenum(VI) and dinuclear oxomolybdenum(V) complexes. On the one hand, reduction of the mononuclear dioxomolybdenum(VI) compounds, achieved by addition of phosphines like PPh_3, leads to dinuclear μ-oxo-bridged complexes. On the other hand, oxidations of the oxomolybdenum(V) complexes depend on electronic features of the ligands. Considering catalytic oxo-transfer reactions, both the formation of dinuclear oxomolybdenum(V) complexes and electronic properties of a given ligand have been elucidated. Formation of μ-oxo-bridged dimers does not necessarily exclude reversible oxo-transfer reactions. However, the introduction of an aromatic pyrazole (H_2L^4) instead of a phenyl unit (H_2L^1–H_2L^3) causes the irreversible formation of the dinuclear μ-oxo-bridged complex $[Mo_2O_3L^4_2]$ **4**.

Experimental

Materials and methods

All experiments involving sulfur-containing materials were performed using Schlenk techniques under a dry nitrogen atmosphere. Solvents were dried by standard methods and degassed prior to use. The compounds $[MoO_2(acac)_2]$,[11] *S*-benzyl dithiocarbazate,[12] 4-(triphenylmethyl)thiosemicarbazide,[13] 2-sulfanylacetophenone,[14] 2,2′-dithiodibenzaldehyde[15] and 4-formyl-3-methyl-1-phenyl-5-sulfanylpyrazole[16] were prepared according to the literature. Infrared spectra were recorded on a Bruker IFS 48 spectrometer, mass spectra of a dmf solution of **4** at the Physikalisches Institut der Universität Münster using a TOF-SIMS/PDMS spectrometer, NMR spectra on a Bruker WM 300 (300 and 75.5 MHz, for ^1H and ^{13}C, respectively; calibrated relative to the chemical shifts of the solvent protons) and UV/VIS spectra with a Shimadzu UV-PC-3100. The analyses (C, H and N) were performed by the Institut für Organische Chemie der Universität Münster using a Perkin-Elmer 240 Elemental Analyser.

Syntheses

H_2L^1. *S*-Benzyl dithiocarbazate (1.98 g, 10 mmol) was dissolved in hot ethanol (200 cm^3) and treated with a solution of 2-sulfanylacetophenone (1.52 g, 10 mmol) in ethanol (10 cm^3). The mixture was stirred for 12 h at room temperature. After evaporation of the solvent under reduced pressure an orange oil remained which was used without further purification (2.1 g, 63%) (Found: C, 58.07; H, 4.91; N, 8.49. $C_{16}H_{16}N_2S_3$ requires C, 57.83; H, 4.82; N, 8.43%); $\tilde{\nu}_{max}/cm^{-1}$ = 3305m (N–H), 3185m, 3059m (aryl C–H), 2927m (alkyl C–H), 1587s (C=N), 1488s, 1457s, 1425s (phenyl C=C), 1368m, 1328s, 1279s, 1253s, 1194w, 1113s, 1064s, 1044s, 978m, 757s, 699s and 655m.

H_2L^2. A solution of 2-sulfanylacetophenone (5.32 g, 35 mmol) in ethanol–water (200 cm^3:50 cm^3) was treated with 4-(triphenylmethyl)thiosemicarbazide (11.6 g, 35 mmol) as a solid. The mixture was refluxed for 2 h and then stirred for 12 h at room temperature. The precipitated pink solid was collected by filtration. The filtrate was treated with water (50 cm^3) and again filtered. The combined solids were washed with ethanol and dried *in vacuo* over $CaCl_2$ (14.6 g, 89%) (Found: C, 72.28; H, 5.52; N, 8.83. $C_{28}H_{25}N_3S_2$ requires C, 71.95; H, 5.35; N, 8.99%); $\tilde{\nu}_{max}/cm^{-1}$ = 3300s (N–H), 3057w, 3019w (aryl C–H), 2496w (S–H), 1595m (C=N), 1504s, 1490s, 1470s, 1447s (phenyl C=C), 1369m, 1301m, 1268m, 1206s, 1110m, 1033m, 754s, 745s and 700s; δ_H([$^2H_6$]dimethyl sulfoxide) 2.41 (3 H, s, CH_3), 5.13 (1 H, br s, SH), 6.63 (1H, br s, NH), 7.08–7.64 (19 H, m, aryl H), 8.95 (s, br, NH) and 10.18 (1 H, br s, NH); δ_C($CDCl_3$) 23.56 (CH_3), 72.18 (*C*Ph_3), 124.80 (aryl C), 126.39 (C*Ph*$_3$, C4), 127.12 (C*Ph*$_3$, C2,6), 127.23 (aryl C), 127.37 (C*Ph*$_3$, C3,5), 128.65 (aryl C),

Table 4 Crystallographic data and experimental details for complexes **1**–**3**

	1	**2**	**3**
M	551.54	697.69	1397.83
Formula	$C_{22}H_{21}MoN_3O_2S_3$	$C_{29}H_{27}MoN_3O_3S_2\cdot 2.25CH_4O$	$C_{54}H_{42}Mo_2N_6O_3S_4\cdot 3CH_2Cl_2$
Crystal size/mm	0.35 × 0.14 × 0.12	0.32 × 0.25 × 0.12	0.25 × 0.24 × 0.22
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$I2/a$
a/Å	10.779(2)	9.715(2)	18.450(4)
b/Å	12.678(2)	10.256(2)	19.763(4)
c/Å	17.567(2)	18.122(3)	18.514(4)
α/°		75.66(1)	
β/°	100.89(2)	83.29(1)	116.51(3)
γ/°		64.60(1)	
U/Å^3	2357	1581	6041
Z	4	2	4
D_c/g cm^{-3}	1.554	1.466	1.537
μ/mm^{-1}	0.846	0.590	0.867
T/K	293	170	293
2*θ* Range/°	4.72–54.12	4.50–48.12	10.60–56.06
hkl Ranges	0–13, 0–16, −22 to 22	0–11, −11 to 11, −20 to 20	−22 to 22, −25 to 23, −24 to 24
Measured reflections	5446	5347	24 807
Unique reflections	5160	4997	6700
Data for refinement	5160	4997	6686
Parameters refined	280	415	354
*R*1 [$I > 2\sigma(I)$]	0.0375	0.0507	0.0682
*wR*2 (all data)	0.0903	0.1339	0.2197

Graphite monochromated Mo-K*α* radiation; no absorption correction.

128.96 (aryl C), 129.66 (aryl C), 130.75 (aryl C), 143.77 (CH=N), 146.30 (C*Ph*$_3$, C1) and 177.48 (C=S).

Disulfide (HL^3)$_2$. A solution of 2,2′-dithiobenzaldehyde (1.37 g, 5 mmol) in ethanol (30 cm^3) was added to a suspension of 4-(triphenylmethyl)thiosemicarbazide (3.33 g, 10 mmol) in ethanol (200 cm^3). The mixture was gently refluxed for 4 h and then cooled to room temperature. The solution was reduced to 50 cm^3 and cooled to −20 °C. The light yellow precipitate was suction filtered, washed with MeCN and dried *in vacuo* over $CaCl_2$ (3.8 g, 84%) (Found: C, 71.30; H, 5.25; N, 9.02. $C_{28}H_{25}N_3S_2$ requires C, 71.94; H, 5.35; N, 8.99%); $\tilde{\nu}_{max}$/cm^{-1} = 3322m (N–H), 3056w, 3023w (aryl C–H), 2939w (alkyl C–H), 1584m (C=N), 1458m, 1431m (phenyl C=C), 1316m, 1253m, 1157m, 1034m, 958m, 752s and 719m; δ_H([$^2H_6$]dimethyl sulfoxide) 7.15–7.50 (38 H, m, aryl H), 8.40 (2 H, s, CHN) and 8.80 (2 H, s, NH).

H$_2$L^3. The disulfide (HL^3)$_2$ (4.5 g, 5 mmol) was added to a solution of NaOH (2.0 g, 50 mmol) in ethanol–water (200 cm^3 : 50 cm^3). Glucose (1.8 g, 10 mmol) was added portionwise. The mixture was stirred at 60 °C for 2 h. The cooled solution was adjusted to pH 3 by half concentrated acetic acid (9 mol l^{-1}. The slightly yellow precipitate was filtered off, washed with water and ethanol and dried *in vacuo* (2.7 g, 60%) (Found: C, 70.78; H, 5.22; N, 9.23. $C_{27}H_{23}N_3S_2$ requires C, 71.52; H, 5.07; N, 9.27%); $\tilde{\nu}_{max}$/cm^{-1} = 3333m (N–H), 3056w, 3023w (aryl C–H), 2923w (alkyl C–H), 2500w (S–H), 1591m (C=N), 1500s, 1442m (phenyl C=C), 1384m, 1246m, 1184m, 1098m, 755s and 703m; δ_H($CDCl_3$) 3.52 (1 H, br s, SH), 6.98–7.70 (19 H, m, aryl H), 7.90 (1 H, s, CHN), 8.82 (1 H, br s, NH) and 10.80 (1 H, br s, NH); δ_C($CDCl_3$) 72.89 (*C*Ph$_3$), 125.67 (aryl C), 127.23 (C*Ph*$_3$, C4), 127.93 (C*Ph*$_3$, C2,6), 129.75 (C*Ph*$_3$, C3,5), 129.81 (aryl C), 130.57 (aryl C), 131.34 (aryl C), 132.16 (aryl C), 132.41 (aryl C), 141.57 (CH=N), 144.35 (C*Ph*$_3$, C1) and 177.71 (C=S).

H$_2$L^4. A solution of 4-formyl-3-methyl-1-phenyl-5-sulfanylpyrazole (2.45 g, 11.2 mmol) in ethanol (50 cm^3) was added to a suspension of 4-(triphenylmethyl)thiosemicarbazide (3.72 g, 11.2 mmol) in ethanol (200 cm^3). The mixture was stirred for 24 h at room temperature and then filtered. The resulting solid was washed with ethanol and Et_2O and dried *in vacuo* (5.3 g, 90%) (Found: C, 67.81; H, 5.32; N, 12.56. $C_{30}H_{27}N_5S_2$ requires C, 68.5; H, 5.13; N, 13.31%); $\tilde{\nu}_{max}$/cm^{-1} = 3315m (N–H), 3055w, 3023w (aryl C–H), 2966w, 2923w (alkyl C–H), 1596m (C=N), 1515s, 1493s, 1443m (phenyl C=C), 1398s, 1298m, 1223s, 1203m, 1156w, 1104m, 1032w, 805w, 767m, 749s and 697s; δ_H($CDCl_3$) 2.27 (3 H, s, CH_3), 4.21 (1 H, s, SH), 7.32–7.48 (20 H, m, aryl H), 8.66 (1 H, s, CHN) and 9.31 (1 H, s, NH); δ_C([$^2H_6$]dimethyl sulfoxide) 14.57 (CH_3), 71.45 (*C*Ph$_3$), 117.2 (pyrazole C), 125.48 (aryl C), 126.90 (C*Ph*$_3$, C4), 127.81 (C*Ph*$_3$, C2,6), 128.25 (aryl C), 128.54 (aryl C), 128.99 (C*Ph*$_3$, C3,5), 132.93 (pyrazole C), 135.44 (CHN), 137.86 (aryl C), 144.45 (C*Ph*$_3$, C1) and 176.62 (C=S).

[MoO$_2$L^1(pic)] 1. A solution of H$_2$L^1 (3.2 g, 10 mmol) in ethanol (50 cm^3) was added dropwise to a solution of [MoO_2(acac)$_2$] (2.4 g, 7.2 mmol) in ethanol (100 cm^3). After a few minutes 4-methylpyridine (3 cm^3) was added. The mixture was stirred for 12 h at room temperature and then filtered. The light brown solid was washed with ethanol and dried *in vacuo*. The solid was treated with the minimum amount of ethyl acetate. Insoluble residues were filtered off. Slow diffusion of *n*-hexane through the gas phase into the filtrate yielded complex **1** as orange needles within a few days (1.2 g, 32%) (Found: C, 47.07; H, 3.83; N, 7.57. $C_{22}H_{21}MoN_3O_2S_3$ requires C, 47.91; H, 3.81; N, 7.62%); $\tilde{\nu}_{max}$/cm^{-1} = 3131w, 3057w, 3027w (aryl C–H), 1569m (C=N), 1541m, 1495m, 1460m, 1423m (picoline and phenyl C=C), 1401m, 1012m, 927s, 896s (Mo=O), 806m, 756m and 700m; δ_H($CDCl_3$) 2.63 (3 H, s, CH_3), 2.78 (3 H, s, CH_3), 4.52 (2 H, s, CH_2), 7.18–7.99 (11 H, m, aryl H) and 8.62 (2 H, s, aryl H).

[MoO$_2$L^2(MeOH)] 2. A suspension of H$_2$L^2 (0.94 g, 2 mmol) in ethanol (150 cm^3) was added to a suspension of MoO_2Cl_2 (0.4 g, 2 mmol) in ethanol (20 cm^3). The reaction mixture was stirred for 12 h and the brown solid was filtered off. The solution was evaporated to dryness and the residue treated with methanol (75 cm^3). After filtering off the undissolved material the solution was slowly evaporated to yield complex **2** as an orange powder along with some small needles (0.19 g, 15%) (Found: C, 54.80; H, 4.04; N, 7.02. $C_{29}H_{27}MoN_3O_3S_2$ requires C, 55.68; H, 4.32; N, 6.72%); $\tilde{\nu}_{max}$/cm^{-1} = 3427m (N–H), 3055w, 3026w (aryl C–H), 2965w (alkyl C–H), 1580m (C=N), 1557m,

1483s (phenyl C=C), 1444m, 1374m, 1277m, 1241m, 1055m, 927s, 893s (Mo=O), 757s, 704s, 654m and 619m; δ_H([$^2H_6$]-dimethyl sulfoxide) 2.38 (3 H, s, CH_3) and 7.10–7.45 (19 H, m, aryl H).

[$Mo_2O_3L^3_2$] 3. A solution of [MoO_2(acac)$_2$] (0.33 g, 1 mmol) in methanol (50 cm^3) was added dropwise to a solution of H_2L^3 (0.45 g, 1 mmol) in methanol (100 cm^3). The reaction mixture was gently refluxed for 2 h and then reduced to a volume of approximately 30 cm^3. Upon cooling to −20 °C a dark red-violet precipitation formed. The solid was filtered off, washed several times with ether and dried *in vacuo* (0.14 g, 24%) (Found: C, 59.75; H, 4.19; N, 7.86. $C_{54}H_{42}Mo_2N_6O_3S_4$ requires C, 57.35; H, 3.86; N, 7.33%); $\tilde{\nu}_{max}$/cm^{-1} = 3408m, (N–H), 3057w, 3026w (aryl C–H), 1582s (C=N), 1548s, 1472m (phenyl C=C), 1056m, 970s (Mo=O), 754s and 700s; δ_H([$^2H_6$]dimethyl sulfoxide) 7.08–7.41 (38 H, m, aryl-H) and 7.86 (2 H, s, CHN). Crystalline product was obtained by vapour diffusion of ether into a concentrated dichloromethane solution of complex **3**. No further elemental analysis of crystalline product was performed.

[$Mo_2O_3L^4_2$] 4. This compound was synthesized in the same manner as for **3**. Dark red crystals were grown from dichloromethane–pentane (0.75 g, 41%) (Found: C, 57.03; H, 4.01; N, 10.67. $C_{62}H_{50}Mo_2N_{10}O_3S_4$ requires C, 57.14; H, 3.84; N, 10.75%); $\tilde{\nu}_{max}$/cm^{-1} 3429m (N–H), 3057w (aryl C–H), 1579s (C=N), 1520m, 1493s, 1478s (phenyl C=C), 1450s, 1336m, 970s (Mo=O), 758s and 699s; δ_H($CDCl_3$) (mixture of diastereomers ≈2:1) 2.29, 2.30 (6 H, 2s, CH_3), 5.97, 5.94 (2 H, 2s, NH), 7.25–7.64 (40 H, m, aryl H) 8.02 and 8.06 (2 H, 2s, CHN); δ_C($CDCl_3$) 11.85 (CH_3), 73.70 (*C*Ph$_3$), 116.58 (pyrazole C), 123.92 (aryl C), 126.87 (C*Ph*$_3$, C4), 127.68 (C*Ph*$_3$, C2,6), 128.45 (aryl C), 128.86 (aryl C), 128.94 (C*Ph*$_3$, C3,5), 138.53 (pyrazole C), 144.34 (C*Ph*$_3$ C1), 145.92 (aryl C), 151.42 (NCS) and 155.26 (CHN); TOF-SIMS (substrate Ag), positive *m*/*z* 1411 (M + Ag$^+$) and 1304 (M^+); negative, *m*/*z* 1303 (M^-).

X-Ray crystallography

Crystals of complexes **1**–**3** were taken directly from solution and mounted on glass fibers at room temperature. Data were collected on a Siemens P3 diffractometer for **1** and **2** and on a Stoe IPDS for **3**. The structures for **1** and **2** were solved by direct methods and for **3** by the heavy atom method (SHELXS 86)[17] and refined by full-matrix least squares on F^2 (SHELXL 93);[18] hydrogen atoms were fixed geometrically. Details of the structure solutions and refinements are listed in Table 4.

CCDC reference number 186/1074.

See http://www.rsc.org/suppdata/dt/1998/2921/ for crystallographic files in .cif format.

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