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# Synthesis and characterization of molybdenum oxo complexes of two tripodal ligands: reactivity studies of a functional model for molybdenum oxotransferases†‡

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Reaction of the tetradentate ligand *N*-(2-hydroxybenzyl)-*N*,*N*-bis(2-pyridylmethyl)amine (L–OH) with $MoO_2Cl_2$ in methanol in the presence of NaOMe and $PF_6^-$ results in the formation of $[MoO_2(L–O)]PF_6$. Similarly, the reaction of *N*-(2-mercaptobenzyl)-*N*,*N*-bis(2-pyridylmethyl)amine (L–SH) with $MoO_2(acac)_2$ leads to the formation of $[MoO_2(L–S)]^+$. The dioxo-molybdenum complex $[MoO_2(L–O)]^+$ reacts with phosphines in methanol to afford phosphine oxides and an air-sensitive molybdenum complex, tentatively identified as $[Mo(IV)O(L–O)(OCH_3)]$. The latter complex is capable of reducing biological oxygen donors such as DMSO or nitrate, thereby mimicking the activity of DMSO reductase and nitrate reductase. Reaction of $[MoO_2(L–O)]PF_6$ with $PPh_3$ in other solvents than methanol leads to the formation of the Mo(V) dimer $[(L–O)OMo(\mu\text{-}O)MoO(L–O)](PF_6)_2$. The crystal structures of $[MoO_2(L–O)]PF_6$ and the μ-oxo bridged dimer are presented.

## Introduction

The mononuclear molybdenum enzymes constitute a diverse set of enzymes that have been found in all types of living systems from bacteria to plants and mammals, including man. These enzymes catalyze reactions that are part of the global carbon, nitrogen and sulfur metabolisms[1,2] and their active sites contain a cofactor (Moco) which consists of a molybdenum atom and one or two organic pterin derivatives (pyranopterindithiolates) called molybdopterins[3] (Fig. 1). The molybdopterin is coordinated to the molybdenum atom *via* the dithiolene unit. Additional ligands that are found in the oxidized Mo(VI) state of the cofactor includes one or two oxo ligands and/or a sulfido ligand and/or an amino acid residue such as serine or cysteine. Corresponding tungsten enzymes containing similar cofactors are known,[2,4] such enzymes have been found in acetate- and methane-producing bacteria as well as in hyperthermophilic archaea.

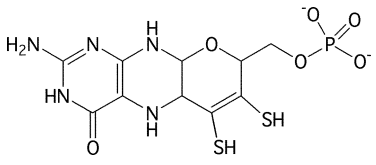

**Fig. 1** The structure of molybdopterin. In several enzymes, nucleotides (AMP, GMP, IMP) are coordinated to the phosphate side chain of the pyran (pyrene) ring. The "open form" of molybdopterin,[3] a bicyclic dihydropterin rather than the tricyclic pyranopterin, has recently been detected in the crystal structure of membrane-bound nitrate reductase from *E. coli*.[55–57]

The mononuclear molybdenum enzymes can be divided into two functional groups, hydroxylases and oxotransferases.[1,2] The general role for enzymes from the latter group is to catalyze oxygen atom transfer to or from a biological oxygen acceptor or donor (eqn. (1)).

$$[Mo^{VI}O_n]^{2+} + X \rightleftharpoons [Mo^{IV}O_{n-1}]^{2+} + XO \; (n = 1, 2) \qquad (1)$$

Examples of well-studied oxotransferases include sulfite oxidase[5–8] and dimethyl sulfoxide (DMSO) reductase.[9–16] In the case of DMSO reductase, isotope labelling experiments[17] indicate that the oxygen atom that is removed from the substrate coordinates to the molybdenum atom in the oxidized state of the enzyme. The presence of a Mo(VI)=O functional moiety is thus an essential feature of this group of enzymes. Several model systems for oxotransferases have been developed in order to better understand the reactivity of the molybdenum cofactors and the mechanisms of oxygen atom transfer.[18–25] The general mechanism proposed for the oxygen atom transfer includes a transition state where the molybdenum atom and the substrate are bridged by the oxygen atom that is either entering or leaving the coordination sphere of the molybdenum atom.[26,27]

The redox potentials, and thus potential reactivity/catalytic activity as well as substrate specificity of the enzymes (and model systems) are expected to be considerably influenced by the direct coordination environment of the molybdenum atom.[28,29] The presence of a molybdopterin (dithiolene) ligand is invariant in all mononuclear molybdenum enzymes and great advances in the preparation of molybdenum dithiolene complexes that replicate important structural, electronic[25] and functional features of molybdenum hydroxylases and oxotransferases have been made in recent years.[19–21,24–26,30] In order to probe the effects of the coordination environment, we have developed a synthetic strategy to obtain a number of tripodal ligands with N,O- and N,S-donor sets that can be varied in a systematic fashion.[31] Here, we would like to describe the preparation and oxygen atom transfer chemistry of molybdenum oxo complexes, in which the functional $\{Mo(VI)O_2\}/\{Mo(IV)O\}$ system, bearing a relationship to the active site of oxotransferase enzymes, is stabilized by the tetradentate ligands *N*-(2-hydroxybenzyl)-*N*,*N*-bis(2-pyridylmethyl)amine) (L–OH) and *N*-(2-mercaptobenzyl)-*N*,*N*-bis(2-pyridylmethyl)amine (L–SH).

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‡ Electronic supplementary information (ESI) available: Synthesis of bis(pyridin-2-ylmethyl)amine (DPA); COSY spectrum of complex **1**. See http://dx.doi.org/10.1039/b505180k

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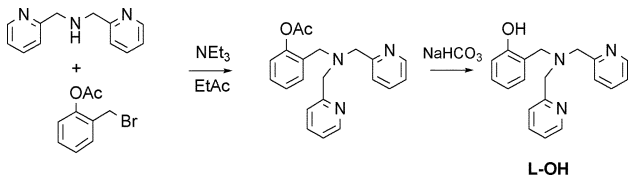
## Results and discussion

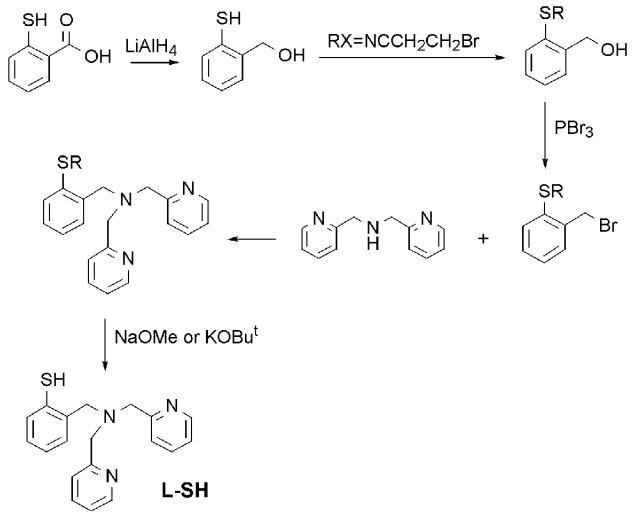
### Ligand synthesis

Preparative routes to L–OH[32] and L–SH[33,34] have been described in the literature, but we have developed new, convenient and relatively high yield syntheses of these ligands. The starting material dipicolylamine (bis(pyridin-2-ylmethyl)amine, DPA) was prepared according to a literature method[35] and isolated as its hydrochloride salt. The ligand L–OH was synthesized by a method used to prepare the closely related ligand *N*-(2-hydroxybenzyl)-*N*,*N*-bis(2-pyridyl*ethyl*)amine[36] (Scheme 1). Dipicolylamine was condensed with 2-bromomethylphenyl acetate;[37] subsequent deacylation afforded L–OH in better than 60% yield.




**Scheme 1** Synthetic route to *N*-(2-hydroxybenzyl)-*N*,*N*-bis(2-pyridylmethyl)amine) (L–OH).

The synthetic route to L–SH is outlined in Scheme 2. Reduction of the carboxylic acid of thiosalicylic acid with $LiAlH_4$[38] and subsequent protection of the thiol with a propionitrile group[34] led to the isolation of 3-(2-hydroxymethylphenylsulfanyl)-propionitrile. Bromination of 3-(2-hydroxymethylphenylsulfanyl)propionitrile with $PBr_3$ gave 3-(2-bromomethylphenylsulfanyl)propionitrile in 80% yield, and this was reacted with an equimolar amount of DPA to give L–$SCH_2CH_2CN$ (yield: 59%). Removal of the protection group by refluxing in methanol with NaOMe, or by addition of $KOBu^t$ at ambient temperature,[34] gave L–SH. The deprotected ligand was isolated as a sticky solid by the removal of the solvent *in vacuo*.




**Scheme 2** Synthetic route to *N*-(2-mercaptobenzyl)-*N*,*N*-bis(2-pyridylmethyl)amine (L–SH).

### Synthesis and characterization of $[MoO_2(L–O)]PF_6$ 1

In order to prepare two isostructural oxomolybdenum complexes with different ligand donor properties, L–OH and L–SH (*vide supra*) were reacted with suitable Mo(VI) starting materials. The dioxo-molybdenum complex of L–OH, $[MoO_2(L–O)]PF_6$ **1** was easily afforded by reaction of $[MoO_2Cl_2]$ or $[MoO_2(acac)_2]$ with the ligand in methanol or dichloromethane in the presence of NaOMe and $KPF_6$. Removal of the solvent and subsequent recrystallization of the product from a diethyl ether–hexane solution gave **1** as an orange microcrystalline powder.

Complex **1** has been characterized by $^1H$ NMR, UV-Vis and IR spectroscopy as well as mass spectrometry. In principle, there are two possible coordination modes for the ligand $L–O^-$ to a *cis*-dioxo molybdenum group - the methylpyridyl arms may be coordinated *cis* or *trans* to each other. Thus, two coordination isomers (one of which consists of a pair of enantiomers) are possible for **1**; these are shown in schematic form in Fig. 2. The crystal structures of mononuclear iron complexes containing $L–O^-$, $[FeCl_2(L–O)]$, and a derivative of $L–O^-$, $[FeCl_2(NO_2–L–O)]$ ($NO_2–L–O$ = *N*-(2-hydroxy-5-nitrobenzyl)-*N*,*N*-bis(2-pyridylmethyl)amine)),[39,40] reveal that the ligand coordinates with the pyridyl arms *cis* to each other (Fig. 2, isomer A). It is reasonable to expect that isomer A should be favoured, as it positions two relatively basic amine moieties in *trans* position to the oxo ligands while in isomer B, the phenolate moiety is *trans* to one oxo ligand. Molecular mechanics minimizations of the two coordination isomers using the SYBYL force field within the Spartan 4.1 program suite, indicate that isomer A is indeed favoured. The one-dimensional $^1H$ NMR spectrum of **1**, as well as $^1H–^1H$ COSY measurements (see ESI‡), support the existence of isomer A (exclusively) in solution. There are twelve resonances in the aromatic region (6.5–9.3 ppm) which may be attributed to the phenoxyl ring protons and the protons of two inequivalent pyridine rings (Fig. 3). Furthermore, the characteristic doublets of the two pyridine rings at 9.22 and 8.78 ppm are well separated and it is possible to detect six methylene resonances in the 4–6 ppm region, which is consistent with all three arms of the $L–O^-$ ligand being inequivalent.

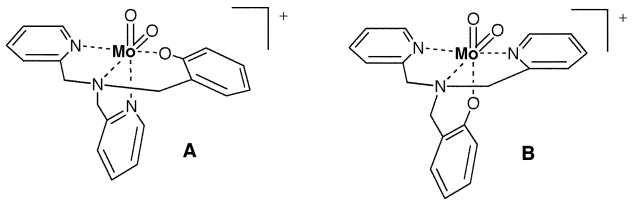



**Fig. 2** Two possible coordination isomers for the coordination of $L–O^-$ to a $MoO_2$ group (see text).

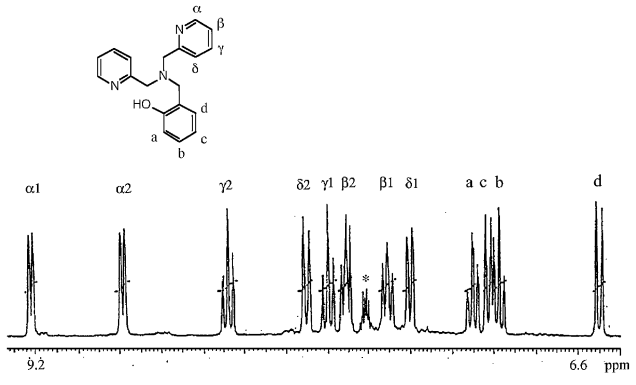



**Fig. 3** The aromatic region of the $^1H$ NMR-spectrum of $[MoO_2(L–O)]^+$ **1** (* = impurity). The resonances have been assigned on the basis of COSY spectroscopy (see text and ESI†).

### Crystal and molecular structure of 1

Crystals of **1** suitable for X-ray diffraction were grown from a concentrated methanol solution and the crystal structure of **1** was determined in order to confirm its structure and determine its conformation in the solid state. The molecular structure of **1** (Fig. 4) shows that the molybdenum atom is in a distorted octahedral environment with the three oxygen donors arranged in a *fac* configuration. The structure confirms that the pyridyls are coordinated *cis* to each other with one nitrogen *trans* to the phenolate and the other *trans* to one oxo ligand; the central

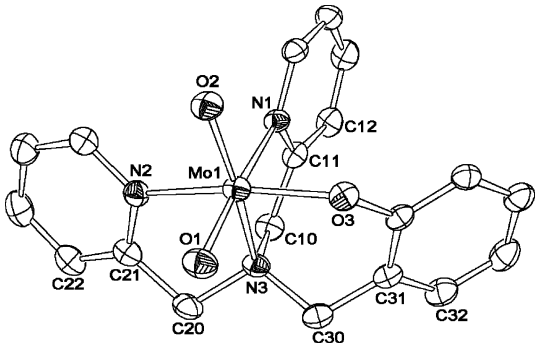



**Fig. 4** An ORTEP-3[58] diagram of the molecular structure of $[MoO_2(L–O)]^+$ **1** showing the atom numbering scheme. Thermal ellipsoids are plotted at the 30% probability level. Hydrogen atoms have been omitted for clarity.

amine is coordinated *trans* to the second oxo ligand. There are two optical isomers of the cation of **1** and both are present in the crystal. The $O_{oxo}$–Mo–$O_{oxo}$ angle (105.0°) and the Mo–$O_{oxo}$ distances (Mo–O1 1.667 Å, Mo–O2 1.676 Å) are similar to those reported in earlier studies of octahedral molybdenum dioxo complexes.[18,28,29,41–43] Due to the larger *trans* influence of the oxo ligand compared to the phenolate, the Mo–N1 bond distance is 0.16 Å longer than the Mo–N2 bond [2.286(3) and 2.128(4) Å, respectively] but almost identical to the Mo–N3 bond distance [2.290(4) Å]. All Mo–N distances are shorter than those observed in the closely related complexes $[MO_2(L–O_2)]$ (M = Mo,[41] W[28]), where $L–O_2^{2-}$ is the corresponding tripodal ligand with one pyridyl and two phenolate arms. The planes of the two pyridyl rings in **1** are almost perpendicular to each other and point straight out from the metal. The phenolate ring is coordinated so that the angle between this ring and the closest pyridyl ring is 40°. As has been observed in related complexes,[41] the Mo–O(3)–C(31) angle is unusually large (134.5°), suggesting partial $sp^2$ (re)hybridization to maximize orbital overlap with the metal.[42] Selected distances and angles are summarized in Table 1.

### Reactivity studies of $[MoO_2(L–O)]PF_6$ 1

Reaction of equimolar amounts of **1** and $PPh_3$ in methanol at low concentrations (0.4 mM) is fast and affords $Ph_3PO$ (as identified by $^{31}P$ NMR) and a complex that is tentatively formulated as $[Mo^{IV}O(L–O)]^+$. However, the reduced molybdenum complex is not stable and decomposes rapidly, $^1H$ NMR of the resultant solution shows only signals from the free ligand. At higher concentrations (>4 mM), reactions of **1** in methanol solution with an equimolar amount of $PPh_3$, or an excess of $PPh_3$ or $PEt_3$, affords a red complex and phosphine oxide. The red complex is tentatively identified as $[MoO(L–O)(OCH_3)]$ **2** on the basis of its $FAB^+$ mass spectrum which exhibits an $M^+$ peak with a characteristic molybdenum pattern corresponding to the formulation. Although **2** is air-sensitive, it is stable for days in anaerobic solutions at room temperature but decomposes slowly at elevated temperatures. Unfortunately, all attempts of isolation by evaporation of solvent or addition of diethyl ether or other solvents have been unfruitful, leading only to the isolation of a dark purple solid. It appears that **2** is a lightly stabilized complex that is present only in solution.

Addition of $OAsPh_3$ to a methanol solution of **2** leads to reduction of the arsine oxide and (re)oxidation of the molybdenum complex to form **1** in a slow reaction. In methanol solutions, the red complex also reduces three biological oxygen donors, *viz.* dimethyl sulfoxide (DMSO), nitrate and diphenyl sulfoxide as evidenced by the (re)formation of **1** (confirmed by UV-Vis spectroscopy), but the addition of $Me_3NO$ leads to decomposition of the molybdenum complex. If $PPh_3$ and **1** are reacted with DMSO as solvent, a red complex is initially formed and, in a slower reaction, **1** is reformed, indicating that the solvent is reduced. Addition of more $PPh_3$ starts the cycle over again, indicating that molybdenum-mediated oxo transfer from DMSO to $PPh_3$ is taking place.

**Table 1** Selected distances (Å) and angles (°) for $[MoO_2(L–O)](PF_6)$ **1**

| | | | |
|---|---|---|---|
| Mo1–O1 | 1.697(3) | Mo1–N2 | 2.194(3) |
| Mo1–O2 | 1.690(3) | Mo1–N3 | 2.312(3) |
| Mo1–O3 | 1.899(3) | O3–C36 | 1.372(4) |
| Mo1–N1 | 2.292(3) | | |
| | | | |
| O1–Mo1–O2 | 105.01(14) | O3–Mo1–N2 | 155.21(12) |
| O1–Mo1–N1 | 163.31(13) | N1–Mo1–N2 | 82.66(12) |
| O2–Mo1–N3 | 155.31(13) | Mo1–O3–C36 | 133.0(2) |

### Preparation of $[(\mu\text{-}O)\{MoO(L–O)\}_2](PF_6)_2$ 3

Upon reaction of **1** with $PPh_3$ in $CH_2Cl_2$, $CHCl_3$, pyridine, THF or acetonitrile, the solution initially turns red but rapidly changes color to dark purple and, in the case of dichloromethane or chloroform, leads to the formation of a dark purple solid. The $^1H$ NMR spectrum of the complex exhibited only very broad signals; this observation indicates that the product is a paramagnetic Mo(V) complex, and very likely a dimer, since the formation of oxo-bridged Mo(V) dimers is prevalent in this type of chemistry. Mass spectrometry of the dark purple complex indicated that it is indeed $[(\mu\text{-}O)\{MoO(L–O)\}_2](PF_6)_2$ **3**.

### Crystal and molecular structure of 3

In order to confirm the dimeric nature of **3**, single crystals were grown from a THF solution of **3** with added excess of $NaBPh_4$. The crystals were needle-shaped and very thin in one dimension. The low volume of the crystals made them weakly diffracting and a good quality data set could not be obtained with a conventional rotating anode X-ray source. However, a high quality data set could be obtained on the Lund University synchrotron (MAX-lab) and a satisfactory structure solution was obtained (*cf.* Experimental section).

The molecular structure of **3**, which is shown in Fig. 5, reveals that the cation is a dinuclear molybdenum complex with an Mo1–Mo2 distance of 3.717(24) Å. Selected distances and angles are summarized in Table 2. The two molybdenum atoms are bridged by an oxygen atom with an Mo1–O3–Mo2 angle of 169.7°. There is one terminal oxo ligand on each molybdenum and the two oxo ligands are in a *trans* configuration with an O1–Mo1···Mo2–O2 torsion angle of 179.8°; such *trans* configuration of the oxo groups is a feature that has been observed for several oxo-bridged Mo dimers.[44–49] On both

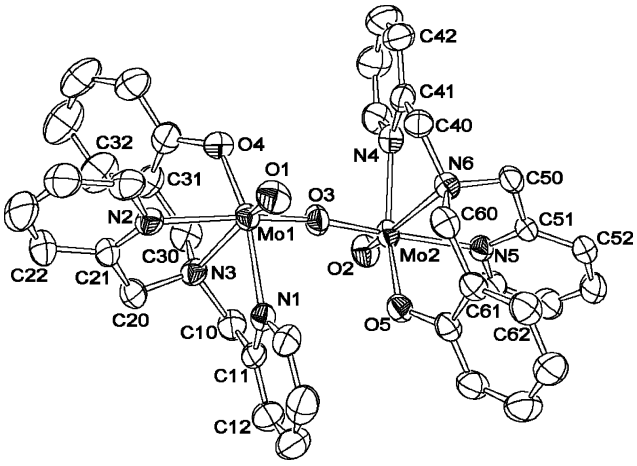



**Fig. 5** A diagram of the molecular structure of $[(\mu\text{-}O)\{MoO(L–O)\}_2]^{2+}$ **3** showing the atom numbering scheme. Thermal ellipsoids are plotted at the 30% probability level. Hydrogen atoms have been omitted for clarity.

**Table 2** Selected distances (Å) and angles (°) and [(μ-O){MoO(L–O)}$_2$](BPh$_4$)$_2$ **3**

| | | | |
|---|---|---|---|
| Mo1–Mo2 | 3.717(24) | Mo2–O2 | 1.681(2) |
| Mo1–O1 | 1.675(1) | Mo2–O3 | 1.868(16) |
| Mo1–O3 | 1.865(7) | Mo2–O5 | 1.956(17) |
| Mo1–O4 | 1.950(5) | Mo2–N4 | 2.194(16) |
| Mo1–N1 | 2.191(5) | Mo2–N5 | 2.211(24) |
| Mo1–N2 | 2.195(11) | Mo2–N6 | 2.326(0) |
| Mo1–N3 | 2.300(1) | | |
| | | | |
| Mo2–O3–Mo1 | 169.64(2) | O2–Mo2–N6 | 158.02(1) |
| O1–Mo1–O3 | 105.36(1) | O4–Mo1–N1 | 157.24(2) |
| O2–Mo2–O3 | 104.74(1) | O5–Mo2–N4 | 157.06(2) |
| O3–Mo1–N2 | 165.05(2) | N1–Mo1–N2 | 91.92(1) |
| O3–Mo2–N5 | 163.51(2) | N4–Mo2–N5 | 93.59(1) |
| O1–Mo1–N3 | 155.60(1) | | |

molybdenum atoms, the amine nitrogen is coordinated *trans* to the oxo group, one pyridyl nitrogen is *trans* to the μ-oxo bridge, and the other pyridyl nitrogen is *trans* to the phenolate oxygen. The geometrical configuration of the ligand donor atoms around each molybdenum in **3** is thus the same as the configuration in **1**, with one of the oxo ligands in **1** (the one *trans* to the pyridyl nitrogen) being replaced by the μ-oxo bridge, but it should be noted that the two molybdenum atoms in **3** have opposite stereochemical octahedral configurations (corresponding to the enantiomeric forms of **1**), probably due to steric reasons. Since there is no inversion center in the position of O3, there are two possible diastereomers of the whole cation of **3** and both of these are found in the unit cell. The Mo1–O1 and Mo2–O2 distances are 1.675(1) and 1.681(2) Å, respectively, while the Mo1–O3 and Mo2–O3 distances are longer, 1.865(7) and 1.868(16) Å, respectively. All four Mo–$N_{py}$ distances in the structure are close to 2.2 Å indicating that the *trans* influences exerted by the phenolate substituent of the ligand and the oxo bridge are approximately equal.

### Synthesis and reactivity studies of [MoO$_2$(L–S)]$^+$ 4

It was found that the preparation of complex **4** is dependent on the method of addition of the reactants. Thus, dropwise addition of a solution of L–SH to methanol or THF solutions of [MoO$_2$Cl$_2$] led to the formation of dark precipitates that were not analyzed further. The reactions were investigated at ambient temperature as well as −20 °C with the same result; at even lower temperature no reaction was found to occur. It is possible that reaction of L-SH with high-valent molybdenum complexes may lead to ligand oxidation and formation of a disulfide bridge. Such reactivity is not unprecedented, reaction of Ni(II) acetate with the protected form of L–SH in the presence of air leads to the dinuclear complex [Ni$_2$(L–S–S–L)(CH$_3$COO)$_2$](BPh$_4$)$_2$.[34] However, the dropwise addition of [MoO$_2$(acac)$_2$] in THF to a methanol solution of L–SH under the rigorous exclusion of air, led to the formation of [MoO$_2$(L–S)]$^+$ **4**, which was recrystallized in the presence of KPF$_6$ to form the hexafluorophosphate salt. The $^1$H NMR spectrum of **4** reveals that the ligand has the same coordination mode as observed for **1** (Fig. 2, isomer A), *i.e.* the two pyridyl moieties are chemically and magnetically inequivalent. The oxo transfer capability of **4** was investigated in NMR tube reactions, where an excess of triphenylphosphine was added to a CD$_2$Cl$_2$ solution of **4**. However, no formation of the corresponding phosphine oxide could be detected. This is in contrast to what has been observed for the oxygen atom transfer capabilities of tungsten dioxo complexes with tetradentate N$_2$O$_2$ and N$_2$S$_2$ phenolate/thiolate ligands[29] where the thiolate-containing complexes were found to be better oxo-transfer reagents than the corresponding phenolate complexes; however, a direct comparison between analogous phenolate and thiophenolate ligands was not made in this study.

In summary, the complex [MoO$_2$(L–O)]$^+$ **1** is capable of effecting oxygen atom transfer reactions with phosphines as oxo acceptors. The (unstable) Mo(IV) mono-oxo species [MoO(L–O)(OCH$_3$)] **2** that is the product of such oxo transfer in methanol, may in turn reduce (deoxygenate) the biological substrates nitrate, DMSO and diphenyl sulfoxide, thus emulating the reductive half reactions of nitrate reductase and DMSO reductase. However, in non-protic solvents, reaction of **1** with phosphines leads to the formation of the Mo(V) dimer [(μ-O){MoO(L–O)}$_2$](PF$_6$)$_2$ **3**. The molybdenum(VI) dioxo complex of the thiolate analogue of L–OH, *i.e.* [MoO$_2$(L–S)]$^+$ **4** was found to be unable to effect oxygen atom transfer to triphenylphosphine.

## Experimental

### General methods

All synthetic procedures were performed under an atmosphere of dry nitrogen using standard Schlenk and vacuum-line techniques or in a glove box. All solvents were dried by distillation over appropriate drying agents and degassed prior to use. All other chemicals were used as received. NMR Spectra were recorded using Varian Unity 300 MHz and Bruker Avance 400 MHz spectrometers using the solvent resonance as an internal standard for the $^1$H NMR spectra while H$_3$PO$_4$ was used as an external standard for the $^{31}$P spectra. IR Spectra were recorded in KBr pellets on Nicolet Avatar 360 and Perkin Elmer 1720 FT-IR instruments. UV-vis spectra were obtained on Varian Cary 50 Scan and Cary 300 Bio spectrometers. FAB-MS spectra were obtained on a JEOL SX-102 instrument; 3-nitrobenzyl alcohol was used as a matrix and CsI as the calibrant. The syntheses of bis(pyridin-2-ylmethyl)amine[35] *via* its hydrochloride salt (*cf.* ESI), 2-bromomethylphenyl acetate[37] and (2-mercaptophenyl)methanol[38] were performed according to literature procedures.

### Synthesis of *N*-(2-hydroxybenzyl)-*N*,*N*-bis(2-pyridylmethyl)amine (L–OH)[33,34]

Bis(pyridin-2-ylmethyl)amine (DPA, 1.70 g, 8.5 mmol) was dissolved in 40 ml ethyl acetate and 2.78 g of a 70 wt% solution of 2-bromomethylphenylacetate (8.5 mmol) and 5 ml triethylamine was added. The reaction was stirred at room temperature for 72 h and a white solid precipitated. The mixture was filtered and the solvent was removed under reduced pressure, yielding a brown oil. The oil was treated with a mixture of 40 ml water, 80 ml ethanol and 40 ml saturated sodium hydrogen carbonate and stirred for 3 h. Sodium hydroxide (2.0 g) dissolved in 20 ml water was added and the mixture extracted with 3 × 40 ml dichloromethane. The organic phase was dried with MgSO$_4$, filtered and evaporated to give 1.8 g of a brown oil. The oil was purified by flash column chromatography on silica using a 70 : 30 mixture of ethanol–ethyl acetate as eluent to give 1.6 g (5.26 mmol, 62% yield) of the product as a light brown oil. $^1$H NMR (CDCl$_3$): $\delta$ 8.56 (d, 2H), 7.64 (t, 2H), 7.35 (d, 2H), 7.14–7.20 (m, 3H), 7.06 (d, 1H), 6.89 (d, 1 H), 6.76 (t, 1H), 3.89 (s, 4H), 3.80 (s, 2H).

### Synthesis of 3-(2-hydroxymethylphenylsulfanyl)propionitrile

A solution of 5.22 g (37.2 mmol) of (2-mercaptophenyl)-methanol in 20 ml ethanol was added to a mixture of 1.45 g NaOH (36.3 mmol) in 2 ml water and 6 ml ethanol. To this solution, 4.98 g (37.2 mmol) 3-bromopropionitrile was added dropwise and the reaction was stirred for 5 h. The sodium bromide formed was filtered off and the solution evaporated to a yellow oil. The oil was dissolved in 40 ml diethyl ether and washed with 20 ml 5% NaOH and 20 ml water. The ether phase was dried and evaporated to give 6.16 g (31.9 mmol, 86% yield) of the product as a light yellow solid. Recrystallization of this solid from ether–pentane gave 4.48 g white crystalline material. $^1$H NMR (CDCl$_3$): $\delta$ 7.28–7.50 (m, 4H), 4.85 (s, 2H), 3.15 (t, 2H), 2.60 (t, 2H).

### Synthesis of 3-(2-bromomethylphenylsulfanyl)propionitrile

A suspension of 3.45 g (17.9 mmol) 3-(2-hydroxymethylphenylsulfanyl)propionitrile in 60 ml diethyl ether was cooled on an ice-bath and 1.61 g (6.0 mmol) $PBr_3$ was added dropwise under stirring. The ice-bath was removed and the reaction left for 3 h at room temperature. The solution was washed with 20 ml 5% NaOH and 20 ml water, dried with $MgSO_4$, filtered and evaporated to give 3.66 g (14.3 mmol, 80% yield) of the product as a light yellow oil. $^1$H NMR ($CDCl_3$): $\delta$ 7.44–7.50 (m, 2H), 7.29–7.33 (m, 2H), 4.74 (s, 2H), 3.20 (t, 2H), 2.62 (t, 2H).

### Synthesis of *N*-(2-propionitrilemercaptobenzyl)-*N*,*N*-bis(2-pyridylmethyl)amine (L–$SCH_2CH_2CN$)[34]

A mixture of 1.752 g DPA (8.79 mmol), 2.25 g 3-(2-bromomethylphenylsulfanyl)propionitrile (8.36 mmol), 3 ml $NEt_3$ and 150 ml ethyl acetate was stirred for 3 days. The reaction was filtered and evaporated to give 2.34 g of a yellow–brown oil. The oil was purified by chromatography on a silica column with a 70 : 30 mixture of ethanol–ethyl acetate as eluent and the product was obtained as 1.82 g (4.9 mmol, 59% yield) of a light yellow oil. $^1$H NMR ($CDCl_3$): $\delta$ 8.49 (d, 2H), 7.62 (t, 2H), 7.54 (dd, 1H), 7.49 (d, 2H), 7.34–7.30 (m, 1H), 7.22–7.18 (m, 2H), 7.10 (dd, 2H), 3.87 (s, 2H), 3.80 (s, 4H), 3.08 (t, 2H), 2.52 (t, 2H)

### Preparation of $[MoO_2(L–O)]PF_6$ 1

To a solution of L–OH (100 mg, 0.33 mmol), $KPF_6$ (72 mg, 0.39 mmol) and NaOMe (22 mg, 0.41 mmol) in 20 ml methanol, 67 mg $MoO_2Cl_2$ (0.34 mmol) was added. The reaction was stirred for 4 h and placed in a freezer overnight. The reaction was filtered to remove a white precipitate. Diethyl ether (5 ml) and hexane (15 ml) was added and more white solid formed and was removed by filtration. The yellow solution was kept at −20 °C overnight. Removal of the solvent at reduced pressure gave 122 mg of **1** (0.21 mmol, 64% yield). IR (KBr): $\nu_{MoO}$ 949, 918 cm$^{-1}$ $^1$H NMR ($CD_3OD$): $\delta$ 9.23 (d, 1H) 8.79 (d, 1H), 8.29 (t, 1H), 7.90 (d, 1H), 7.81 (t, 1H), 7.72 (t, 1H), 7.52 (t, 1H), 7.39 (d, 1H), 7.11 (t, 1H), 7.03 (d, 1H), 6.98 (t, 1 H), 6.51 (d, 1H), 5.32 (s, br, 1H), 5.28 (d, 1H), 4.92 (d, 1H), 4.51 (d, 1H), 4.46 (d, 1H), 4.17 (d, 1H). MS-FAB$^+$ ($m/z$): 434 ($M^+$). UV-vis (MeCN), $\lambda_{max}$/nm ($\varepsilon$/$M^{-1}$ cm$^{-1}$): 228, 261 (9400 ± 300), 355 (2350 ± 60).

### Preparation of [MoO(OMe)(L–O)] 2

In a typical reaction, **1** (10 mg, 0.02 mmol) was dissolved in 5 ml of methanol and $PPh_3$ (7 mg, 0.03 mmol) was added under nitrogen atmosphere, whereupon the solution immediately turned red. UV-vis (MeOH), $\lambda_{max}$/nm: 220, 255, 290 (sh) MS-FAB$^+$ ($m/z$): 465 ($M^+$). Removal of solvent under reduced pressure leads to the isolation of a small amount of complex **3** (*vide infra*).

### Preparation of $[(\mu\text{-}O)\{MoO(L–O)\}_2](PF_6)_2$ 3

To a solution of 40 mg (0.070 mmol) of **1** in 5 ml dichloromethane, 10 mg $PPh_3$ (0.038 mmol, 0.5 eq.) dissolved in 2 ml dichloromethane was added. The color changed from yellow to dark purple within 5 min. After 10 min a purple precipitate started to form and 10 ml diethyl ether was added. The product $[(\mu\text{-}O)\{MoO(L–O)\}_2](PF_6)_2$ was isolated by filtration after 30 min as 26 mg (0.023 mmol, 65% yield) of dark purple powder. MS-FAB$^+$ ($m/z$): 848 ($M^+$). UV-vis (MeCN), $\lambda_{max}$/nm ($\varepsilon$/$M^{-1}$ cm$^{-1}$): 228, 265, 383 (5000 ± 300), 534 (10700 ± 700).

### Preparation of $[MoO_2(L–S)]PF_6$ 4

A total of 163 mg $[MoO_2(acac)_2]$ (0.5 mmol) in 10 ml THF was added dropwise to a solution of L–SH (180 mg, 0.5 mmol) in 10 ml methanol, resulting in a yellow solution that slowly turned dark red. The solution was left stirring at ambient temperature overnight after which the solvent was removed *in vacuo* to yield **4** as a dark red microcrystalline product which was dried under vacuum for more than 2 h. Recrystallization from an acetonitrile solution in the presence of $KPF_6$ gave $[MoO_2(L–S)]PF_6$. Yield: 130 mg (0.3 mmol, 60%). IR (KBr): $\nu_{MoO}$ 952s, 898m cm$^{-1}$. $^1$H NMR (dmso-$d_6$): $\delta$ 8.97 (m, 1H) 8.79 (m, 1H), 8.18 (t, 1H), 7.74 (d, 1H), 7.60 (m, 1H), 7.53 (t, 1H), 7.44 (d, 1H), 7.34 (d, 1H), 7.21 (m, 1H), 7.16 (m, 2H), 6.88 (t, 1 H), 5.19 (d, 1H), 4.87 (d, 1H), 4.64 (d, 1H), 4.34 (d, 1H), 4.20 (d, 1H), 3.95 (d, 1H). MS-FAB$^+$ ($m/z$): 450 ($M^+$). UV-vis (MeCN), $\lambda_{max}$/nm: 253 (sh), 362, 450, 537.

**Table 3** Crystallographic data for $[MoO_2(L–O)](PF_6)$ **1** and $[(\mu\text{-}O)\{MoO(L–O)\}_2](BPh_4)_2$ **3**

| | **1** | **3** |
|---|---|---|
| Formula | $C_{19}H_{18}F_6Mo_1N_3O_3P_1$ | $C_{86}H_{76}B_2Mo_2N_6O_5$ |
| $M_r$ | 577.27 | 1487.03 |
| $\lambda$/Å | 0.71073 | 1.515 |
| Crystallographic system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ |
| $Z$ | 2 | 4 |
| $a$/Å | 8.4549(17) | 16.499(3) |
| $b$/Å | 9.2820(19) | 21.562(4) |
| $c$/Å | 14.303(3) | 20.882(4) |
| $\alpha$/° | 89.61(3) | 90 |
| $\beta$/° | 78.13(3) | 91.28(3) |
| $\gamma$/° | 76.02(3) | 90 |
| $V$/Å$^3$ | 1064.8(4) | 7427(3) |
| $D_c$/g cm$^{-3}$ | 1.800 | 1.330 |
| $2\theta$ Range/° | 1.5–31.7 | |
| $R_1$,[a] $wR_2$[b] | 0.0538, 0.1282 | 0.0538, 0.1682 |

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

### Crystallography

Relevant data about the collections and structure solutions are summarized in Table 3. Crystals of **1** suitable for X-ray crystallography were grown by slow evaporation of a methanol solution of **1**. Crystals of **3** were grown from a THF solution of $[(\mu\text{-}O)\{MoO(L–O)\}_2](PF_6)_2$ with an added excess of $NaBPh_4$. The intensity data sets for both **1** and **3** were collected with a SMART CCD detector at room temperature using $\omega$-scans.[50] For complex **1**, a rotating anode was used as the radiation source and no decay was detected. The intensity was corrected for Lorentz, polarisation and absorption effects using SADABS.[51] Complex **3** crystallised as needle-shaped crystals that were very thin in one dimension and therefore weakly diffracting. The data was therefore collected at the I711 beamline[52] at the MAX laboratory in Lund, Sweden, using synchrotron radiation at a wavelength of 1.515 Å. The data was collected with 2 s/frame where each frame scanned −0.2° in $\omega$. The whole reflection sphere was collected twice, with the detector at two different $2\theta$ angles (31 and 75°). The two sets of data, collected directly after each other, were merged. The intensity data set was corrected for decay in the incoming beam current when integrating the reflection using SAINT.[53] The intensity data set was also corrected for Lorentz, polarisation, and absorption effects using SADABS.[51] The structure of **1** was solved by the Patterson method and the structure of **3** was solved by direct methods using the SHELXTL97 program package.[54] All non-hydrogen atoms were refined anisotropically.

CCDC reference numbers 268641 (**1**) and 268642 (**3**).

See http://dx.doi.org/10.1039/b505180k for crystallographic data in CIF or other electronic format.

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