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Communication

X-ray crystal structure of a novel alkoxide-bridged dimolybdenum complex

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Summary – Reaction of $CR_2(CH_2SCH_2CMe_2CH_2OLi)_2$ (R = Me, hduLi$_2$; R = H, tduLi$_2$) with $[MoCl_4(NCMe)_2]$ in boiling CH_2Cl_2 gave the dithioether-dialkoxide complexes $[MoCl_2(hdu)]$ and $[MoCl_2(tdu)]$. Recrystallization of the latter from tetrahydrofuran (THF) plus ether gave the novel dimolybdenum complex $[MoCl_2(\mu\text{-tdu})MoOCl_2(THF)]\cdot Et_2O$, **1**. The X-ray crystal structure of **1** shows the complex to have an edge-sharing bioctahedral structure in which the two molybdenum atoms are in markedly different coordination environments. The pattern of bond angles suggests the presence of a Mo-Mo bond (Mo-Mo distance 2.814(1) Å).

molybdenum / bridging alkoxide / dinuclear complex / thioether

It has been established in recent years that the active site of nitrogenase is located on a metal-sulfur cluster of stoichiometry Fe_7MoS_9, in which the molybdenum atom at one end of the cluster is coordinated by three inorganic sulfurs, two oxygens from the alkoxide and carboxylate functions of the homocitrate ion, and a nitrogen from a histidine residue of the surrounding protein [1]. We are currently developing a strategy for modelling this coordination environment based on molybdenum complexes of mixed dithioether-dialcohols such as 2,2,6,6,10,10-hexamethyl-4,8-dithio-undecane-1,11-diol (hduH$_2$) and 2,2,10,10-tetramethyl-4,8-dithio-undecane-1,11-diol (tduH$_2$), figure 1.

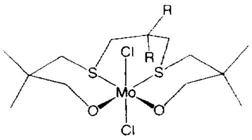

Fig 1. Molybdenum(IV) dithioether-dialkoxide complexes. $[MoCl_2(hdu)]$ R = Me, $[MoCl_2(tdu)]$ R = H.

We have previously described the preparation of hduH$_2$ from 2,2-dimethylpropane-1,3-dithiol and 3-bromo-2,2-dimethylpropan-1-ol [2]; tduH$_2$ can be prepared by an analogous procedure, but with the advantage that the propane-1,3-dithiol starting material is commercially available. Reaction of the dilithium salts hduLi$_2$ and tduLi$_2$ with $[MoCl_4(NCMe)_2]$ in boiling dichloromethane gives the expected complexes $[MoCl_2(hdu)]$ and $[MoCl_2(tdu)]$ (fig 1), obtained as air-sensitive, very dark brown microcrystalline powders. In contrast to the related, d^2, Schiff base complex $[MoCl_2(salen)]$ [H$_2$salen = *N,N'*-bis(salicylidene)ethylenediamine] which is high spin ($\mu_{eff} = 2.61\ \mu_B$) [3], $[MoCl_2(hdu)]$ is diamagnetic, whilst $[MoCl_2(tdu)]$ is weakly paramagnetic ($\mu_{eff} = 1.3 \pm 0.2\ \mu_B$ at 292 K). This leads to a broadening of the NMR spectrum when recorded in solvents such as CD_2Cl_2, but the spectrum is much sharper in coordinating solvents such as CD_3CN and CD_3OD. Conductivity measurements on both complexes confirm that they are non-conducting in acetone and nitromethane, but ionize to become 1:1 electrolytes in methanol (see *Experimental section*), which in the case of $[MoCl_2(tdu)]$ is evidently sufficient to induce a change to the low spin configuration.

Although $[MoCl_2(hdu)]$ and $[MoCl_2(tdu)]$ are readily soluble in medium-polarity solvents such as dichloromethane, THF and acetone, repeated attempts to grow crystals suitable for X-ray analysis have been unsuccessful. However, in one experiment when $[MoCl_2(tdu)]$ was recrystallized from THF/ether under dinitrogen, a few well-formed crystals were obtained in addition to the bulk microcrystalline powder. One of these was subjected to X-ray crystallographic analysis, and proved to be the unprecedented dinuclear derivative $[MoCl_2(\mu\text{-tdu})MoOCl_2(THF)]\cdot Et_2O$, **1**. The structure of **1** is shown in figure 2, along with the atom labelling scheme and selected bond distances and angles. Formation of **1** could arise from the reaction of a species such as $MoOCl_3$ [4] (formed by partial oxidation of the starting material $[MoCl_4(NCMe)_2]$) with $[MoCl_2(tdu)]$. Since $[MoCl_2(tdu)]$ is stable in boiling THF, the oxo ligand in **1** is most likely to have come from a trace of air rather than the solvent.

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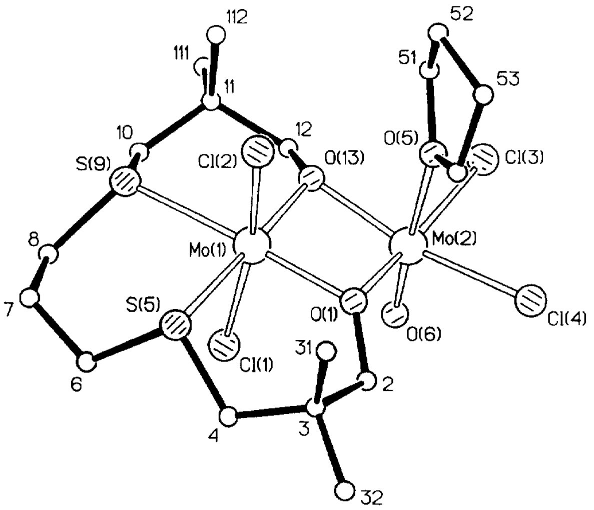

Fig 2. Molecular structure of $[MoCl_2(\mu\text{-tdu})MoOCl_2(THF)]\cdot Et_2O$, **1**. Hydrogen atoms and solvent have been omitted for clarity. Selected bond lengths and angles : mean Mo(1)-O 2.049(4), Mo(1)-Cl(1) 2.426(2), Mo(1)-Cl(2) 2.308(2), mean Mo(1)-S 2.493(1), mean Mo(2)-O (tdu) 2.038(3), mean Mo(2)-Cl 2.396(2), Mo(2)-O(5) 2.284(5), Mo(2)-O(6) 1.665(5) Å ; mean S-Mo(1)-O 90.3(3), S(5)-Mo(1)-S(9) 87.4(1), mean Cl-Mo(2)-O (tdu) 87.6 (4), Cl(3)-Mo(2)-Cl(4) 88.9(1)°.

Compound **1** is an unusual example of an edge-sharing bioctahedral complex in that the two metal atoms are in markedly different coordination environments. Thus in addition to the shared *cis*-bridging alkoxide groups, Mo(1) has two *trans*-chloride and two *cis*-thioether ligands, whereas Mo(2) has two *cis*-chloride ligands, one THF and one oxo-ligand. Mo(1) is located close to the mean plane of the equatorial S_2O_2 ligand, but Mo(2) is displaced by 0.265(2) Å out of the equatorial plane towards the oxo-ligand.

Cotton [5] has reviewed the structural features of dimeric edge-sharing bioctahedral complexes, and observed that the pattern of bond angles around the shared donor atoms and the metal centers, as much as the metal-metal distance, may be used to identify metal-metal bonding. On this basis, there appears to be a Mo-Mo bonding interaction in **1** since the Mo-O-Mo angles are both acute at 87.0(2)°, whilst the O-Mo-O angles are obtuse at 92.1(2)° for O(1)-Mo(1)-O(13) and 92.7(2)° for O(1)-Mo(2)-O(13); furthermore, the axial ligands are displaced away from their neighbors to relieve steric crowding (Cl(1)-Mo(1)-Cl(2) 171.0(1), O(5)-Mo(2)-O(6) 177.3(2)°), although there is minimal twisting of the axial ligands about the Mo-Mo axis (torsion angles Cl(1)-Mo(1)-Mo(2)-O(6) 0.0(2), Cl(2)-Mo(1)-Mo(2)-O(5) 1.5(1)°). The Mo-Mo distance in **1** is 2.814(1) Å, somewhat longer than the values of 2.731(1) Å (X = Cl) and 2.739(1) Å (X = Br) encountered in the isopropoxide-bridged molybdenum(V) dimers $[\{MoX_2(O^iPr)_2(\mu\text{-}O^iPr)\}_2]$ [6] for which a molybdenum-molybdenum single bond was assigned, but significantly shorter than the distances of 3.335(2) Å and 3.390(2) Å observed, respectively, in the complexes $[\{Mo(O^iPr)_2(NO)(\mu\text{-}O^iPr)\}_2]$ and $[\{Mo(O^iPr)_2(NO)(HNMe_2)(\mu\text{-}O^iPr)\}_2]$, which are considered to have no Mo-Mo bonding [7].

Consideration of the oxidation states of the metal atoms in **1** raises some interesting questions. If **1** is regarded as an adduct in which the parent molybdenum(IV) complex $[MoCl_2(tdu)]$ acts as a neutral chelating ligand to $\{MoOCl_2(THF)\}$, it can be formulated as a IV/IV (d^2-d^2) species. However, the alternative III/V (d^3-d^1) mixed formulation, which is conceptually related to the isopropoxide bridged dimers mentioned above, is also possible. There are very few comparable structures in the literature, but a loosely related example of a mixed oxidation state dimolybdenum species is furnished by the triple aryloxide-bridged complex $[Et_4N]_2[Mo(S,O\text{-}C_6H_4\text{-}1,2)_3Mo(CO)_3]$ which was considered to be approximately Mo^{III}/Mo^{I} on the basis of X-ray structural and photoelectron data [8]. If there are any qualitative differences in the bonding of the bridging alkoxides to the two molybdenum centres in **1**, these are not reflected in the Mo-OR(bridge) distances; all four are virtually equal (Mo(1)-O 2.049(4) Å, Mo(2)-O 2.038(3) Å), and lie well within the normal range of 2.03-2.15 Å [9].

Complex **1** was found to be paramagnetic (μ_{eff} = 5.2 ± 0.5 μ_B per molecule at 292 K; the relatively large uncertainty of this value reflects the small quantity of material available for the measurement). Given that the spin-only values for d^1-d^3 and high spin d^2-d^2 systems are 5.60 and 5.66 μ_B respectively [10], the observed magnetic moment is of little help in assigning formal oxidation states for **1**. However, it does suggest that the metal-metal bonding is relatively weak. We are currently developing a rational synthesis for **1** to enable a fuller study of its magnetic properties.

Experimental section

Caution. The lithium alkoxides $hduLi_2$ and $tduLi_2$ are very fine powders which are extremely irritating to the mucous membranes if inhaled. These compounds must be handled in the fume cupboard.

All preparations were done under a nitrogen atmosphere. Solvents were dried and distilled under nitrogen before use. Chemicals were purchased from Aldrich. Carbon, hydrogen and nitrogen elemental analyses were obtained from the Microanalytical Service, University of Surrey. Sulfur and chlorine analyses were obtained from Butterworth Laboratories. Magnetic moments were measured with a recording Faraday balance and corrected for diamagnetism using Pascal's constants. Solution conductivities were obtained with a Portland Electronics conductivity bridge.

The preparation and properties of 2,2,6,6,10,10-hexamethyl-4,8-dithiaundecane-1,11-diol have been reported previously [2]. 2,2,10,10-Tetramethyl-4,8-dithiaundecane-1,11-diol was prepared in 82% yield using the same procedure and has the following properties :

IR (liquid film, NaCl plates) : 3 389, 2 957, 1 472, 1 364, 1 246, 1 044, 986, 899 cm^{-1}.

^1H NMR (CD_2Cl_2, 270 MHz) : δ 0.92 (s, 12H), 1.83 (p, J = 7.1 Hz, 2H), 2.51 (s, 4H), 2.59 (t, J = 7.1 Hz, 4H), 2.86 (s, 2H), 3.34 (s, 4H).

^{13}C NMR ($CDCl_3$, 67.9 MHz) : δ 23.9 (q, J = 127 Hz), 29.4 (t, J = 129 Hz), 32.5 (t, J = 139 Hz), 36.5 (s), 42.1 (t, J = 138 Hz), 70.2 (t, J = 140 Hz).

The alcohols were lithiated with two equivalents of methyl lithium in ether; the lithium alkoxide was filtered off and dried under vacuum (yield typically 80-90%).

Preparation of [MoCl$_2$(hdu)]

A mixture of [MoCl$_4$(NCMe)$_2$] (18.6 g, 5.8 × 10^{-2} mol) and hduLi$_2$ (19.0 g, 5.9 × 10^{-2} mol) in dichloromethane (500 mL) was boiled under reflux for 4 h. After cooling, the mixture was filtered and the pale brown residue discarded. The filtrate was concentrated under vacuum to *ca* 50 mL, and ether (400 mL) was added. The mixture was stirred for 1 h, then filtered to give a dark brown powder, which was washed with ether and dried under vacuum (yield 21.5 g, 78%). The complex was purified if desired by dissolving in acetone or dichloromethane and re-precipitating with ether.

IR (KBr and CsI pellets) : 2 960, 1 470, 1 390, 1 365, 1 015, 985, 705, 630, 520, 325 cm^{-1}.

^{1}H NMR (CD$_3$CN, 270 MHz) : δ 0.92 (s, 12H), 1.00 (s, 6H), 2.56 (s, 4H), 2.60 (s, 4H), 3.32 (s, 4H).

^{13}C{^{1}H} NMR (CD$_3$CN, 67.9 MHz) : δ 24.0, 26.6, 37.5, 37.6, 44.9, 46.8, 70.0.

Anal calc for $C_{15}H_{30}Cl_2MoO_2S_2$: C, 38.1; H, 6.4; S, 13.5; Cl, 15.0%. Found : C, 38.3; H, 6.7; S, 13.5; Cl, 11.8%.

Λ_M (cm^2 Ω^{-1} mol^{-1}) : 88 (methanol), 11 (acetone), 16 (nitromethane).

Preparation of [MoCl$_2$(tdu)]

The above procedure was used to obtain [MoCl$_2$(tdu)] from tduLi$_2$ in 83% yield. The complex was purified by dissolving in dichloromethane or THF and re-precipitating with ether.

IR (KBr and CsI pellets) : 2 960, 1 470, 1 390, 1 370, 1 020, 985, 700, 630, 505, 330 cm^{-1}.

^{1}H NMR (CD$_3$OD, 270 MHz) : δ 0.93 (s, 12H), 1.82 (p, J = 7.1 Hz, 2H), 2.51 (s, 4H), 2.61 (t, J = 7.0 Hz, 4H), 3.32 (s, 4H).

^{13}C{^{1}H} NMR (CD$_3$OD, 67.9 MHz) : δ 24.1, 30.9, 33.6, 37.8, 42.9, 70.6.

Anal calc for $C_{13}H_{26}Cl_2MoO_2S_2$: C, 35.1; H, 5.9; S, 14.4; Cl, 15.9%. Found : C, 34.2; H, 5.9; S, 15.5; Cl, 16.2%.

Λ_M (cm^2 Ω^{-1} mol^{-1}) : 86 (methanol), 10 (acetone), 14 (nitromethane).

X-ray analysis of [MoCl$_2$(μ-tdu)MoOCl$_2$(THF)]·Et$_2$O, 1

Crystal data : $C_{17}H_{34}Cl_4O_4S_2Mo_2 \cdot C_4H_{10}O$, M = 774.4; monoclinic, space group $P2_1/a$, a = 19.395(6), b = 11.997(7), c = 13.362(2) Å, β = 93.94(2)°, U = 3 102(2) Å^3, Z = 4, D_c = 1.658 g cm^{-3}, $F(000)$ = 1 576, μ(Mo-K$_\alpha$) = 13.0 cm^{-1}, λ(Mo-K$_\alpha$) = 0.71069 Å.

Dark-brown crystals; one, *ca* 0.26 × 0.5 × 0.86 mm, was mounted in air on glass fibre; Enraf-Nonius CAD4 diffractometer for accurate cell dimensions (from 25 reflections, each in four orientations, θ *ca* 10.5°) and intensity measurements (to θ_{max} 25°). 5 449 Unique reflections were corrected for Lorentz-polarization effects, absorption and to eliminate negative intensities statistically. The structure was determined by heavy atom method in SHELX [11].

Refinement was made by full-matrix least-squares methods to R = 0.074, R_g [11] = 0.083 for 4 763 reflections (those with $I > \sigma_I$), weighted $w = (\sigma_F^2 + 0.00166F^2)^{-1}$. Hydrogen atoms were included in idealized positions (methyl groups staggered) with independent U_{iso} thermal parameters; all non-hydrogen atoms were anisotropic. The ether molecule was slightly disordered, showing two sites for one carbon atom. Final difference peaks were 0.7-1.4 eÅ^{-3} close to the Mo atoms.

Supplementary material data have been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication no = SUP 90380 and are available on request from the Document Supply Centre; material available atomic coordinates and anisotropic thermal parameters, hydrogen atom parameters, bond lengths and angles, observed and calculated structure factors, and full experimental details for the determination.

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