Dioxomolybdenum(VI) Complexes of Chelating Alkoxides

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Molybdenum trioxides MoO₃ or MoO₃·2H₂O reacted with alcohol ethers (HOROR) to form complexes having the general formula [MoO₃(OROR)₂] where HOROR = 2-methoxyethanol (Hmet) or tetrahydropryran-2-methanol (Hpyr). In these compounds the Mo⁶⁺ has a distorted octahedral coordination geometry. The reaction of [MoO₃(pyrr)₂] with diertitary diol 1,1'-bicyclohexane-1,1'-diol (H₂bicy) in acetonitrile solution produced the complex [MoO₃(Hbicy)(pyrr)] and in the presence of methanol the product was the dimeric complex [{MoO₂(Hbicy)(OMet)₂}₂·2MeOH. The structures of four complexes were confirmed by X-ray diffraction.

High-valent transition metals bearing multiple bonded oxo ligands¹ are of interest in organometallic chemistry as catalysts in olefin metathesis reaction² and as model compounds for the active catalyst site in oxidation reactions.³ Moreover, molybdenum complexes containing the cis-dioxomolybdenum(VI) unit coordinated to ligands having nitrogen, oxygen or sulfur donors are intensely investigated because such complexes are proposed as model compounds for the active site in a number of oxo-transfer molybdoenzymes.⁴

Alkoxide groups are widely employed ancillary ligands in combination with multiply bonded functionalities. Mo⁶⁺ dioxoalkoxides with the general formula of MoO₃(OR)₂ are typically prepared by displacement of chloride ion from MoO₃Cl₂ using lithium alkoxides.⁵,⁶ Other methods are the reaction of [Mo₂(OR)₄] with molecular oxygen⁷ and low-temperature co-condensation reactions of MoO₃ with silolated alcohols.⁸ These tetra-coordinated dioxomolybdenum(VI) alkoxides are usually unstable in the solid state, but they can be stabilised as nitrogen-based adducts. High-temperature reaction between molybdenum oxide and diols produces more stable, coordinatively saturated, six-coordinated hydrogendiolato complexes, e.g. [MoO₂(Heg)$_2$] and [MoO₂(Hbpu)$_2$]·2H₂bu (He₉ₑ = 1,2-ethanediol, H₂bu = 1,2-butanediol).⁹,¹⁰

In our previous investigations, we have studied the coordination chemistry of tungsten and rhenium oxoalkoxides.¹¹,¹² In this paper we discuss the syntheses and crystal structures of two monomeric dioxomolybdenum(VI) complexes with chelating monofunctional ether alkoxides, [MoO₂(met)$_2$] I and [MoO₂(pyrr)$_2$] 2 (Hmet = 2-methoxyethanol, Hpyr = tetrahydropryran-2-methanol). We also report reactions of complex 2 with a diertitary diol, H₂bicy (H₂bicy = 1,1'-bicyclohexane-1,1'-diol) including crystal structures of a mononuclear hydrogendiolato complex [MoO₂(Hbicy)(pyrr)] and a methoxy-bridged dimer [{MoO₂(Hbicy)(OMet)₂}₂·2MeOH.

Results and discussion

Synthesis. One of the general methods to prepare metal alkoxides is a condensation reaction between alcohol and a metal oxide.¹³ In the present experiments, direct reactions between molybdenum trioxide (MoO₃ or MoO₃·2H₂O) and monohydric, chelating ether alcohols, 2-methoxyethanol (Hmet) and tetrahydropryran-2-methanol (Hpyr) without a solvent were studied. When white molybdenum trioxide MoO₃ was used as a metal oxide source, the oxide was suspended in excess alcohol at a temperature over 120°C for 15–30 min. Compounds [MoO₂(met)$_2$] I and [MoO₂(pyrr)$_2$] 2 crystallised out from filtered solutions upon cooling. A dark blue solid, presumably Mo₂O₁₀(OH)$_₂$, ⁹ is formed as a by-product during the reaction, and the yields of Mo⁶⁺ alkoxides are low (<30%). The low yields suggested us to use different molybdenum oxides as metal precursors. Yellow molybdenum trioxide dihydrate MoO₃·2H₂O is known to be more reactive than MoO₃ at temperatures near room temperature, e.g. it reacts with methanol under reflux to form dimeric oxomethoxide [Mo₂O₃(OMet)$_₂$].¹⁴ We found that when MoO₃·2H₂O was mixed with excess Hmet or Hpyr at 20-30°C temperature, it reacted slowly
and some white precipitate formed during 24 h stirring. The reaction vessels were warmed to dissolve solids, and filtered solutions were cooled to $-18^\circ$C to obtain complexes 1 and 2 as colourless crystals in high yields.

Crystals of 1 are stable in their mother liquor, but as isolated solids they decompose to afford an intractable dark blue material, especially if exposed to light. Complex 1 is insoluble in alcohols, chloroform or acetonitrile, but dissolves in DMSO forming a blue solution. Compound 2 is stable in the solid state if stored in a dark place under dry air, but it also turned blue if exposed to light and humidity. Complex 2 dissolves in methanol and ethanol. It is also soluble in acetonitrile and tetrahydrofuran in the presence of alcohols, but decomposes rapidly when dissolved in chloroform. Generally 2 seems to be more stable and soluble and so more useful in further reactions than 1.

Our attempts to prepare analogous complexes from other ether-functionalised alcohols e.g. 2-ethoxyethanol, 2-(2-methoxyethoxy) ethanol and tetrahydrofurural alcohol were unsuccessful. They reacted with MoO$_3$ only with prolonged heating leading finally to the formation of dark solids and green–blue solutions without any isolable products. These alcohols also dissolved MoO$_3$·2H$_2$O, resulting in blue solutions.

As complex 2 is stable and soluble in organic solvents, it could be a suitable source for exploring the chemistry of dioxomolybdenum complexes. We found that it can undergo an alkoxide displacement reaction with a bulky, ditertiary diol H$_2$bic$_2$. If complex 2 and H$_2$bic$_2$ are dissolved in acetonitrile, the reaction leads to the displacement of one pyridyl ligand by singly deprotonated Hbic$_2$ group yielding monomeric complex [MoO$_3$(Hbic)$_2$(pyr)]. Complex 3 is moderately stable in the solid state if kept in dark and dry conditions. If the ligand displacement reaction is done in the presence of methanol, the product is the methoxide-bridged dimeric complex [[MoO$_3$(Hbic)$_2$(OMe)$_2$]$\cdot$2MeOH (4), in which one pyridyl ligand is displaced by an Hbic$_2$ ligand and another one by a bridging methoxide group. Crystals of 4 are stable in their mother liquor but when dry they slowly become dark blue.

**Structures of complexes.** The molecular structures of monomeric complexes 1–3 are shown in Figs. 1–3 respectively, with the relevant bond distances and angles collected in Table 1. The coordination sphere around the Mo$^{VII}$ cation is quite similar in all three complexes. Coordination around the molybdenum atom presents distorted octahedral geometry with the terminal oxo ligands cis to each other. Two anionic alkoxide oxygens and two neutral ether oxygen donor atoms of the ligands are trans and cis, respectively, as expected for an octahedral dioxo complex. Neutral oxygen atoms of the ligands are trans to the terminal oxo groups where the considerably longer Mo–O bond distances are observed. The strong trans-influencing ability of multiply bonded oxo ligand explains the disposition of the ligands, which are arranged with the weakest π-bonding donor atom trans to the oxide group.$^1$ The O–Mo–O angles vary from 104.7(2) to 105.7(3)$^\circ$. Also the O–Mo–O (O = alkoxide) angles are quite similar [from 143.9(2) to 148.6(1)$^\circ$], as are all other angle values around Mo$^{VII}$ in all three complexes. The torsion angle values of O–C–C–O chains in the ligands vary from 39.9(9) to $-49.5(5)^\circ$. The ligands adopt λδ conformations in 1 and 3. The ligand has a λα (δδ) conformation in 2. Coordination spheres around the Mo$^{VII}$ ion in these structures are closely similar to those found in dioxomolybdenum(VI) complexes with simple diols.$^9,10$

The molecular structure of the dinuclear complex 4 is shown in Fig. 4, with the relevant bond distances and

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**Fig. 1. ORTEP plot of 1 showing the labelling system of heavy atoms. Displacement ellipsoids are plotted at the 30% probability level.**

**Fig. 2. ORTEP plot of 2 showing the labelling system of heavy atoms. Displacement ellipsoids are plotted at the 30% probability level.**

**Fig. 3. ORTEP plot of 3 showing the labelling system of heavy atoms. Displacement ellipsoids are plotted at the 30% probability level.**

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Table 1. Selected bond distances (in Å) and angles (in °) for complexes 1–4.

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<td>2.426(5)</td>
<td>2.354(3)</td>
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O(1)–Mo–O(2) 105.2(1) 105.7(3) 104.7(2) 104.4(1)*
O(1)–Mo–O(4) 165.0(1) 166.1(2) 164.2(2) 164.8(1)*
O(2)–Mo–O(6) 166.6(1) 165.7(3) 165.9(2) 158.3(1)*
O(3)–Mo–O(4) 72.3(1)   72.5(2)   72.3(1)   72.3(1)
O(3)–Mo–O(5) 145.0(1) 143.9(2) 145.3(2) 148.6(1)
O(5)–Mo–O(6) 72.7(1)   71.7(2)   73.5(1)   68.6(1)*
Mo–O(3)–C(1) 122.9(2) 121.3(5) 123.2(3) 125.4(2)
Mo–O(4)–C   111.6(2) 112.2(4) 114.6(3) 114.3(2)
Mo–O(5)–C   125.5(2) 121.9(5) 121.6(3) –
Mo–O(6)–C   105.3(2) 114.6(3) 110.0(3) –
O(3)–C–O–(4) 45.7(3)  41.6(8)  43.5(4)  42.3(3)
O(5)–C–O–(6) 46.8(3)  39.9(9)  49.5(5) –

*In 4 O(5’) = O(6) (I = 1 – x, 1 – y, –z).

Fig. 4. ORTEP plot of 4 showing the labelling system of heavy atoms. The CH hydrogens are not depicted. Displacement ellipsoids are plotted at the 30% probability level.

angles collected in Table 2. The dinuclear species of 4 consists of two identical molybdenum-centred units linked together by two methoxy bridges around a crystallographic centre of inversion. Each molybdenum(VI) ion is bonded to one singly deprotonated Hbicy chelate ligand, two terminal oxide groups and two methoxide ligands, with the latter forming bridges to another molybdenum(VI) ion. The oxygen atom of the methanol is bonded to the hydrogen atom of the alcohol group of the diol via an H-bond [the O(4)–O(6) distance is 2.748(2) Å]. The hydrogen at methanol forms a weak H-bond to O(1) [the O(6)–O(1) distance is 3.006(4) Å, I = x–1, y, z]. On the whole the structure of 4 resembles closely that found in the hydrogenpinacolato complex [MoO2(Hpin)(OMe)2]·2MeOH.16

Conclusions

This work has shown that molybdenum trioxides MoO3 or MoO3·2H2O react with monohydrate, ether alcohols 2-methoxyethanol (Hmet) or tetrahydropropyan-2-methanol (Hpyr) to form distorted octahedral dioxomolybdenum(VI) complexes. If yellow dihydrate MoO3·2H2O is used as starting material, high yields are reached even at low temperatures near RT. These compounds can be used as starting materials for new molybdenum(VI) complexes. The reaction of [MoO2(pyr)2] with the ditertiary diol 1,1’-bicyclohexene-1,1’-dial (Hbicy) in acetonitrile solution produces the complex [MoO2(Hbicy)(pyr)], and in the presence of methanol the product is the dimeric complex [MoO2(Hbicy)(OMe)2]·2MeOH.

Experimental

MoO3·2H2O (Ref. 17) and H2bicy (Ref. 18) were prepared by known methods. Other chemicals were from commercial origins and were used without subsequent purification. IR spectra were recorded on a Mattson Galaxy FTIR spectrometer as Nujol mulls. Elemental analyses were performed on a Perkin–Elmer series II analyser. NMR spectra of studied compounds were not recorded owing to low stability and/or solubility in common NMR solvents.

Preparation of [MoO2(meet)2]·2H2O (1).

(a) From MoO3. A suspension of white MoO3 (1.0 g, 6.9 mmol) in 2-methoxyethanol (10 ml) was stirred in an open vessel at 120 °C for 30 min, upon which period the colour of the suspension turned dark blue. The dark solid residue was removed by filtration, and the clear filtrate was allowed to stand overnight at –18 °C. Separation of the crystalline product by filtration and washing with diethyl ether yielded clear crystals (550 mg) in ca. 30% yield based on molybdenum oxide. IR: 1265 (m), 1235 (m), 1095 (s, br), 1040 (s, br), 1005 (s), 950
Table 2. Crystal data and experimental details for 1-4.

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<td>$U$/Å$^3$</td>
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<td>$wR_2$</td>
<td>0.052 (0.050)</td>
<td>0.070 (0.065)</td>
<td>0.090 (0.075)</td>
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*Values in parentheses for reflections with $I>2.0\sigma(I)$.

$R_1 = \sum |F_o| - |F_c|)/\sum |F_o|$, $wR_2 = (\sum [w(F_o^2 - F_c^2)^2]/\sum [w(F_o^2)^2])^{1/2}$ and $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP)$, where $P = (2F_o^2 + F_c^2)/3$.

(s), 910 (s, br), 840 (s), 720 (m), 560 (s, br). Found C: 25.45; H: 4.70. Calcld. C: 25.90; H: 5.05.

(b) From MoO$_3$·2H$_2$O. The suspension of yellow MoO$_3$·2H$_2$O (1.0 g, 5.6 mmol) in 2-methoxyethanol (15 ml) was stirred at 20°C for 1 hour. After 1 hour, the formation of a white precipitate was noted. When the reaction had proceeded for 24 hours, the mixture was warmed to 50°C for 20 minutes to dissolve the white solid which had been formed during the reaction. The reaction mixture was filtered as a warm and clear filtrate, and then cooled to room temperature, and finally to −18°C, giving a white precipitate. The product was filtered and washed with diethyl ether, yielding 1020 mg of colourless crystals (66%). This product was identical to that obtained from MoO$_3$.

Preparation of [MoO$_2$(Hbicy)(pyr)$_2$] (2).

(a) From MoO$_3$. MoO$_3$ (1.0 g, 6.9 mmol) was suspended in tetrahydropropylene-2-methanol (10 ml), and the mixture was stirred in an open vessel at 160°C for 15 minutes. A dark solid residue was formed and removed by filtration. The clear filtrate was allowed to stand overnight at −18°C to obtain a white solid. The crystalline product was separated by filtration with washed with diethyl ether yielding 720 mg of clear crystals (30%). IR: 1280 (m), 1180 (m), 1011 (s), 1070 (s), 1035 (s), 1000 (s), 920 (s, br), 880 (s), 855 (s), 830 (s), 790 (s), 600 (m), 565 (s), 515 (m). Found C: 40.85; H: 6.40. Calcld. C: 40.25; H: 6.20.

(b) From MoO$_3$·2H$_2$O. A suspension of MoO$_3$·2H$_2$O (1.0 g, 5.6 mmol) in 15 ml of tetrahydropropylene-2-methanol was stirred for 24 hours at 30°C. The reaction mixture was then warmed to 60°C to dissolve the white solid which was formed during the reaction. The solution was filtered while warm, and the clear filtrate was cooled to room temperature and finally to −18°C. A white solid was formed during 24 hours. The product was filtered and washed with diethyl ether, yielding 1.55 g of white crystals (77%). This product was identical to that obtained from MoO$_3$. Preparation of [MoO$_2$(Hbicy)(pyr)$_2$] (3). 180 mg of [MoO$_2$(pyr)$_2$] (0.50 mmol) were added to the solution of Hbicy (200 mg, 1.0 mmol) in 10 ml of acetonitrile. The mixture was kept at −18°C for 2 days until pale yellow crystals had been formed. The crystals were separated and washed with diethyl ether. Yield 130 mg, 60% based on molybdenum. IR: 1275 (m), 1252 (m), 1180 (m), 1156 (m), 1148 (m), 1121 (m), 1076 (s), 1032 (s, br), 961 (s), 910 (s, br), 876 (s), 856 (m), 829 (w), 789 (s), 737 (s), 681 (m), 604 (m), 586 (s), 536 (s), 520 (s), 503 (s), 498 (m). Found C: 49.05; H: 7.25. Calcld. C: 49.10; H: 7.30.

Preparation of [{MoO$_2$(Hbicy)(OMe)$_2$}/2·MeOH] (4). 200 mg (1.0 mmol) of Hbicy dissolved in 2 ml of methanol were added to the solution of [MoO$_2$(pyr)$_2$] (180 mg, 0.50 mmol) at 5 ml of acetonitrile. The pale yellow mixture was kept at −18°C for 2 days, and the bright crystals formed were separated and washed with diethyl ether. Yield 135 mg, 69% based on molybdenum. IR: 3500 (s, br), 3160 (s, br), 1287 (m), 1258 (m), 1180 (m), 1156 (m), 1148 (m), 1125 (s), 1061 (s), 1005 (s), 907 (s, br), 862 (s), 841 (m), 822 (w), 739 (s), 679 (m), 582 (s), 519 (m). Found C: 43.15; H: 7.25. Calcld. C: 43.30; H: 7.30.

Crystal structure determinations. Crystal data for compounds 1-4, along with other experimental details, are summarised in Table 2. Single-crystal data collections were performed at ambient temperature on a Rigaku AFCSS diffractometer using graphite monochromatized Mo K$_\alpha$ radiation ($\lambda = 0.710 69$ Å). The unit-cell parameters were determined by least-squares refinement of 25 carefully centred reflections. Data reduction and subsequent calculations were performed with teXsan for Windows. The data were corrected for Lorentz and polarisation effects and for absorption (PSI scans).

The structures were solved by direct methods using

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the SIR92 program, and full-matrix least-squares refinements on $F^2$ were performed using the SHELXL-97 program. Non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms were included in the calculations at fixed distances from their host atoms. Figures were drawn with ORTEP-3 for Windows.

References


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