Dioxomolybdenum(VI) Complexes of Chelating Alkoxides

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Molybdenum trioxides MoO_3 or $MoO_3 \cdot 2H_2O$ reacted with alcohol ethers (HOROR') to form complexes having the general formula $[MoO_2(OROR')_2]$ where HOROR' = 2-methoxyethanol (Hmet) or tetrahydropyran-2-methanol (Hpyr). In these compounds the Mo^{VI} has a distorted octahedral coordination geometry. The reaction of $[MoO_2(pyr)_2]$ with ditertiary diol 1,1'-bicyclohexane-1,1'-diol (H_2bicy) in acetonitrile solution produced the complex $[MoO_2(Hbicy)(pyr)]$ and in the presence of methanol the product was the dimeric complex $[\{MoO_2(Hbicy)(OMe)\}_2] \cdot 2MeOH$. The structures of four complexes were confirmed by X-ray diffraction.

High-valent transition metals bearing multiple bonded oxo ligands[1] are of interest in organometallic chemistry as catalysts in olefin metathesis reaction[2] 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. Mo^{VI} dioxoalkoxides with the general formula of $MoO_2(OR)_2$ are typically prepared by displacement of chloride ion from MoO_2Cl_2 using lithium alkoxides.[5,6] Other methods are the reaction of $[Mo_2(OR)_6]$ with molecular oxygen[7] and low-temperature co-condensation reactions of MoO_3 with silylated alcohols.[8] These tetra-coordinated dioxomolybdenum(VI) alkoxides are usually unstable in the solid state, but they can be stabilised as nitrogen-base adducts. High-temperature reaction between molybdenum oxide and diols produces more stable, coordinatively saturated, six-coordinated hydrogendiolato complexes, e.g. $[MoO_2(Heg)_2]$ and $[MoO_2(Hbu)_2] \cdot 2H_2bu$ (H_2eg = 1,2-ethanediol, H_2bu = 1,2-butanediol).[9,10]

In our previous investigations, we have studied the coordination chemistry of tungsten and rhenium oxo-alkoxides.[11,12] In this paper we discuss the syntheses and crystal structures of two monomeric dioxomolybdenum(VI) complexes with chelating

monofunctional ether alkoxides, $[MoO_2(met)_2]$ 1 and $[MoO_2(pyr)_2]$ 2 (Hmet = 2-methoxyethanol, Hpyr = tetrahydropyrane-2-methanol). We also report reactions of complex 2 with a ditertiary diol, H_2bicy (H_2bicy = 1,1'-bicyclohexane-1,1'-diol) including crystal structures of a mononuclear hydrogendiolato complex $[MoO_2(Hbicy)(pyr)]$ and a methoxy-bridged dimer $[\{MoO_2(Hbicy)(OMe)\}_2] \cdot 2MeOH$.

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 (MoO_3 or $MoO_3 \cdot 2H_2O$) and monohydric, chelating ether alcohols, 2-methoxyethanol (Hmet) and tetrahydropyran-2-methanol (Hpyr) without a solvent were studied. When white molybdenum trioxide MoO_3 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 $[MoO_2(met)_2]$ (1) and $[MoO_2(pyr)_2]$ (2) crystallised out from filtered solutions upon cooling. A dark blue solid, presumably $Mo_4O_{10}(OH)_2$,[9] is formed as a by-product during the reaction, and the yields of Mo^{VI} alkoxides are low (<30%). The low yields suggested us to use different molybdenum oxides as metal precursors. Yellow molybdenum trioxide dihydrate $MoO_3 \cdot 2H_2O$ is known to be more reactive than MoO_3 at temperatures near room temperature, e.g. it reacts with methanol under reflux to form dimeric oxomethoxide $[Mo_2O_5(OMe)_2]$.[14] We found that when $MoO_3 \cdot 2H_2O$ was mixed with excess Hmet or Hpyr at 20–30 °C temperature, it reacted slowly

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and some white precipitate formed during 24 h stirring. The reaction vessels were warmed to dissolve solids, and filtered solutions were cooled to −18°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 tetrahydrofurfuryl 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 $MoO_3 \cdot 2H_2O$, 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_2bicy. If complex **2** and H_2bicy are dissolved in acetonitrile, the reaction leads to the displacement of one pyr ligand by singly deprotonated Hbicy group yielding monomeric complex [MoO_2(Hbicy)(pyr)] (**3**). 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_2(Hbicy)(OMe)}$_2$] · 2MeOH (**4**), in which one pyr ligand is displaced by an Hbicy 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^{VI} 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.[15] 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
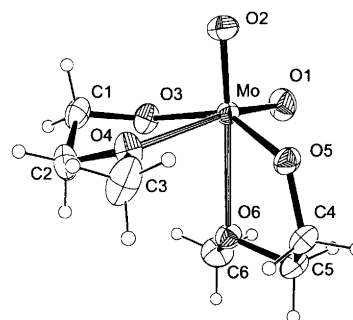

Fig. 1. ORTEP plot of **1** showing the labelling system of heavy atoms. Displacement ellipsoids are plotted at the 30% probability level.
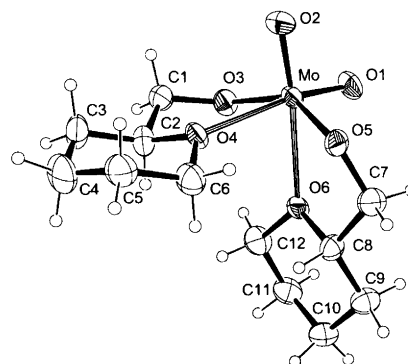

Fig. 2. ORTEP plot of **2** showing the labelling system of heavy atoms. Displacement ellipsoids are plotted at the 30% probability level.
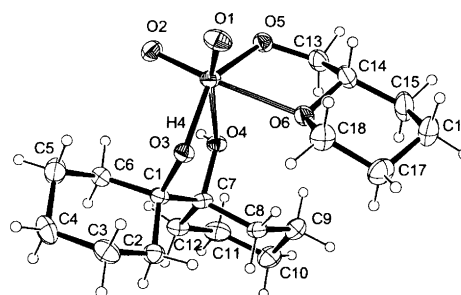

Fig. 3. ORTEP plot of **3** showing the labelling system of heavy atoms. Displacement ellipsoids are plotted at the 30% probability level.

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)°. Also the O–Mo–O (O = alkoxide) angles are quite similar [from 143.9(2) to 148.6(1)°], as are all other angle values around Mo^{VI} 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)°. The ligands adopt λδ conformations in **1** and **3**. The ligand has a λλ (δδ) conformation in **2**. Coordination spheres around the Mo^{VI} 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

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

	1	2	3	4
Mo–O(1)	1.699(2)	1.693(6)	1.699(4)	1.703(2)
Mo–O(2)	1.696(2)	1.704(5)	1.698(3)	1.699(2)
Mo–O(3)	1.910(2)	1.915(5)	1.923(3)	1.910(2)
Mo–O(4)	2.358(2)	2.384(4)	2.321(4)	2.330(2)
Mo–O(5)	1.920(2)	1.913(5)	1.970(3)	2.037(2)
Mo–O(6)	2.402(2)	2.426(5)	2.354(3)	2.221(2)[a]
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)[a]
O(3)–Mo–O(4)	72.1(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)[a]
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(6)	110.0(3)	—
O(3)–C–C–O(4)	−45.7(3)	−41.6(8)	43.5(4)	42.3(3)
O(5)–C–C–O(6)	46.8(3)	−39.9(9)	−49.5(5)	—

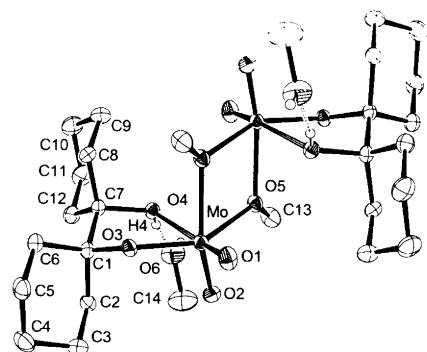[a] In **4** O(5^{II}) = O(6) (II = 1 − x, 1 − y, −z).

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^{I}) [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 [{ MoO$_2$(Hpin)(OMe)}$_2$]·2MeOH.[16]

Conclusions

This work has shown that molybdenum trioxides MoO$_3$ or MoO$_3$·2H$_2$O react with monohydric, ether alco-

hols 2-methoxyethanol (Hmet) or tetrahydropyran-2-methanol (Hpyr) to form distorted octahedral dioxomolybdenum(VI) complexes. If yellow dihydrate MoO3·2H$_2$O 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 [MoO$_2$(pyr)$_2$] with the ditertiary diol 1,1'-bicyclohex-ane-1,1'-diol (H$_2$bicy) in acetonitrile solution produces the complex [MoO$_2$(Hbicy)(pyr)], and in the presence of methanol the product is the dimeric complex [{ MoO$_2$(Hbicy)(OMe)}$_2$]·2MeOH.

Experimental

MoO$_3$·2H$_2$O (Ref. 17) and H$_2$bicy (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 [MoO$_2$(met)$_2$] (**1**).

(a) *From MoO$_3$.* A suspension of white MoO$_3$ (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**.

	1	**2**	**3**	**4**
Formula	$C_6H_{14}O_6Mo$	$C_{12}H_{22}O_6Mo$	$C_{18}H_{32}O_6Mo$	$C_{14}H_{28}O_6Mo$
M	278.11	358.24	440.38	388.30
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group (no.)	$P2_1/n$ (14)	$Pna2_1$ (33)	$Pbca$ (61)	$P2_1/c$ (14)
$a/\text{Å}$	8.7150(8)	18.676(2)	22.958(7)	7.956(3)
$b/\text{Å}$	11.0476(7)	6.9445(13)	16.139(4)	15.557(4)
$c/\text{Å}$	10.9625(7)	11.4529(15)	10.672(5)	13.901(3)
$\beta/°$	102.698(6)	90	90	98.03(2)
$U/\text{Å}^3$	1029.65(13)	1485.4(4)	3954(3)	1703.6(8)
Z	4	4	8	4
$\mu(\text{Mo K}_\alpha)/\text{cm}^{-1}$	12.71	9.01	6.92	7.92
Observed reflections	1812	1368	3469	3009
Parameters	119	172	229	196
*R*1	0.026 (0.020)[a]	0.049 (0.030)	0.116 (0.042)	0.047 (0.028)
*wR*2	0.052 (0.050)	0.070 (0.065)	0.090 (0.075)	0.068 (0.062)

[a]Values in parentheses for reflections with $I>2.0\sigma(I)$.
$R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ and $w=1/[\sigma^2(F_o^2)+(aP)^2+bP)]$, where $P=(2F_c^2+F_o^2)/3$.

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

(b) *From* $MoO_3 \cdot 2H_2O$. The suspension of yellow $MoO_3 \cdot 2H_2O$ (1.0 g, 5.6 mmol) in 2-methoxyethanol (15 ml) was stirred at 20 °C. After 1 h, the formation of a white precipitate was noted. When the reaction had proceeded for 24 h, the mixture was warmed to 50 °C for 20 min to dissolve the white solid which had been formed during the reaction. The reaction mixture was filtered as a warm and clear filtrate, and was 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 $[MoO_2(pyr)_2]$ (**2**).

(a) *From* MoO_3. MoO_3 (1.0 g, 6.9 mmol) was suspended in tetrahydropyrane-2-methanol (10 ml), and the mixture was stirred in an open vessel at 160 °C for 15 min. 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 and washed with diethyl ether yielding 720 mg of clear crystals (30%). IR: 1280 (m), 1180 (m), 1101 (s), 1070 (s), 1035 (s), 1000 (s), 920 (s, br), 880 (s), 855 (s), 830 (m), 790 (s), 600 (m), 565 (s), 515 (m). Found C; 40.85, H; 6.40, Calcd. C; 40.25, H; 6.20.

(b) *From* $MoO_3 \cdot 2H_2O$. A suspension of $MoO_3 \cdot 2H_2O$ (1.0 g, 5.6 mmol) in 15 ml of tetrahyropyran-2-methanol was stirred for 24 h 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 h. 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 $[MoO_2(Hbicy)(pyr)]$ (**3**). 180 mg of $[MoO_2(pyr)_2]$ (0.50 mmol) were added to the solution of H_2bicy (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, Calcd. C; 49.10, H; 7.30.

Preparation of $[\{MoO_2(Hbicy)(OMe)\}_2] \cdot 2MeOH$ (**4**). 200 mg (1.0 mmol) of H_2bicy 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, Calcd. 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 AFC5S diffractometer using graphite monochromatized Mo K_α 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.[19] The data were corrected for Lorenz and polarisation effects and for absorption (PSI scans[20]).

The structures were solved by direct methods using

the SIR92 program,[21] and full-matrix least-squares refinements on F^2 were performed using the SHELXL-97 program.[22] 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.[23]

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