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Molybdenum(VI) Methoxyethoxides. Synthesis and Structure of $MoO_2(OC_2H_4OMe)_2$ and Polymeric $NaMoO_2(OC_2H_4OMe)_3$

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Reaction of $MoO(OEt)_4$ with an excess of methoxyethanol leads to the formation of $MoO(OC_2H_4OMe)_4$, which decomposes to give complex $MoO_2(OC_2H_4OMe)_2$ **1**, an X-ray structural study of which shows that its crystals are constructed of monomeric molecules with both methoxyethoxide groups forming chelate rings around the molybdenum atoms; interaction of **1** with $NaOC_2H_4OMe$ in methoxyethanol results in the formation of a complex $NaMoO_2(OC_2H_4OMe)_3$ **2**, whose polymeric structure, established by X-ray analysis, contains a planar tetranuclear fragment analoguous to that found in $Ti_4(OMe)_{16}$.

Methoxyethoxides $M(OC_2H_4OR)_n$, are readily soluble in organic solvents and, in many cases, are more stable than derivatives of aliphatic alcohols, containing only one hydroxy group. Recently they have thus attracted considerable interest as starting materials for the synthesis of oxides. The preparation of solutions containing both molybdenum alkoxides and derivatives of other metals is hindered by decomposition with elimination of ether. This decomposition reaction is especially characteristic of the bimetallic complexes, the rate of the reaction (1) increasing with increase in the Na:Mo ratio.

$$MoO(OR)_4 + nNaOR \rightarrow [NaMoO(OR)_5] \rightarrow Na_2MoO_4 + 3R_2O \qquad (1)$$

Crystallization of complex oxide phases occurs directly from the organic solvent, and the composition of the oxide compound usually does not correspond at all to the composition of the initial alkoxide solution.[1]

Reaction of $MoO(OEt)_4$ (its synthesis has been described in ref. 2) with an excess of $MeOC_2H_4OH$ (ROH) followed by evacuation of solvent at 60–70 °C resulted in isolation of the liquid $MoO(OR)_4$. On storage for 1–2 days decomposition occurs with elimination of diglyme and formation of crystalline $MoO_2(OR)_2$ **1** [eqn. (2)]. This compound is quite stable; m.p.

$$MoO(OR)_4 \rightarrow MoO_2(OR)_2 + R_2O \qquad (2)$$

$$\mathbf{1};\ R = C_2H_4OMe$$

(decomp.) 102–105 °C. It is readily soluble in ROH but practically insoluble in hydrocarbons.

Conductometric titration of 0.05 mol dm^{-3} solutions in ROH of $MoO_2(OR)_2$ by sodium methoxyethoxide (the latter was obtained by dissolution of Na in ROH) proved the formation in solution of the 1:1 bimetallic complex. Colourless crystals of $NaMoO_2(OR)_3$ **2** precipitated from the solution

$$NaMoO_2(OR)_3$$

$$\mathbf{2};\ R = C_2H_4OMe$$

with Na:Mo (≥ 1.05):1. In the IR spectra of the synthesized methoxyethoxides bands corresponding to vibrations of Mo=O groups and Mo—OR were observed **1**: μ/cm^{-1} 945s, 910vs, 830m, 580s, 565vs, 540s; **2**: μ/cm^{-1} 960w, 905vs, 885vs, 825m, 605s, 520m,br, 480w, 450w. The considerable stability of the bimetallic methoxyethoxides in comparison with the corresponding aliphatic derivatives is noteworthy: *e.g.* solutions containing both **1** and $Bi(OR)_3$ are quite stable, and **2** does not decompose, even in the presence of an excess of NaOR.

Table 1 Powder diffractogram of **1** and **2**

1			**2**		
I	*d*/Å	*hkl*	*I*	*d*/Å	*hkl*
10	6.68	110	5	9.17	110
100	6.09	$11\bar{1}$	40	8.93	002
50	6.01	101	80	8.86	$1\bar{1}1$
10	5.40	020	100	8.16	020
40	5.24	111	5	7.85	021
8	4.78	012	20	6.88	112
8	3.93	210	90	6.81	200
10	3.53	212	8	4.39	003
15	3.34	220	10	4.11	$1\bar{1}3$
45	3.26	$13\bar{1}$	8	3.92	130
5	3.03	032	5	3.71	$3\bar{3}0$
10	2.518	320	45	3.06	330
10	2.484	$30\bar{3}$	25	2.90	$1\bar{3}4$
8	2.358	321	20	2.73	$\bar{4}60$
10	2.324	232	5	2.60	005
5	2.127	400	10	2.46	$3\bar{3}3$
5	2.045	$32\bar{4}$	40	2.35	$\bar{6}60$
7	1.8039	234	8	2.12	$3\bar{5}1$

The crystal and molecular structures of both complexes have been solved by X-ray structural analysis.† Powder diffraction data for **1** and **2** is given in Table 1.

The molybdenum atom in the molecule of **1** (Fig. 1), as in the majority of other oxo-complexes of molybdenum,[5] has a distorted octahedral coordination of the 2 + 2 + 2 type. There are three types of Mo—O bonds: two short *cis*-Mo=O(1) and Mo=O(2) [1.698(2) and 1.699(3) Å], the two longest bonds with the ether oxygen atoms Mo—O(3) and Mo—O(5) *trans* to the Mo=O bonds [2.399(2) and 2.354(2)], and two σ-bonds with the alkoxide atoms Mo—O(4) and Mo—O(6) [1.916(2) and 1.910(2) Å] (*trans* to each other). Considerable elongation of the donor–acceptor bonds in positions *trans* to double bonds involving metal atoms has been observed earlier in the

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† *Crystal data* for $C_6H_{14}O_6Mo$ **1**: $M = 277.9$, monoclinic, space group $P2_1/n$, $a = 8.695(2)$, $b = 11.016(3)$, $c = 10.938(3)$ Å, $\beta = 102.71(1)°$, $V = 1022.0(8)$ Å^3, $D_c = 1.816$ g cm^{-3}, $Z = 4$. λ (Mo-Ka) = 13.0 cm^{-1}, 2507 reflections with $F^2 \geqslant 3\sigma(F^2)$ were collected at + 20 °C up to $\theta_{max} = 30°$ with a Syntex $P2_1$ diffractometer using Mo-Kα radiation.

For $C_{18}H_{42}O_{16}Mo_2Na_2$ **2**: $M = 751.8$, monoclinic, space group $C2/c$, $a = 14.357(7)$, $b = 12.343(5)$, $c = 17.573(8)$ Å, $\beta = 108.57(4)°$, $V = 2952(2)$ Å^3, $D_c = 1.701$ g cm^{-3}, $Z = 4$. λ (Mo-Kα) = 9.22 cm^{-1}, 2764 reflections with $F^2 \geqslant 4\sigma(F^2)$ were collected at + 20 °C up to $\theta_{max} = 28°$ with a Siemens P3/PC diffractometer using Mo-Kα radiation.

Both structures were solved by the standard heavy-atom technique; the coordinates of the Mo atoms were found from Patterson Syntheses; all other non-hydrogen atoms were located in subsequent approximations of the electron-density syntheses. The structures were refined by full-matrix least-squares techniques, first in the isotropic and then in the anisotropic approximation. All H atoms were located by difference Fourier syntheses and included in the final cycles of refinement in the isotropic approximation. Final discrepancy factors are $R = 0.027$, $R_w = 0.037$ for **1** and $R = 0.040$, $R_2 = 0.040$ for **2**. All calculations were performed with an Eclipse S/200 computer using the INEXTL[3] program package for **1** and with an IBM PC by means of the SHELXTL PC[4] programs for **2**. Atomic coordinates, bond lengths and angles and thermal parameters for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, Issue 1.

‡ The structure of the corresponding tungsten complex $NaWO_2(OC_2H_4OMe)_3$ was recently shown to be analogous to that of the molybdenum one. Unit cell parameters $a = 14.394(2)$, $b = 12.344(2)$, $c = 17.452(4)$ Å, $\beta = 108.60(20)°$.

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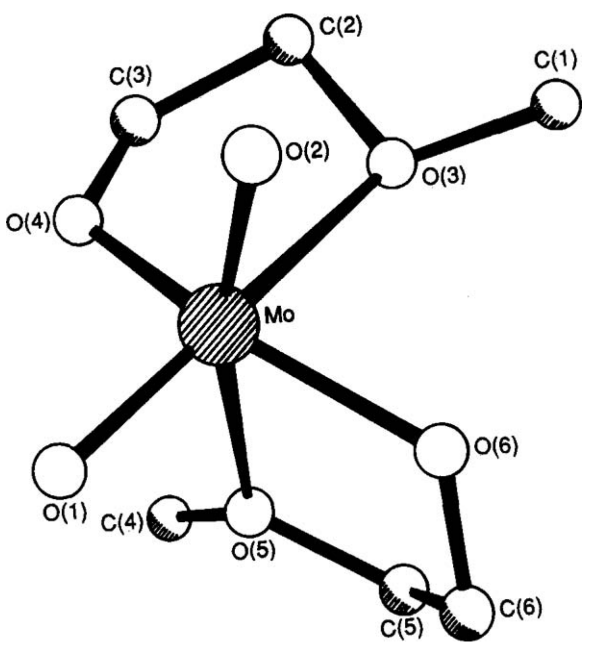

Fig. 1 The molecular structure of $MoO_2(OC_2H_4OMe)_2$ **1**. Main bond lengths (Å) and angles (°): Mo═O(1) 1.698(2), Mo═O(2) 1.699(3), Mo—O(3) 2.399(2), Mo—O(4) 1.916(2), Mo—O(5) 2.354(2), O(1)MoO(2) 105.5(1), O(3)MoO(4) 72.72(7), O(5)MoO(6) 72.02(8)

$MoO_2(OC_2H_4OH)_2$[6] and $Se{=}WCl_3(OC_2H_4OMe)$[7] molecules. Complex **2** is constructed of dimeric centrosymmetric 'molecules', the metal-oxygen core is analogous to that of $[Mg_4(OC_2H_4OMe)_6(MeOC_2H_4OMe)_2]^{2+}$ (ref. 8) or the tetramers $Ti_4(OR)_{16}$.[9,10]‡ However, in contrast to the abovementioned structures the tetranuclear fragments of the bimetallic methoxyethoxide are linked in chains by pairs of asymmetric bridges formed by the ether oxygen atoms O(4) and O(4′) of one of the three methoxyethoxide groups (Fig. 2).

The alkoxide O-atoms form bridges (μ_3 and μ_2), while the ether oxygens are monodentate [excluding O(4)] and participate in the coordination sphere of Na, thus forming chelate rings around them. Mo atoms are attached to them due to enhancement of the coordination number of the oxygen atoms. Tridentate O(1) and O(1′) are located at distances of 2.255(3) and 2.162(3) Å from Mo, while the distance from the bidentate atoms O(2) and O(3) are 1.964(3) and 1.975(3) Å respectively. The Mo octahedra are completed by two terminal Mo═O groups [1.703(4) and 1.706(3) Å]. The sums of the lengths of the Mo—O bonds located in *trans* to one another are very close and are in the range 3.86–3.96 Å.

The considerably distorted polyhedron with seven vertices round the Na atom is formed by three alkoxide oxygen atoms, tridentate O(1) and two bidentate O(2) and O(3), [at distances of 2.689(3), 2.341(4) and 2.308(4) Å respectively] and three ether oxygen atoms, O(4), O(5) and O(6) (Na—O 2.493–2.529 Å). The seventh place is occupied by the ether O(4′) oxygen of the neighbouring tetranuclear 'molecule', which is located at a distance of 2.881(4) Å, which exceeds the value for a normal Na—O bond. The Na—O (alkoxide) bond lengths are close to those observed in sodium alkoxides;[11] in addition, the Mo—O bond lengths correlate with the coordination of the oxygen atoms; both these facts testify to the molecular character of the methoxyethoxide. The absence of the terminal OR-groups (compare ref. 12) and formation of the chelate rings both ensure high stability of the molecules to decomposition with elimination of ether.

Both complexes described differ from other methoxyethoxides of Bi and Y[13–15] by the absence of the terminal OR groups in their structures, which is presumably due to the trend of Na and Mo atoms to formation of chelates with the polyoxoligands. At the same time the existence of tridentate alkoxyl O atoms in molecule **2** emphasizes its similarity with the bimetallic complex $Ba_2Cu_2(\mu_3\text{-}OC_2H_4OMe)_4(acac)_4(MeOC_2H_4OH)_2$ (Hacac = acetylacetone).[16]

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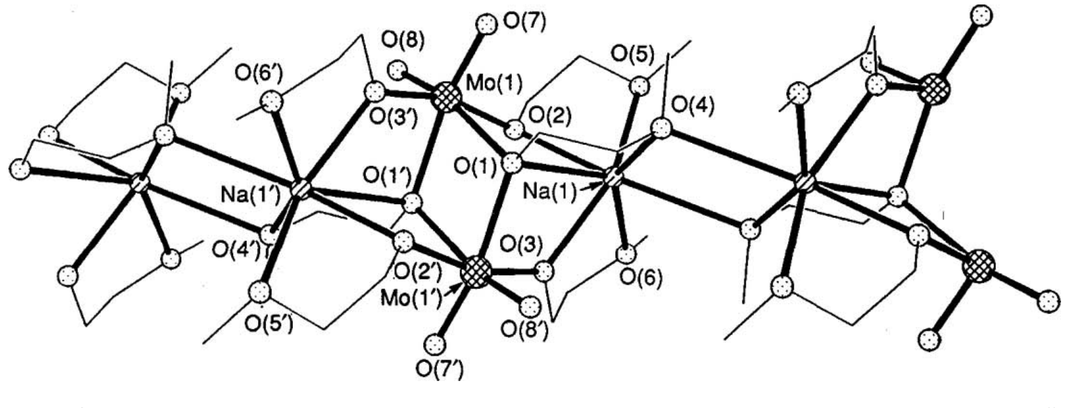

Fig. 2 The fragment of the infinite chain in the structure of $[NaMoO(OC_2H_4OMe)_3]_2$ **2**. The C atoms are designated by dot shading. Main bond lengths (Å) and angles (°): Mo(1)—O(1) 2.255(3), Mo(1)—O(1′) 2.162(3), Mo(1)—O(2) 1.964(3), Mo(1)—O(3′) 1.975(3), Mo(1)═O(7) 1.703(4), Mo(1)═O(8) 1.706(3), Na(1)—O(1) 2.689(3), Na(1)—O(2) 2.341(4), Na(1)—O(4) 2.494(4), Na(1)—O(4′) 2.881(4), Na(1)—O(5) 2.493(4), Na(1)—O(6) 2.529(4), O(1)Mo(1)O(1′) 69.5(1), O(1)Mo(1)O(2) 79.5(1), O(7)Mo(1)O(8) 193.7(2), O(1)Mo(1′)O(3) 80.0(1), O(1)Na(1)O(2) 64.7(1), O(1)Na(1)O(3) 63.9(1), O(1)Na(1)O(4′) 70.1(1), Mo(1)O(1)Mo(1′) 110.5(1), Mo(1)O(1)Na(1) 95.8(1), Mo(1′)O(1)Na(1) 97.5(1), Mo(1)O(2)Na(1) 117.2(2), Mo(1′)O(3)Na(1) 117.4(2)

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