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Preparation and Crystal Structure of Two Oxo-Molybdenum Complexes with Dimethoxyethane

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We have already reported the preparation and crystal structure of the tetrameric acetato [$\{Mo_2ClO_3(OCOCH_3)_3\}$] and benzoato [$\{Mo_2ClO_3(OCOC_6H_5)_3\}$] complexes of molybdenum [1, 2]. In the attempt to prepare the analogous formato complex from dimethoxyethane as solvent, we obtained two complexes containing dimethoxyethane as a neutral ligand. One is dimeric μ-oxobis[dichlorooxo(dimethoxyethane)]dimolybdenum(V) (A), while the other is the analogous but monomeric dichlorodioxo(dimethoxyethane)molybdenum(VI) (B).

Among many structures of Mo(V) complexes containing the O=Mo–O–Mo=O unit with terminal oxo-oxygen atoms in either *cis* or *trans* configuration with respect to the Mo–O–Mo bridge [3–7], there are only a few examples with oxygen donating ligands [8]. All of them as the complex (A) contain terminal oxo-oxygen atoms in the *trans* configuration.

Experimental

Preparation

(A) $MoCl_5$ (4 g) was dissolved in dimethoxyethane (25 ml), the solution acidified with formic or acetic acid (3 ml) and warmed for 15 hours under reflux. The deep olive-green crystalline substance obtained by cooling the solution was washed with dry dimethoxyethane and dried under vacuum. The complex was identified as $Mo_2O_3Cl_4(CH_3OCH_2CH_2OCH_3)_2$. *Anal.* Found: Mo 34, 22; Cl 25.22; C 17.25, H 3.71%. Calcd. for $Mo_2O_7Cl_4C_8H_{20}$. Mo 34.15; Cl 25.24; C 17.10; H 3.59%. Crystals were sensitive when exposed to air, and for protection were sealed in Lindemann glass capillaries.

(B) This complex was prepared by dissolving MoO_2Cl_2 (5 g) in dimethoxyethane (10 ml). The solution was warmed up under reflux and filtered. A white substance crystallized immediately on cooling, identified as $MoO_2Cl_2(CH_3OCH_2CH_2OCH_3)$ *Anal.* Found· Mo 33.20; Cl 24.54; C 16.63; H 3.49%. Calcd. for $MoO_4Cl_2C_4H_{10}$: Mo 32.84; Cl 24.94, C 16.43, H 3.49%.

Crystal Data and Intensity Measurements

Space groups and preliminary unit cell dimensions were obtained from rotation and Weissenberg photographs while the final unit cell parameters listed in Table I were obtained by refinement of the single crystal diffraction data. The intensity data were collected by the ω–2θ scan method on a Philips PW 1100 automated diffractometer using monochromatized MoKα radiation (λ = 0.7107 Å). Using the criterion $I > 3\sigma(I)$, 2030 of the 2176 for (A) and

TABLE I. Crystal Data.

Molecular Formula (MW)	$Mo_2O_7Cl_4C_8H_{20}$ (561.7)	$MoO_4Cl_2C_4H_{10}$ (289.0)
Space group	$P2_1/n$	$P2_1/n$
Cell dimensions: *a*	9.641(4) Å	12.163(4) Å
b	11.127(6)	11.191(4)
c	8.672(6)	7.243(3)
β	96.79(4)°	92.39(2)°
V	923.8 Å^3	985.0 Å
Z	2	4
Calculated density	2.02 g cm^{-3}	1.96 g cm^{-3}
Observed density	1.96	2.04
F(000)	552	568
Crystal size	0.34 × 0.20 × 0.37 mm^3	0.50 × 0.17 × 0.16 mm^3
Range of data $2\theta_{max}$	60°	60°
μ(MoKα)	21.4 cm^{-1}	18.2 cm^{-1}

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TABLE II. Positional Parameters ($\times 10^4$, for Mo $\times 10^5$ and for H $\times 10^3$) with Estimated Standard Deviations in Parentheses.

	(A) $Mo_2O_3Cl_4(CH_3OCH_2CH_2OCH_3)_2$			(B) $MoO_2Cl_2(CH_3OCH_2CH_2OCH_3)$		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
Mo	17318(3)	7242(2)	4210(3)	1176(1)	24379(1)	38445(1)
Cl(1)	1218(1)	1317(1)	2930(1)	1712(3)	1406(4)	3060(6)
Cl(2)	2126(1)	735(1)	−2243(1)	−1560(4)	3442(4)	3386(6)
O(1)	0	0	0	751(10)	3491(10)	5122(12)
O(2)	2811(3)	−393(2)	1006(3)	−320(10)	1439(9)	5367(11)
O(3)	3471(2)	2039(2)	777(3)	480(6)	3424(7)	1168(9)
O(4)	868(3)	2596(2)	−204(3)	−583(6)	1363(7)	1391(9)
C(1)	4894(4)	1643(4)	702(6)	1395(13)	4226(14)	1119(21)
C(2)	3216(4)	3205(4)	39(6)	329(13)	2705(16)	−480(14)
C(3)	1776(4)	3579(3)	298(5)	−665(12)	2020(13)	−322(14)
C(4)	−602(4)	2873(4)	−112(7)	−1501(11)	579(14)	1604(22)
H(11)	561	230	127	146	474	240
H(12)	506	79	126	129	483	−3
H(13)	507	157	−51	215	372	98
H(21)	398	385	52	101	210	−61
H(22)	328	312	−121	26	327	−170
H(31)	174	375	152	−137	264	−29
H(32)	147	437	−37	−79	143	−147
H(41)	−76	312	104	−139	10	290
H(42)	−124	213	−52	−154	−6	48
H(43)	−88	365	−88	−225	109	161

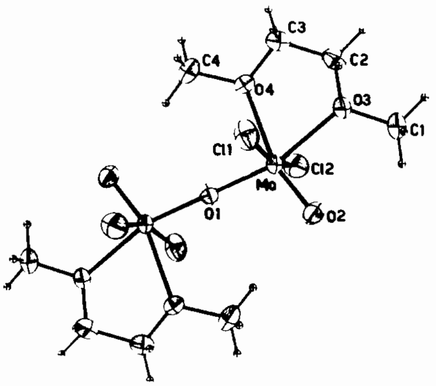

Fig. 1. A perspective ORTEP drawing of the $Mo_2O_3Cl_4(CH_3OCH_2CH_2OCH_3)_2$ molecule with the atom numbering scheme. Thermal ellipsoids are scaled at the 50% probability level.

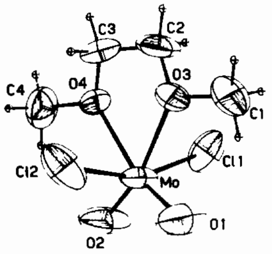

Fig. 2. An ORTEP drawing of the $MoO_2Cl_2(CH_3OCH_2CH_2OCH_3)$ molecule with the atom numbering scheme. Thermal ellipsoids are scaled at the 50% probability level.

1730 of the 1955 for (B) were used in the structure determinations and refinements. Corrections for Lorentz and polarization factors were applied but no correction for absorption was made.

Structure Solutions and Refinement

The Mo atom positions in both structures were found from three-dimensional Patterson syntheses, while the remaining non-hydrogen atoms were located in subsequent Fourier maps. The structures were refined by full matrix refinement procedure using anisotropic temperature factors for all non-hydrogen atoms. The positions of hydrogen atoms were calculated and used in structure factor calculations with fixed isotropic temperature factors. The scattering factors of ref. 9 were used and both the real and imaginary components of anomalous dispersion for Mo and Cl atoms were included. The final *R* factors were 0.031 and 0 073 for the structures of (A) and (B), respectively.

Description of the Structures

The final positional parameters for both structures are given in Table II. The Mo(V) complex (A)

TABLE III. Bond Lengths and Angles in $Mo_2O_3Cl_4(CH_3OCH_2CH_2OCH_3)_2$ (A) and $MoO_2Cl_2(CH_3OCH_2CH_2OCH_3)$ (B).

Bond Lengths (Å)	(A)	(B)
Mo–Cl(1)	2.380(1)	2.347(4)
Mo–Cl(2)	2.385(1)	2.340(4)
Mo–O(1)	1.851(1)	1.667(11)
Mo–O(2)	1.655(3)	1.673(10)
Mo–O(3)	2.217(3)	2.289(7)
Mo–O(4)	2.283(3)	2.281(7)
O(3)–C(1)	1.449(5)	1.432(18)
O(3)–C(2)	1.448(6)	1.445(15)
O(4)–C(3)	1.436(5)	1.443(13)
O(4)–C(4)	1.452(6)	1.434(16)
C(2)–C(3)	1.496(7)	1.440(21)
Bond Angles (°)		
Cl(1)–Mo–O(1)	91.2(1)	96.6(4)
Cl(1)–Mo–O(2)	96.8(1)	96.9(4)
Cl(1)–Mo–O(3)	85.8(1)	80.9(2)
Cl(1)–Mo–O(4)	81.5(1)	80.6(2)
Cl(2)–Mo–O(1)	93.1(1)	96.8(4)
Cl(2)–Mo–O(2)	97.7(1)	96.6(4)
Cl(2)–Mo–O(3)	85.8(1)	81.1(2)
Cl(2)–Mo–O(4)	82.1(1)	81.2(2)
O(1)–Mo–O(2)	104.5(1)	105.0(5)
O(1)–Mo–O(3)	164.4(1)	91.6(4)
O(1)–Mo–O(4)	93.1(1)	162.6(4)
O(2)–Mo–O(3)	91.0(1)	163.4(4)
O(2)–Mo–O(4)	162.4(1)	92.4(4)
O(3)–Mo–O(4)	71.4(1)	70.9(3)
Mo–O(3)–C(1)	120.0(3)	120.0(7)
Mo–O(3)–C(2)	116.5(2)	114.1(7)
C(1)–O(3)–C(2)	111.0(4)	113.6(10)
Mo–O(4)–C(3)	115.3(2)	114.3(7)
Mo–O(4)–C(4)	121.1(3)	120.4(7)
C(3)–O(4)–C(4)	112.2(4)	112.2(9)
O(3)–C(2)–C(3)	106.9(4)	108.0(10)
O(4)–C(3)–C(2)	106.8(4)	108.1(10)

is dimeric while Mo(VI) (B) is monomeric (Figs. 1 and 2, Table III), as expected from the known stereochemistry of molybdenum [4, 5, 10]. The coordination polyhedra in both structures are significantly distorted octahedra with angles at Mo atoms ranging from 71.4 to 104.5° in (A) and from 70.9 to 105.0° in (B), respectively. In both complexes the oxo-oxygen atoms are *cis* to each other. In the dimeric molecule (A) the two octahedra share a bridging oxygen atom located on a space group inversion centre so that the Mo–O–Mo bridge is linear and the terminal oxo-oxygen atoms are *trans* to it. In both structures the Mo atoms are surrounded by two chlorine atoms, two oxo-oxygen atoms (one of which in (A) is terminal and one bridging), and two dimethoxyethane-oxygen atoms. The molybdenum-to-terminal oxo-oxygen bond lengths, 1.655 Å in (A) and 1.667 and 1.673 Å in (B), as well as the angles within the *cis*-MoO_2 groups (104.5 in (A) and 105.0° in (B)), are in very good agreement with the corresponding values reported for numerous dioxomolybdenum compounds (see for example refs. 4 and 5). The molybdenum-to-bridging oxo-oxygen bond length is significantly longer, 1.851 Å, as would be expected from published data [11]. The molybdenum-to-dimethoxyethane-oxygen atom bond lengths *trans* to the terminal oxo-oxygen atoms have almost the same value [2.283 Å in (A) and 2.281 and 2.289 Å in (B)], while the same bond length *trans* to the bridging oxo-oxygen atom in (A) is slightly shorter [2.217 Å], thus showing a weaker *trans* influence of the bridging oxo-oxygen atom. The Mo–Cl bond lengths in (A) were 2.380 and 2.385 Å, while those in (B) were 2.340 and 2.347 Å, respectively. In both structures dimethoxyethane acts as a neutral bidentate ligand with normal interatomic distances and angles.

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