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Synthesis of Two Novel Tetranuclear Molybdenum(V) Complexes. Crystal Structure of Hexa-μ-propionato-dichlorodi-μ_3-oxotetraoxotetramolybdenum(V)[†]

Boris Kamenar,[*] *Branka Korpar-Čolig, and Maja Penavić*

Laboratory of General and Inorganic Chemistry, Faculty of Science,
University of Zagreb, P.O.Box 153, 10000 Zagreb, Croatia

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In the reaction of MoO_2Cl_2 and MoO_2Br_2 with propionic anhydride, new complexes of molybdenum(V), $Mo_4O_6Cl_2(OCOC_2H_5)_6$ and $Mo_4O_6Br_2(OCOC_2H_5)_6$, respectively, have been prepared. The crystal structure of the former was determined from single crystal diffractometer data and refined to the final R value of 0.046. The complex crystallizes in the monoclinic space group $P2_1/n$ with cell dimensions a = 11.713(2) Å, b = 9.292(3) Å, c = 30.957(6) Å, β = 96.71(2)°, D_{calc} = 1.963 g cm^{-3}, Z = 4. The tetranuclear complex molecule contains four molybdenum atoms bridged through two oxo-oxygen atoms and six bidentate propionato-ligands. Two of the four molybdenum atoms form a Mo-Mo bond at 2.592(3) Å.

INTRODUCTION

While dinuclear complexes are dominant in molybdenum(V) chemistry, tetranuclear complexes are relatively rare. Such complexes are formed by a simple linkage of two dinuclear species, such as in $K_6[\{Mo_2O_3(mal)_2\}_2(mal)] \cdot 4H_2O$, in which one malonato ion acts as a quadridentate ligand bridging two $Mo_2O_2(mal)_2$ moieties,[1] or by building $Mo_4X_aY_bZ_c$ cluster complexes such as suggested for a large class of metal alkoxides. However, while in the alkoxides $a + b + c = 16$, as it was found in the propoxo complexes Mo_4O_8(O-*i*-Pr)$_4$(py)$_4$[2] and in $Mo_4Cl_4O_6(OPr)_6$,[3] in the carboxylates, such as in

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[†] Dedicated to the memory of Stanko Borčić.

[*] Author to whom correspondence should be addressed.

$Mo_4O_6Cl_2(OCOCH_3)_6$[4] and $Mo_4O_6Cl_2(OCOC_6H_5)_6$,[5] $a + b + c = 14$. Also, while in the alkoxides four Mo-octahedra are fused, allowing formation of localized metal-metal single bonds between two pairs of molybdenum atoms, in the carboxylates only two of four molybdenum atoms participate in the Mo-Mo bonding.

We report here the syntheses of the chloro- and bromo-propionato molybdenum(V) complexes and the crystal structure of $Mo_4O_6Cl_2(OCOC_2H_5)_6$.

EXPERIMENTAL

Synthesis of $Mo_4O_6Cl_2(OCOC_2H_5)_6$

The complex was prepared by dissolving MoO_2Cl_2 (2 g) in propionic anhydride (10 cm^3) and by warming the reaction mixture up to 89–90 °C. The resulting crystalline precipitate obtained by cooling the solution in a refrigerator (5 °C) was filtered off (1.8 g, yield 73%) and recrystallized from hot propionic anhydride. The olive-green crystals were moderately stable in dry atmosphere at room temperature.

Anal. calcd. for $C_{18}H_{30}Cl_2Mo_4O_{18}$: C 21.86, H 3.06, Mo 38.80, Cl 7.17%; found: C 21.59, H 3.27, Mo 38.71, Cl 6.89%.

The infrared spectrum (FTIR 1600 Fourier transform spectrophotometer): bands at 985s and 754s cm^{-1} were assigned to $\nu(Mo\text{-}O_t)$ and $\nu(Mo\text{-}O_b)$ while those at 1567vs and at 1430s cm^{-1} were attributed to $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$, respectively.[6]

Magnetic measurements at 294 K gave μ = 2.48 M.B. for tetranuclear unit, or 0.62 per one molybdenum atom.

Synthesis of $Mo_4O_6Br_2(OCOC_2H_5)_6$

The preparation was performed as described above by dissolving MoO_2Br_2 (1 g) in propionic anhydride (10 cm^3). The olive-green crystals (0.38 g, yield 40%) obtained were less stable in air than the corresponding chloro-derivative.

Anal. calcd. for $C_{18}H_{30}Br_2Mo_4O_{18}$: C 20.06, H 2.81, Mo 35.60, Br 14.82%; found; C 20.36, H 3.02, Mo 35.88, Br 14.53%.

The IR spectrum ν_{max}/cm^{-1}: 982s, 756m, 1569vs, 1429s (v = very, s = strong, m = medium). Magnetic moment μ = 0.59 M.B.

Crystal Structure Determination and Refinement

Three-dimensional data were collected on a Philips PW 1100 diffractometer. Unit cell dimensions (Table I) were determined by least-squares refinement of the angular positions of 18 reflections in the 11–16° θ range during the normal alignment procedure. Intensity data were not corrected for absorption. Five low angle reflections were omitted due to secondary extinction.

Calculations were performed on a IBM PC/AT compatible microcomputer with a 80386/20 MHz processor and mathematical 80387 co-processor. All non-hydrogen atoms were located in several successive Fourier maps and then refined by full-matrix least-squares procedure assuming anisotropic temperature parameters for molybdenum and chlorine atoms and isotropic parameters for all other non-hydrogen

TABLE I

Crystal data and summary of intensity data collection and structure refinement

Compound	$Mo_4O_6Cl_2(OCOC_2H_5)_6$	Crystal dimensions/mm	0.09 × 0.12 × 0.50
Colour/shape	Olive-green/prisms	Scan width	1.2
Formula weight	989.09	Standard reflections	034; 800; 6 0 14
Space group	$P2_1/n$	Decay of standards	± 1%
Temp./°C	18	Reflections measured	4670
		$2\,\theta$ range/deg	$4 \leq 2\,\theta \leq 30$
Cell constants[a]		Range of h, k, l	± 17, +13, +14
a/Å	11.713(2)	Reflections observed	2094
b/Å	9.292(3)	$[I > 2\,\sigma(I)]$	
c/Å	30.957(6)	Computer programs[b]	SHELX[7]
β/deg	96.71(2)	No. of parameters varied	199
		$\Delta/\sigma_{\max}$	0.002
Cell volume/Å^3	3346(1)	Weight	1
Formula units/unit cell	4	GOF	4.70
D_{calc} /g cm^{-3}	1.963	$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.0046
μ_{calc} /cm^{-1}	16.6	Max. and min. height in	
		final diff. map	+ 0.60, –0.54 e$^-$ Å^3
Diffractometer/scan	Philips PW 1100/ω-2θ		
Radiation, graphite			
monochromator	Mo-Kα (λ = 0.71069)		

[a] Least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 18 reflections in the range $11 \leq \theta \leq 16°$.

[b] Neutral scattering factors and anomalous dispersion corrections.

TABLE II

Atomic coordinates, equivalent isotropic thermal parameters and isotropic thermal parameters (× 10^3) with e.s.d.'s in parentheses in the structure of $Mo_4O_6Cl_2(OCOC_2H_5)_6$

Atom	*x*	*y*	*z*	U_{eq}/U_{iso}[a,b]
Mo1	0.4528(1)	0.1604(1)	0.1780(1)	28(1)
Mo2	0.3022(1)	0.2120(1)	0.1116(1)	30(1)
Mo3	0.5823(1)	0.1066(1)	0.0709(1)	38(1)
Mo4	0.1692(1)	–0.0037(1)	0.1994(1)	37(1)
Cl1	0.0668(4)	0.2003(5)	0.2104(2)	69(3)
Cl2	0.6830(4)	0.3140(5)	0.0897(2)	76(3)
O1	0.4707(8)	0.3271(10)	0.1948(4)	47(3)
O2	0.2896(8)	0.3883(10)	0.1176(4)	45(3)
O3	0.6638(9)	0.0343(11)	0.0363(5)	58(3)
O4	0.0833(8)	–0.1224(10)	0.2183(4)	50(3)
O5	0.4658(7)	0.1778(9)	0.1152(5)	34(2)
O6	0.2870(7)	0.1335(9)	0.1689(4)	34(2)
O11	0.6273(8)	0.1064(10)	0.1868(4)	43(3)
O12	0.6651(9)	0.0077(10)	0.1237(5)	48(3)
O21	0.4527(8)	–0.0768(9)	0.1696(4)	38(3)
O22	0.2829(8)	–0.1604(10)	0.1838(4)	43(3)
O31	0.2993(9)	0.2500(10)	0.0439(5)	50(3)
O32	0.4773(9)	0.2189(11)	0.0269(4)	58(3)
O41	0.4551(8)	0.0857(10)	0.2426(4)	43(3)
O42	0.2750(8)	0.0325(10)	0.2540(4)	50(3)
O51	0.2964(8)	–0.0095(10)	0.0849(4)	46(3)
O52	0.4660(9)	–0.0624(10)	0.0643(4)	49(3)
O61	0.1262(8)	0.1747(10)	0.0967(4)	47(3)
O62	0.0862(8)	–0.0128(10)	0.1375(4)	49(3)
C11	0.6860(13)	0.0313(15)	0.1649(8)	44(4)
C12	0.7936(17)	–0.0376(21)	0.1863(10)	80(6)
C13	0.7874(23)	–0.0668(28)	0.2356(11)	122(10)
C21	0.3853(11)	–0.1771(13)	0.1752(6)	34(4)
C22	0.4220(12)	–0.3304(16)	0.1716(7)	48(4)
C23	0.5455(14)	–0.3483(17)	0.1583(7)	58(5)
C31	0.3751(15)	0.2609(17)	0.0184(7)	55(5)
C32	0.3435(15)	0.3292(19)	–0.0269(8)	67(5)
C33	0.2165(20)	0.3432(24)	–0.0397(9)	100(8)
C41	0.3776(13)	0.0553(15)	0.2671(7)	45(4)
C42	0.4122(14)	0.0503(17)	0.3166(8)	55(5)
C43	0.5402(19)	0.0563(22)	0.3295(9)	91(7)
C51	0.3650(12)	–0.0936(15)	0.0699(6)	44(4)
C52	0.3282(13)	–0.2442(16)	0.0541(7)	52(5)
C53	0.2056(15)	–0.2841(19)	0.0644(7)	66(5)
C61	0.0638(13)	0.0742(16)	0.1079(7)	50(4)
C62	–0.0504(20)	0.0459(25)	0.0767(9)	98(8)
C63	–0.0608(28)	0.1413(35)	0.0389(12)	161(13)

[a] Mo and Cl atoms only were refined anisotropically.

[b] Equivalent isotropic *U* defined as $U_{eq} = 1/3\ \Sigma_i\Sigma_j \boldsymbol{U}_{ij}\alpha_i^*\alpha_j^*\boldsymbol{a}_i\boldsymbol{a}_j$.

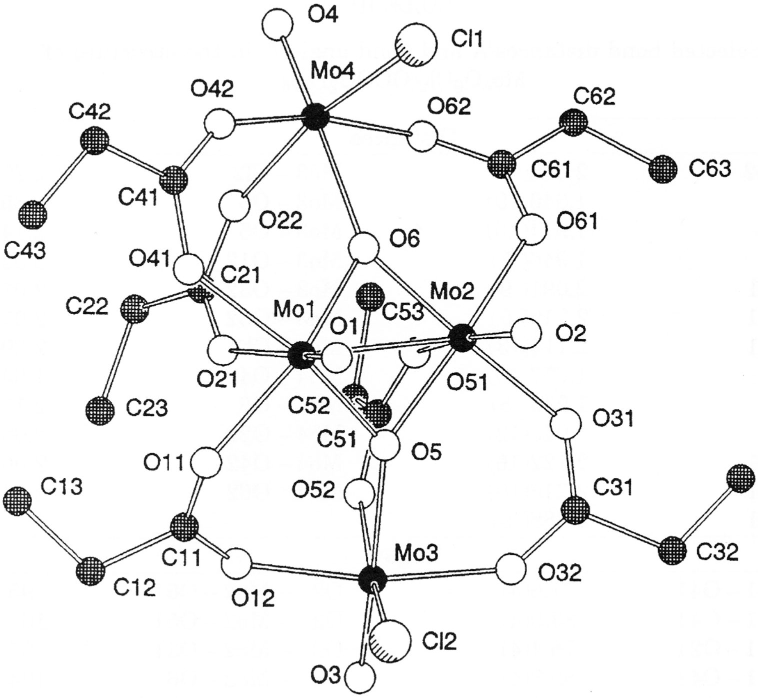

Figure 1. A view of the structure of $Mo_4O_6Cl_2(OCOC_2H_5)_6$ showing the atom-numbering scheme. Hydrogen atoms were not included in the refinement.

atoms. Hydrogen atoms were omitted. The final positional parameters and their estimated standard deviations are listed in Table II.

Several crystals of different shape were also found among the crystals of the title compound. They were extremely sensitive to moisture and, in spite of all possible protection, they decomposed during the data collection. Their crystal data were a = 21.678(7) Å, b = 9.439(1) Å, c = 35.266(13) Å, β = 95.40(3)°, V = 7184 Å^3, D_{calc} = 1.878 g cm^{-3}, Z = 8, space group $C2/c$. Preliminary and not very accurate Fourier maps indicated that the complex was actually a solvate $Mo_4O_6Cl_2(OCOCH_2CH_3)_6 \cdot 0.5(CH_3CH_2CO)_2O$ with a disordered solvent molecule of propionic anhydride, as found in the structure of the corresponding acetate complex solvated with acetic anhydride.[4]

RESULTS AND DISCUSSION

A view of the structure is shown in Figure 1, selected bond lengths and angles given in Table III. Although the title molecule does not possess any crystallographically imposed symmetry, since the related acetato[4] and ben-

TABLE III

Selected bond distances/Å and bond angles/° in the structure of $Mo_4O_6Cl_2(OCOC_2H_5)_6$

Distances			
Mo1 – Mo2	2.592(3)	Mo3 – Cl2	2.299(5)
Mo1 – O1	1.640(10)	Mo3 – O3	1.658(14)
Mo1 – O5	1.974(16)	Mo3 – O5	2.149(13)
Mo1 – O6	1.946(8)	Mo3 – O12	2.022(13)
Mo1 – O11	2.091(9)	Mo3 – O32	2.016(11)
Mo1 – O21	2.219(9)	Mo3 – O52	2.073(10)
Mo1 – O41	2.114(13)	Mo4 – Cl1	2.290(5)
Mo2 – O2	1.657(10)	Mo4 – O4	1.646(10)
Mo2 – O5	1.933(8)	Mo4 – O6	2.174(10)
Mo2 – O6	1.945(12)	Mo4 – O22	2.068(10)
Mo2 – O31	2.122(16)	Mo4 – O42	2.004(11)
Mo2 – O51	2.216(10)	Mo4 – O62	2.047(12)
Mo2 – O61	2.088(9)		

Angles			
O21 – Mo1 – O41	77.6(4)	O2 – Mo2 – O61	95.2(4)
O11 – Mo1 – O41	83.9(4)	O2 – Mo2 – O51	163.9(5)
O11 – Mo1 – O21	76.4(4)	O2 – Mo2 – O31	87.4(5)
O6 – Mo1 – O41	89.8(4)	O2 – Mo2 – O6	104.5(5)
O6 – Mo1 – O21	82.5(3)	O2 – Mo2 – O5	104.9(4)
O6 – Mo1 – O11	158.7(4)	O32 – Mo3 – O52	89.1(4)
O5 – Mo1 – O41	164.7(4)	O12 – Mo3 – O52	89.0(4)
O5 – Mo1 – O21	88.0(4)	O12 – Mo3 – O32	168.2(5)
O5 – Mo1 – O11	87.8(4)	O5 – Mo3 – O52	80.6(4)
O5 – Mo1 – O6	93.4(4)	O5 – Mo3 – O32	83.6(4)
O1 – Mo1 – O41	91.3(5)	O5 – Mo3 – O12	84.5(5)
O1 – Mo1 – O21	166.8(5)	O3 – Mo3 – O52	92.9(5)
O1 – Mo1 – O11	95.7(4)	O3 – Mo3 – O32	97.2(6)
O1 – Mo1 – O6	104.8(4)	O3 – Mo3 – O12	94.6(5)
O1 – Mo1 – O5	102.3(5)	O3 – Mo3 – O5	173.5(4)
O51 – Mo2 – O61	77.1(4)	O42 – Mo4 – O62	167.4(4)
O31 – Mo2 – O61	84.7(4)	O22 – Mo4 – O62	90.0(5)
O31 – Mo2 – O51	77.9(4)	O22 – Mo4 – O42	87.9(4)
O6 – Mo2 – O61	86.9(4)	O6 – Mo4 – O62	82.8(4)
O6 – Mo2 – O51	89.4(4)	O6 – Mo4 – O42	84.6(4)
O6 – Mo2 – O31	166.1(4)	O6 – Mo4 – O22	81.5(4)
O5 – Mo2 – O61	158.8(4)	O4 – Mo4 – O62	93.6(5)
O5 – Mo2 – O51	81.7(4)	O4 – Mo4 – O42	99.0(5)
O5 – Mo2 – O31	89.2(6)	O4 – Mo4 – O22	92.8(4)
O5 – Mo2 – O6	94.7(5)	O4 – Mo4 – O6	173.2(5)

zoato[5] complexes have a two-fold symmetry axis, its structure is close to it. All four molybdenum atoms are octahedrally coordinated and the octahedra are connected through two oxo-oxygen and six bidentate propionato bridges. The octahedra about Mo(1) and Mo(2) share a commonm edge and have common corners with the octahedra about Mo(3) and Mo(4). The octahedra are considerably distorted, the angles at the molydenum atoms range from 76.4 to 104.8°. Such structure permits formation of only one Mo(1)-Mo(2) bond of 2.592(3) Å, the value close to those found in $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$,[2] $Mo_4Cl_4O_6(OPr)_6$,[3] $Mo_4O_6Cl_2(OCOCH_3)_6$,[4] and $Mo_4O_6Cl_2(OCOC_6H_5)_6$,[5] amounting to 2.600(1), 2.669(2), 2.609(3) and 2.611(1) Å, respectively. This bond length is almost the same as that considered as a Mo-Mo single bond.[8,9] Also, the two pairs of molybdenum atoms have different environments. Mo(1) and Mo(2) are surrounded by three propionato-oxygen atoms at Mo-O bond distances ranging from 2.088(9) to 2.219(10) Å and three oxo-oxygen atoms with mean values of 1.649(10) and 1.950(11) Å for the $Mo\text{-}O_t$ and $Mo\text{-}O_b$ bond lengths, respectively. Mo(3) and Mo(4) are also surrounded by three propionato-oxygen atoms at distances ranging from 2.004(11) to 2.073(10) Å, but only by two oxo-oxygen atoms, one terminal at a mean value of 1.652(12) Å and one bridging at a mean value of 2.162(12) Å. Finally, their coordination polyhedra are completed with chlorine atoms at a mean value for the Mo–Cl bond lengths of 2.295(5) Å. The molybdenum-propionato-oxygen bond lengths vary according to their positions, *i.e. cis* or *trans* to the oxo-oxygen atoms. The oxo-oxygens 0(5) and 0(6) are unsymmetrical triple bridges between three molybdenum atoms. The central Mo_2O_2 four-membered ring is folded at an angle of 156.56(3)° along a line connecting these two bridging oxo-oxygen atoms.

The complex is paramagnetic, the magnetic moment has a lower value (μ_{eff} = 0.62 B.M.) than one would expect for such molybdenum(V) complexes, thus indicating a coupling of the molybdenum atoms through the bridging oxo-oygen atoms and/or of a direct spin-spin interaction.

The infrared spectrum is in accordance with the structure determined by the X-ray diffraction analysis.

Supplementary Materials. – Crystallographic data (excluding structure factors which are available from the authors) for the structure reported in this paper will be deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax; 44 (0) 1223-336033; E-mail: teched@chemcrys. cam.ac.uk).

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SAŽETAK

Sinteza dva nova tetranuklearna kompleksa molibdena(V). Kristalna struktura heksa-μ-propionato-diklorodi-μ_3-okso-tetraoksomolibdena(V)

Boris Kamenar, Branka Korpar-Čolig i Maja Penavić

U reakciji MoO_2Cl_2 i MoO_2Br_2 s anhidridom propionske kiseline priređeni su novi kompleksi molibdena(V), $Mo_4O_6Cl_2(OCOC_2H_5)_6$ i $Mo_4O_6Br_2(OCOC_2H_5)_6$. Kristalna struktura prvog kompleksa određena je iz difraktometrijskih podataka na monokristalu i utočnjena do R = 0,046. Kompleks kristalizira u monoklinskom sustavu, prostorna grupa $P2_{1/n}$, ima dimenzije jedinične ćelije a = 11,713(2) Å, b = 9,292(3) Å, c = 30,957(6) Å, β = 96,71(2)°, $D_{izr.}$ = 1,963 g cm^{-3}, Z = 4. Tetranuklearna molekula kompleksa sadržava četiri atoma molibdena premošćena sa dva atoma okso-kisika i šest bidentatno vezana propionato-liganda. Dva od četiri atoma molibdena stvaraju vezu Mo–Mo od 2,592(3) Å.