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Synthesis and Characterization of New Molybdenum(VI) Oxalate Complexes. Crystal Structure of Tetramethylammonium Salt of μ-Oxo-diaquadioxalatotetraoxodimolybdenum(VI)*

*Marina Cindrić,** Neven Strukan, and Višnja Vrdoljak*

Laboratory of General and Inorganic Chemistry, Chemistry Department,
Faculty of Science, University of Zagreb, Ul. kralja Zvonimira 8,
P.O. Box 153, 10001 Zagreb, Croatia

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In the reaction of molybdenum(VI) oxide with oxalic acid and RCl (R = pyH and γ-picH), new dinuclear complexes of molybdenum(VI) $R_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ have been prepared. When molybdenum(VI) oxide was treated with aqueous solution of tetramethylammonium oxalate complex, $[(CH_3)_4N]_2[MoO_3(C_2O_4)] \cdot H_2O$ was isolated. The unknown crystal structure of $[(CH_3)_4N]_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ was determined from single crystal diffractometer data and refined to the final R value of 0.0317. When irradiated, this class of compounds shows considerable photochromic properties. The photochemical process is of the redox type: molybdenum(VI) centers are reduced to molybdenum(V) moieties. The presence of molybdenum(V) species was confirmed by the ESR spectra.

Key words: molybdenum(VI) complexes, oxalate complexes, photochemical behaviour, crystal structure.

INTRODUCTION

In addition to the multitude of mononuclear and polynuclear complexes of Mo(VI), there is also a significant number of its dinuclear complexes. Nevertheless, the dinuclear species are not characteristic of Mo(VI) as they

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* Dedicated to Professor Boris Kamenar on the occasion of his 70th birthday. We would like to thank him for his teaching and his help in our research over many years.

** Author to whom correspondence should be addressed. (E-mail: marina@chem.pmf.hr) are of Mo(V). Such complexes usually contain anions built up from two MoO_3 moieties bridged through one complexing ligand, such as ethylenediamminetetracetate (edta), as found in $Na_4[(MoO_3)_2edta] \cdot 8H_2O$[1] or $Mo_2O_5^{2+}$ core, with a single oxygen atom as found in $Na_2[Mo_2O_5(Hnta)_2] \cdot 8H_2O$[2] (Hnta = nitrilotriacetic acid). Whereas the structures containing MoO_3 structural units are considerably rare, those with $Mo_2O_5^{2+}$ core are found in a number of Mo(VI) complexes.[3]

The Mo(VI) oxalate complexes have been known for many years[4–10] and the structures of some of them, such as $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$,[11] $NaNH_4[MoO_3(C_2O_4)] \cdot 8H_2O$[12] and $[(-)Co(en)_3][MoO_3(C_2O_4)(H_2O)] \cdot 2H_2O$,[13] have been reported in the literature. However, for $R_2[MoO_3(C_2O_4)] \cdot H_2O$[14] and $R_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$[14] (R = K, NH_4), only their unit cell parameters have been published but no X-ray crystal structures have been done so far. The syntheses of complexes[15] of the $R_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ type (R = K, Rb, Cs, NH_4, $N(CH_3)_4$), were reported in 1977 and their structures were speculated only on the basis of spectral data. According to these results, salts with the Rb^+ and NH_4^+ cations should contain anions with a linear symmetric Mo–O–Mo bridge, while for the Cs^+ and $[(CH_3)_4N]^+$ salts the authors claimed that the bridge must be of a different kind. Such findings stimulated our structure determination of $[(CH_3)_4N]_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$. We found that the bridge between two Mo atoms is of the Mo–O–Mo type with an angle of 177.6(2)° at the oxygen atom.

The present work also deals with the preparation and characterization of molybdenum(VI) oxalate complexes of the above general formula but with pyridinium and γ-picolinium cations. In the course of this investigation, a new complex, $[(CH_3)_4N]_2[MoO_3(C_2O_4)] \cdot H_2O$, was also prepared.

EXPERIMENTAL

Reagents and Apparatus

All chemicals were of reagent grade and used as purchased from commercial sources. The IR spectra were recorded in KBr with a FT IR 1600 Fourier-transform spectrophotometer in the 4000–450 cm^{-1} region.

The ESR spectra were recorded with a polycrystalline sample on a Varian E-109 spectrometer operating at 100 kHz modulation. DPPH (α,α′-diphenil-β-picrylhydrazyl) was used as an internal reference. All measurements were made at room temperature.

Synthesis of Pyridinium μ-Oxo-diaquadioxalatotetraoxodimolybdenum(VI)
$[pyH]_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$

To a mixture of pyridine (1.3 cm^3) and 1 M HCl (15.9 cm^3), equivalent amounts of oxalic acid dihydrate (1 g in 15 cm^3 H_2O) and molybdenum(VI) oxide (1.14 g) were added. The mixture (pH ≈ 1) was heated for 2 h at 90 °C, then unreacted MoO_3 was filtered off and the filtrate was allowed to stand in dark at room temperature. Colourless crystals (0.26 g, yield 10.19%), very sensitive to sunlight, appeared after 10 days. They were collected by filtration and dried under vacuum.

Anal. Calcd. for $C_{14}H_{16}Mo_2N_2O_{15}$ ($M_r = 644.17$): C 26.10, H 2.50, Mo 29.79, N 4.35%; found: C 25.99, H 2.78, Mo 29.81, N 4.50%.

IR (KBr) ν_{max} / cm^{-1}: 1718 $(CO_2)_{as}$, 1485 $(CO_2)_s$, 949 (MoO_t), 787 (Mo_2O_b).

Synthesis of Picolinium μ-Oxo-diaquadioxalatotetraoxodimolybdenum(VI) $[picH]_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$

To a mixture of a γ-picoline (1.6 cm^3) and 1 M HCl (15.9 cm^3), an equivalent amount of oxalic acid dyhidrate (1 g in 25 cm^3 H_2O) was added, followed by the molybdenum(VI) oxide (1.14 g). The mixture (pH ≈ 1) was heated for 1.5 h at about 90 °C, then unreacted MoO_3 was filtered off and the solution was allowed to stand in dark at room temperature. After 20 days, colourless crystals were collected by filtration and dried under vacuum (0.25 g, yield 9.5%). The product was light sensitive.

Anal. Calcd. for $C_{16}H_{20}Mo_2N_2O_{15}$ ($M_r = 670.20$): C 28.59, H 2.99, Mo 28.54, N 4.17%; found: C 28.80, H 3.00, Mo 28.20, N 4.36%.

IR (KBr) ν_{max} / cm^{-1}: 1673 $(CO_2)_{as}$, 1501 $(CO_2)_s$, 939 (MoO_t), 773 (Mo_2O_b).

Synthesis of Tetramethylammonium Oxalatotrioxomolybdenum(VI) Hydrate $[(CH_3)_4N]_2[MoO_3(C_2O_4)]\cdot H_2O$

An aqueous solution of tetramethylammonium chloride (1.74 g in 10 cm^3) was passed through the anion exchanger column (DOWEX-2). Tetramethylammonium cation was removed down the column by water (150 cm^3). To combined effluent and washings, oxalic acid dihydrate (0.5 g) was added. The solution was evaporated to half of its volume and then MoO_3 (0.55 g) was added. The mixture (pH ≈ 6) was heated for two hours at 90 °C and then unreacted MoO_3 was filtered off. After 30 days, colourless crystals (0.34 g, yield 44.68%) were collected by filtration and dried under vacuum.

Anal. Calcd. for $C_{10}H_{26}MoN_2O_8$ ($M_r = 398.27$): C 30.16, H 6.58, Mo 24.09, N 7.03%: found: C 29.89, H 6.90, Mo 24.49, N 6.67%.

IR (KBr) ν_{max} / cm^{-1}: 1684 $(CO_2)_{as}$, 1486 $(CO_2)_s$, 906 (MoO_t), 736 (Mo_2O_b).

Crystal Structure Determination and Refinement

Crystal Data

$C_{12}H_{28}Mo_2N_2O_{15}$, monoclinic, space group $C2/c$, $M_r = 632.24$, $a = 34.770(13)$, $b = 11.190(5)$, $c = 11.544(4)$ Å, $\beta = 102.89(4)°$, $V = 4378(3)$ Å^3, $Z = 8$, $D_x = 1.918$ g cm^{-3}, $F(000) = 2544$, μ(Mo-Kα) = 12.21 cm^{-1}. A single crystal of dimensions 0.30 × 0.30 × 0.20 mm^3 was used for data collection on a Philips PW 1100 diffractometer with graphite monochromatized Mo-Kα radiation ($\lambda = 0.7107$ Å). Cell dimensions were determined using fitting angles for 21 strong reflections in the range $26 < 2\theta < 32°$. The 6686 reflections were collected by the $\omega - 2\theta$ scan technique ($4 \le 2\theta \le 60°$, $-48 < h < 47°$, $0 < k < 15°$, $0 < l < 16°$) at room temperature.

The structure was solved by the heavy atom method and then refined on F^2 by full matrix least-squares calculations. Intensity data were not corrected for absorption. Hydrogen atoms of the tetramethylammonium cations were positioned on geometrical grounds [$d(\mathrm{C_{sp3}}\text{–H}) = 0.96$ Å], and water molecule H-atoms were located in the difference electron density map. Coordinates of hydrogen atoms were not refined, but they were all included in structure factor calculations. The calculations converged at $R(F) = 0.0317$ for a total of 4073 reflections with $I \geq 2\sigma(I)$ and 281 refined parameters, $wR(F^2) = 0.0867$ for 6331 data. The largest remaining difference peak was 0.91 e Å^{-3}. All calculations were performed on an IBM ThinkPad microcomputer (Pentium II 300 MHz) using SHELXS 97[16] and SHELXL 97.[17] The molecular and crystal structure drawings were prepared by ORTEP[18] and PLUTON[19] programmes.

RESULTS AND DISCUSSION

Depending upon the pH of the reaction solutions, different types of molybdenum(VI) complexes can be synthesized. When molybdenum(VI) oxide reacts with oxalic acid in the presence of pyridinium chloride, or picolinium chloride new dinuclear complexes of the type $R_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ (R = pyH and γ-picH) appear as crystalline products, but when molybdenum(VI) oxide reacts with tetramethylammonium oxalate the $[(CH_3)_4N]_2[MoO_3(C_2O_4)] \cdot H_2O$ complex was prepared. Consequently, in the reaction of molybdenum(VI) oxide with oxalic acid in the presence of tetramethylammonium chloride, a dinuclear complex of the type $[(CH_3)_4N]_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ was synthesized.[15] Owing to the interesting photochromic properties of such complexes, the crystal structure of $[(CH_3)_4N]_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ was undertaken.

Figure 1 shows dinuclear $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$ anion, selected bond lengths and angles are listed in Table I. The complex salt is built up of the dimeric anion and tetramethylammonium cations. The dimeric anion contains two octahedrally coordinated molybdenum(VI) atoms sharing common corners at the bridging oxygen atoms. The bridge is close to linearity, with the Mo–O–Mo angle amounting to 177.6(2)°. In the first reported structure containing such $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$ anion,[11] the Mo–O–Mo bridge was rigorously linear due to the fact that the bridging oxygen atom occupies the crystallographic centre of symmetry. However, many examples of such linear[20] as well as angular structures have been found so far.[21] The six Mo–O bond lengths cover a large range from 1.700 to 2.328 Å. They depend upon the bond order as well as upon their positions in the structure, *i.e. cis* or *trans* to the oxo-oxygen atoms.[11] Consequently, two Mo–OH_2 bonds, 2.319(3) and 2.328(2) Å, are the longest.[22] All bond lengths and angles are comparable to those already known from similar crystal structures.[3] Dinuclear anions are mutually hydrogen bonded (Figure 2) through water molecule, with O–H···O distances varying from 2.597(4) to 2.859(3) Å, thus forming endless layers parallel to (011) plane.

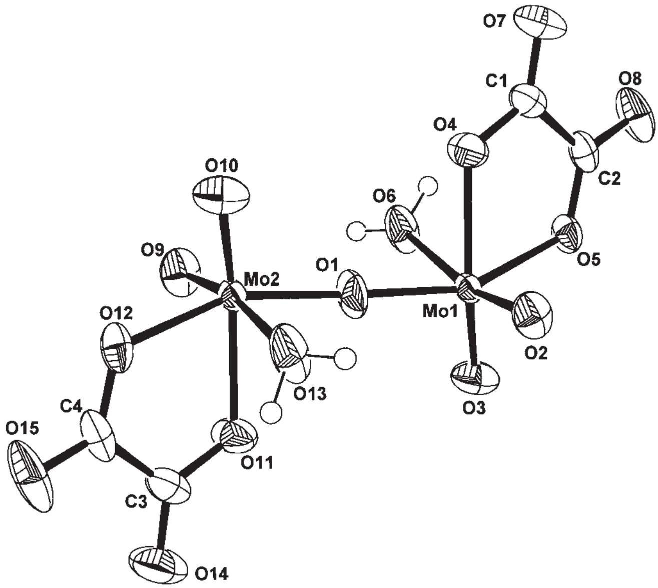

Figure 1. Wiew of the binuclear anion $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$ with the atomic numbering scheme. Ellipsoids are drawn at 50% probability level, H atoms are shown as small circles.

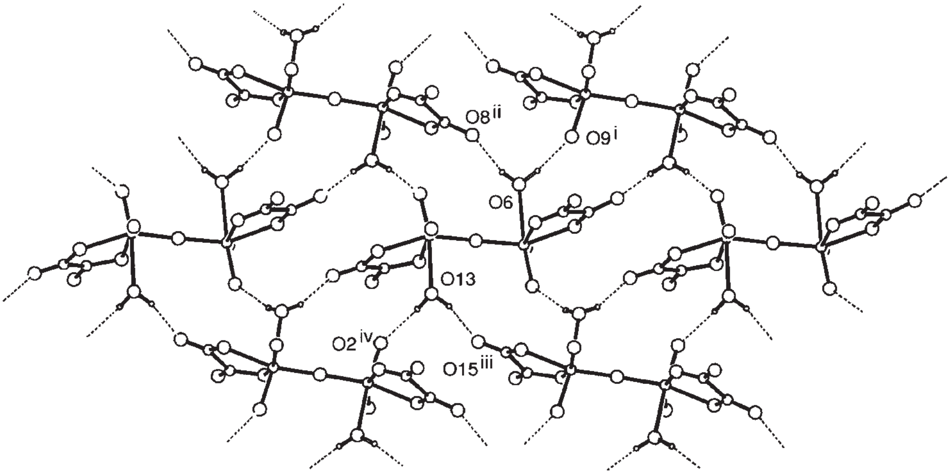

Figure 2. Hydrogen bonds between $[Mo_2O_5(C_2O_4)_2(H_2O)_2]^{2-}$ anions.

The infrared spectra of all complex salts are in accord with X-ray structure analyses, as well as with the examples found in the literature.[13]

TABLE I

Selected bond lengths / Å and angles / ° for $[(CH_3)_4N]_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$

Bond lengths			
Mo(1)–O(2)	1.700(2)	Mo(2)–O(9)	1.700(2)
Mo(1)–O(3)	1.704(2)	Mo(2)–O(10)	1.705(2)
Mo(1)–O(1)	1.880(2)	Mo(2)–O(1)	1.880(2)
Mo(1)–O(5)	2.076(2)	Mo(2)–O(12)	2.077(2)
Mo(1)–O(4)	2.132(2)	Mo(2)–O(11)	2.129(2)
Mo(1)–O(6)	2.328(2)	Mo(2)–O(13)	2.319(3)
O(4)–C(1)	1.281(4)	O(11)–C(3)	1.281(4)
O(5)–C(2)	1.300(3)	O(12)–C(4)	1.307(4)
O(7)–C(1)	1.211(3)	O(14)–C(3)	1.224(4)
O(8)–C(2)	1.215(3)	O(15)–C(4)	1.220(4)
C(1)–C(2)	1.542(4)	C(3)–C(4)	1.523(5)
Bond angles			
Mo(2)–O(1)–Mo(1)	177.6(2)		
O(2)–Mo(1)–O(3)	103.3(1)	O(9)–Mo(2)–O(10)	103.1(1)
O(2)–Mo(1)–O(1)	102.0(1)	O(9)–Mo(2)–O(1)	101.5(1)
O(3)–Mo(1)–O(1)	103.1(1)	O(10)–Mo(2)–O(1)	103.7(1)
O(2)–Mo(1)–O(5)	96.7(1)	O(9)–Mo(2)–O(12)	96.2(1)
O(3)–Mo(1)–O(5)	89.1(1)	O(10)–Mo(2)–O(12)	89.2(1)
O(1)–Mo(1)–O(5)	154.5(1)	O(1)–Mo(2)–O(12)	155.0(1)
O(2)–Mo(1)–O(4)	92.5(1)	O(9)–Mo(2)–O(11)	93.4(1)
O(3)–Mo(1)–O(4)	158.5(1)	O(10)–Mo(2)–O(11)	158.0(1)
O(1)–Mo(1)–O(4)	87.4(1)	O(1)–Mo(2)–O(11)	86.9(1)
O(5)–Mo(1)–O(4)	74.5(1)	O(12)–Mo(2)–O(11)	74.4(1)
O(2)–Mo(1)–O(6)	168.8(1)	O(9)–Mo(2)–O(13)	169.1(1)
O(3)–Mo(1)–O(6)	84.4(1)	O(10)–Mo(2)–O(13)	83.5(1)
O(1)–Mo(1)–O(6)	83.8(1)	O(1)–Mo(2)–O(13)	85.0(1)
O(5)–Mo(1)–O(6)	75.1(1)	O(12)–Mo(2)–O(13)	75.1(1)
O(4)–Mo(1)–O(6)	78.1(1)	O(11)–Mo(2)–O(13)	78.2(1)
C(1)–O(4)–Mo(1)	119.5(2)	C(3)–O(11)–Mo(2)	119.5(2)
C(2)–O(5)–Mo(1)	119.9(2)	C(4)–O(12)–Mo(2)	119.3(2)
O(7)–C(1)–O(4)	126.6(3)	O(14)–C(3)–O(11)	125.9(4)
O(7)–C(1)–C(2)	121.3(3)	O(14)–C(3)–C(4)	121.8(3)
O(4)–C(1)–C(2)	112.1(2)	O(11)–C(3)–C(4)	112.3(3)
O(8)–C(2)–O(5)	125.4(3)	O(15)–C(4)–O(12)	124.6(4)
O(8)–C(2)–C(1)	120.9(3)	O(15)–C(4)–C(3)	121.3(3)
O(5)–C(2)–C(1)	113.7(2)	O(12)–C(4)–C(3)	114.1(3)

TABLE I (cont.)

D–H ⋯ A	d(D–H)	d(H ⋯ A)	d(D ⋯ A)	DHA angles
$O(6)–H(1) \cdots O(9)_{i}$	0.923	1.941	2.859(3)	172.7
$O(6)–H(2) \cdots O(8)_{ii}$	0.770	1.913	2.650(3)	160.1
$O(13)–H(3) \cdots O(15)_{iii}$	0.803	1.812	2.597(4)	165.3
$O(13)–H(4) \cdots O(2)_{iv}$	0.912	1.968	2.850(3)	162.4

Superscripts correspond to equivalent positions as follows:
i = x, $-y + 1$, $z - 1 / 2$; ii = x, $-y + 1$, $z + 1 / 2$; iii = x, $-y$, $z - 1 / 2$; iv = x, $-y$, $z + 1 / 2$.

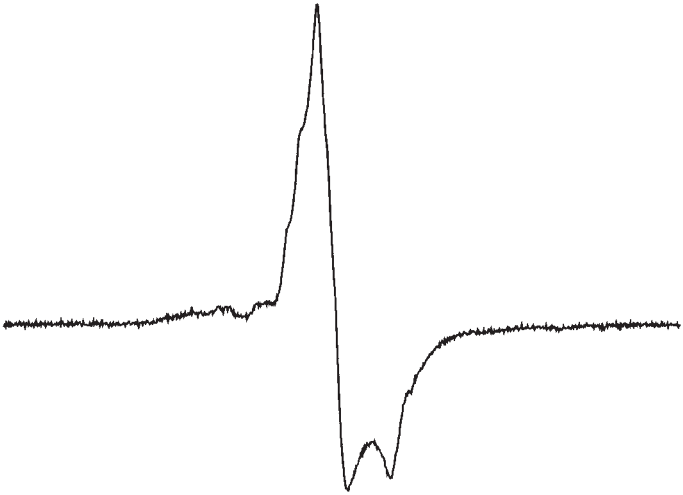

Figure 3. ESR spectrum of $[picH]_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$.

The oxalate complexes of Mo(VI) are of interest owing to their photochromic properties.[14,23] Such behaviour was observed by A. Rosenheim[4] at the end of the last century and confirmed many years later by B. F. Mentzen and H. Sauterean.[14] Our complexes show analogous behaviour. Being exposed to UV radiation, they changed considerably: from colourless to light green in the case of tetramethylammonium and to deep blue in pyridinium salt. The ESR spectrum of $[picH]_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ (Figure 3) clearly shows that, during exposure to UV radiation the oxidation number of Mo partially changes from + 6 to + 5. Such photochemical redox processes can be explained by the reduction of Mo(VI) to Mo(V) centres.[24] A similar redox process has been observed also for uranyl formate where the redox process was explained by the reduction of U(VI) to U(V) and by oxidation of formato groups to CO_2.[14] According to our experience, the photochromic properties are characteristic also of the complexes with the dinuclear Mo_2O_5 core and not only those containing MoO_3 core as it has been suggested earlier.[25]

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Supplementary Materials. – Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. 103209.

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SAŽETAK

Sinteza i karakterizacija novih oksalato-kompleksa molibdena(VI). Kristalna struktura tetrametilamonijeve soli μ-oksodiakvadioksalatotetraoksodimolibdena(VI)

Marina Cindrić, Neven Strukan i Višnja Vrdoljak

Novi dinuklearni kompleksi molibdena(VI) $R_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ priređeni su reakcijom molibdenova(VI) oksida s oksalnom kiselinom i RCl (R = pyH i γ-picH). Mononuklearni kompleks $[(CH_3)_4N]_2[MoO_3(C_2O_4)] \cdot H_2O$ izoliran je u reakciji molibdenova(VI) oksida i vodene otopine tetrametilamonijeva oksalata. Kristalna struktura $[(CH_3)_4N]_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ određena je rentgenskom difrakcijom na monokristalu do $R = 0{,}0317$. Pod utjecajem zračenja ta skupina spojeva pokazuje fotokromna svojstva. Fotokemijski je proces redoks-tipa: centri molibdena(VI) reduciraju se do molibdena(V). Prisutnost molibdena(V) potvrđena je ESR spektrom.