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Complexation of Molybdenum(V) with Glycolic Acid: An Unusual Orientation of Glycolato Ligand in $\{Mo_2O_4\}^{2+}$ Complexes‡

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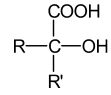
$(PyH)_5[Mo^VOCl_4(H_2O)]_3Cl_2$ and $(PyH)_n[Mo^VOBr_4]_n$ reacted with glycolic acid (H_2glyc) or its half-neutralized ion ($Hglyc^-$) to afford a series of novel glycolato complexes based on the $\{Mo^V_2O_4\}^{2+}$ structural core: $(PyH)_3[Mo_2O_4Cl_4(Hglyc)]\cdot {}^1/_2CH_3CN$ (**1**), $(PyH)_3[Mo_2O_4Br_4(Hglyc)]\cdot Pr^iOH$ (**2**), $(PyH)_2[Mo_2O_4(glyc)_2Py_2]$ (**3**), $(PyH)_4[Mo_4O_8Cl_4(glyc)_2]\cdot 2EtOH$ (**4**), and $[Mo_4O_8(glyc)_2Py_4]$ (**5**) (Py = pyridine, C_5H_5N; PyH^+ = pyridinium cation, $C_5H_5NH^+$ and $glyc^{2-}$ = a doubly ionized glycolate, $^-OCH_2COO^-$). The compounds were fully characterized by X-ray crystallography and infrared spectroscopy. The $Hglyc^-$ ion binds to the $\{Mo_2O_4\}^{2+}$ core through a carboxylate end in a bidentate bridging manner, whereas the $glyc^{2-}$ ion adopts a chelating bidentate coordination through a deprotonated hydroxyl group and a monodentate carboxylate. The orientations of $glyc^{2-}$ ions in **3**–**5** are such that the alkoxyl oxygen atoms occupy the sites opposite the multiply bonded oxides. $\{(C_6H_5)_4P\}[Mo^{VI}O_2(glyc)(Hglyc)]$ (**6**), an oxidized complex, features a reversed orientation of the $glyc^{2-}$ ion. The theoretical DFT calculations on the $[Mo^V_2O_4(glyc)_2Py_2]^{2-}$ and $[Mo^{VI}O_2(glyc)_2]^{2-}$ ions confirm that binding of glycolate with the alkoxyl oxygen to the site opposite the Mo═O bond is energetically more favorable in $\{Mo^V_2O_4\}^{2+}$ species, whereas a reversed orientation of the ligand is preferred in Mo(VI) complexes. An explanation based on the orbital analysis is put forward.

Introduction

Molybdenum forms part of the active site of many metalloenzymes that execute key transformations in the metabolism of nitrogen, sulfur and carbon compounds.[1] The active site of nitrogenase, an enzyme that catalyzes the reduction of dinitrogen, possesses a cagelike $MoFe_7S_9$ cluster with a homocitrate ion coordinated to molybdenum in a chelating manner through the alkoxyl oxygen and the vicinal carboxylate.[2] Although the precise function of homocitrate is not yet fully understood, it has been shown that its presence in the FeMo cofactor is crucial for the efficient N_2 reduction.[3] Homocitrate may also play an important role during biosynthesis of the cofactor: it is believed to mobilize molybdenum, which is taken up by the organisms in the form of MoO_4^{2-} ion.[4] The coordination chemistry of molybdenum(VI) is thus important in the transport of molybdenum from its natural aqueous environment into its ultimate form in biological systems. This has motivated studies of interactions with α-hydroxycarboxylic acids that possess a hydroxyl group in a vicinal position to a carboxylic group (Scheme 1) and, optionally, additional hydroxyl and/or carboxylic groups. The X-ray structure analysis of the only known homocitrato molybdenum complex revealed its composition to be $[(Mo^{VI}O_2)_4(\mu_2\text{-}O)_3(R,S\text{-}Hhomocit)_2]^{4-}$ with homocitrate ions $Hhomocit^{3-}$ engaged in an intricate tridentate coordina-

Scheme 1. General Formula of α-Hydroxycarboxylic Acids



i) homocitric acid: R = CH_2COOH, R' = CH_2CH_2COOH
ii) glycolic acid: R = R' = H
iii) citric acid: R = R' = CH_2COOH

‡ This paper is dedicated to Prof. F. A. Cotton, in memoriam.

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tion.[5] Tetranuclear complexes of the same type were prepared with two other α-hydroxycarboxylates, malate and citrate.[6,7] On the other hand, the same type of ligation as found for homocitrate in the FeMo cofactor was observed in a series of mononuclear complexes $[MoO_2L_2]^{2-}$ (L = glycolate, *S*-lactate,[8] *S*-malate,[9,10] *R,R*-tartrate,[11] *S*- and *R*-mandelate,[12] benzilate,[13] and citrate[14]). With the research focused mainly on systems with molybdenum in VI oxidation state, we deemed it important to investigate the oxidation states other than VI as well. Being largely involved in the studies of molybdenum(V) complexes with multidentate oxygen donor ligands,[15] it seemed logical to test this oxidation state first. The purpose of our work was to prepare molybdenum(V) complexes with glycolic acid, the simplest member of the series. Likewise to Mo(VI) chemistry, the Mo═O unit pervades the chemistry of V oxidation state.[16] We were interested to see in what way and to what extent the multiply bonded oxide influences the coordination of the glycolato ligand. Herein, we report the syntheses and the structural characterization of a series of complexes, all obtained from $(PyH)_5[Mo^{V}OCl_4(H_2O)]_3Cl_2$ or $(PyH)_n[Mo^{V}OBr_4]_n$.

Experimental Section

Most chemicals were purchased from Aldrich Chemical Co., triethylamine from Fluka and tetraphenylphosphonium bromide from Johnson Matthey. They were used without further purification. Acetonitrile solutions of pyridinium or triethylammonium glycolate were prepared by dissolving the appropriate amounts of base and glycolic acid in a 1:1 molar ratio. $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ and $(PyH)_n[MoOBr_4]_n$ were prepared by published procedures.[17] The compounds **1**–**5** were found to decompose on prolonged exposure to the air. Elemental analyses were performed by the Chemistry Department service at the University of Ljubljana. The infrared spectra were measured on solid samples as nujol or poly(chlorotrifluoroethylene) mulls using a Perkin-Elmer 2000 series FT-IR spectrometer.

Preparation of $(PyH)_3[Mo_2O_4Cl_4(Hglyc)]\cdot{}^1/_2CH_3CN$, 1. Ethanol (2 mL) was added to the acetonitrile solution of pyridinium glycolate (6.2 mL of 1.0 M solution, 6.2 mmol of glycolate). To this solution was added $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (1.287 g, 3.0 mmol of Mo). The clear, orange solution was left to stand in a closed Erlenmeyer flask at ambient conditions. Orange, block-shaped crystals of **1** that formed within 2 h were filtered off and washed with the hexanes. Yield: 875 mg (80%). Anal. Calcd. for $C_{17}H_{21}Cl_4Mo_2N_3O_7$ (dried sample): C, 28.64; H, 2.97; N, 5.89. Found: C, 28.85; H, 3.12; N, 5.74.

Preparation of $(PyH)_3[Mo_2O_4Br_4(Hglyc)]\cdot Pr^iOH$, 2. 2-propanol (1 mL) was added to the acetonitrile solution of pyridinium glycolate (3.1 mL of 1.0 M solution, 3.1 mmol of glycolate). To this solution was added $(PyH)_n[MoOBr_4]_n$ (950 mg, 1.86 mmol of Mo). The orange solution was left to stand in a closed Erlenmeyer flask at ambient conditions. Orange, block-shaped crystals of **2** that formed within a week were filtered off and washed with the hexanes. Yield: 593 mg (67%). Anal. Calcd. for $C_{20}H_{29}Br_4Mo_2N_3O_8$: C, 25.26; H, 3.07; N, 4.42. Found: C, 25.10; H, 2.99; N, 4.59.

Preparation of $(PyH)_2[Mo_2O_4(glyc)_2Py_2]$, 3. A mixture of pyridine (3 mL) and *iso*-butanol (4 mL) was added to $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (134 mg, 0.31 mmol of Mo) and glycolic acid (70 mg, 0.92 mmol). The reaction mixture was stirred and left to stand in a closed Erlenmeyer flask at ambient conditions. Red crystals of **3** that formed overnight were filtered off and washed with the hexanes. Yield: 64 mg (57%). Anal. Calcd. for $C_{24}H_{26}Mo_2N_4O_{10}$: C, 39.91; H, 3.63; N, 7.76. Found: C, 39.71; H, 3.65; N, 7.67.

Reaction of $(PyH)_3[Mo_2O_4Cl_4(Hglyc)]\cdot{}^1/_2CH_3CN$ (1) with Pyridine/Glycolic Acid. Freshly prepared $(PyH)_3[Mo_2O_4Cl_4(Hglyc)]\cdot{}^1/_2CH_3CN$ (**1**) (198 mg, 0.27 mmol) was dissolved in the solution of glycolic acid (152 mg, 2.0 mmol) in pyridine (2 mL). To this solution was added *iso*-butanol (3 mL) dropwise. The clear, orange solution was left to stand in a closed Erlenmeyer flask at ambient conditions for 2 days. Red crystals of **3** were separated from almost colorless solution by filtration and washed with the hexanes. Yield: 137 mg (70%).

Preparation of $(PyH)_4[Mo_4O_8Cl_4(glyc)_2]\cdot 2EtOH$, 4. Acetonitrile solution of triethylammonium glycolate (0.65 mL of 1.0 M solution, 0.65 mmol of glycolate) was added to ethanol (6 mL). To this solution was added $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (107 mg, 0.25 mmol of Mo). The clear, orange solution turned cloudy within a few minutes. The reaction mixture was left to stand in a closed Erlenmeyer flask at ambient conditions. Orange, needle-shaped crystals of **4** that formed overnight were filtered off and washed with the hexanes. Yield: 35 mg (46%). Anal. Calcd. for $C_{24}H_{28}Cl_4Mo_4N_4O_{14}$ (dried sample): C, 25.69; H, 2.52; N, 4.99. Found: C, 25.40; H, 2.80; N, 4.87.

Preparation of $[Mo_4O_8(glyc)_2Py_4]$, 5. A glass tube was charged with $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (50 mg, 0.12 mmol of Mo), glycolic acid (76 mg, 1.0 mmol), pyridine (1 mL), and methanol (3 mL). The tube was sealed and heated for 120 h in an electric oven maintained at 120 °C. The tube was allowed to cool slowly to room temperature. Orange crystals of **5** were filtered off. Yield: 11 mg (38%). Anal. Calcd. for $C_{24}H_{24}Mo_4N_4O_{14}$: C, 29.53; H, 2.48; N, 5.74. Found: C, 29.64; H, 2.67; N, 5.63.

Preparation of $\{(C_6H_5)_4P\}[MoO_2(glyc)(Hglyc)]$, 6. $(PyH)_5[MoOCl_4(H_2O)]_3Cl_2$ (322 mg, 0.75 mmol of Mo) was dissolved in acetonitrile (12.5 mL). To this solution was added pyridinium glycolate (3.75 mL of 1.0 M solution in acetonitrile, 3.75 mmol of glycolate). The reaction mixture, initially of an orange color, was left to stand in a closed Erlenmeyer flask at ambient conditions. The reaction mixture became colorless within 2 days. Tetraphenylphosphonium bromide (470 mg, 1.12 mmol) was added.

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Colorless crystals of **6** were filtered off after 1 week. Yield: 197 mg (43%). Anal. Calcd. for $C_{28}H_{25}MoO_8P$: C, 54.56; H, 4.09. Found: C, 54.61; H, 4.29.

Computational Details. DFT calculations were carried out with the aid of the Jaguar suite of programs.[18] Geometry optimizations were carried out at a 6−311+G** level using the LACV3P+ pseudopotential for Mo. Since the geometries optimized with the B3LYP functional did not match the experimental data very well, other functionals (MPW1PW91, BP86, and MPW1K) were tested as well. The best fit with the experimentally determined geometry was obtained using the MPW1K functional[19] (see the Supporting Information), which was primarily developed for the calculations involving the transition states, but has also found applications in the field of hypervalent main group compounds[20] and transition metal complexes.[21] Analytic vibrational frequencies were not scaled.

X-ray Structure Determinations. The crystals used were mounted on the tip of glass fibers with a small amount of silicon grease and transferred to a goniometer head. Data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation at 150 K. Data reduction and integration were performed with the software package DENZO-SMN.[22] Averaging of the symmetry-equivalent reflections largely compensated for the absorption effects. The coordinates of some or all of the nonhydrogen atoms were found via direct methods using the structure solution program SHELXS.[23] The positions of the remaining nonhydrogen atoms were located by use of a combination of least-squares refinement and difference Fourier maps in the SHELXL-97 program.[23] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure factor calculations at idealized positions. **1** contained interstitial solvent, acetonitrile, which was refined with 50% occupancy. The structure of **4** contains cavities which are filled with disordered solvent molecules of ethanol. Attempts to model the ethanol molecule into the solvent density did not result in an acceptable model. The contribution of the disordered solvent to the scattering factors was accounted for by the SQUEEZE program.[24] Figures depicting the structures were prepared by ORTEP3,[25] SHELXTL,[26] and CrystalMaker.[27] Cell parameters and refinement results are summarized in Table 1. Listings of relevant bond distances and angles are given in the Supporting Information.

Table 1. Crystallographic Data for **1**–**6**

	1	**2**	**3**
empirical formula	$C_{18}H_{22.5}Cl_4Mo_2N_{3.5}O_7$	$C_{20}H_{29}Br_4Mo_2N_3O_8$	$C_{24}H_{26}Mo_2N_4O_{10}$
fw	733.58	950.98	722.37
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$C2/c$
T (K)	150(2)	150(2)	150(2)
a (Å)	16.3989(2)	16.6351(2)	21.3058(4)
b (Å)	7.0547(1)	7.1047(1)	8.9699(2)
c (Å)	24.3709(4)	25.0450(3)	16.9880(3)
α (deg)	90	90	90
β (deg)	102.5585(6)	101.2174(5)	123.507(1)
γ (deg)	90	90	90
V (Å^3)	2752.00(7)	2903.46(6)	2707.06(9)
D_{calcd} (g/cm^3)	1.771	2.176	1.772
Z	4	4	4
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	1.341	6.415	0.989
collected reflns	11200	11771	5397
unique reflns, R_{int}	6253, 0.0188	6620, 0.0322	3015, 0.0212
obsd reflns	5288	5612	2691
R1[a] ($I > 2\sigma(I)$)	0.0355	0.0400	0.0293
wR2[b] (all data)	0.0961	0.1077	0.0722

	4	**5**	**6**
empirical formula	$C_{28}H_{40}Cl_4Mo_4N_4O_{16}$	$C_{24}H_{24}Mo_4N_4O_{14}$	$C_{28}H_{25}MoO_8P$
fw	1214.20	976.23	616.39
cryst syst	triclinic	monoclinic	orthorhombic
space group	P−1	$P2_1/a$	*Pbcm*
T (K)	150(2)	150(2)	150(2)
a (Å)	9.0021(2)	10.1235(4)	9.2901(1)
b (Å)	10.3807(3)	13.3136(6)	12.8418(2)
c (Å)	12.8333(4)	10.8652(4)	21.7419(3)
α (deg)	78.253(1)	90	90
β (deg)	70.527 (1)	91.640(3)	90
γ (deg)	65.034(1)	90	90
V (Å^3)	1022.22(5)	1463.8(1)	2593.84(6)
D_{calcd} (g/cm^3)	1.972	2.215	1.578
Z	1	2	4
λ (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	1.532	1.752	0.618
collected reflns	7310	4562	5635
unique reflns, R_{int}	4098, 0.0288	2641, 0.0258	3048, 0.0134
obsd reflns	3262	2255	2691
R1[a] ($I > 2\sigma(I)$)	0.0326	0.0311	0.0306
wR2[b] (all data)	0.0798	0.0747	0.0918

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Results and Discussion

Structural Studies. The structures of $(PyH)_3[Mo_2O_4Cl_4(Hglyc)]\cdot{}^1/_2CH_3CN$ (**1**) and $(PyH)_3[Mo_2O_4Br_4(Hglyc)]\cdot Pr^iOH$ (**2**) are isotypic. The anions $[Mo_2O_4X_4(Hglyc)]^{3-}$ (X = Cl^-, Br^-) (Figure 1) possess the frequently encountered dinuclear structural fragment, the doubly bridged $\{Mo^V_2O_4\}^{2+}$ core with a direct metal−metal bonding interaction and with a well-defined geometry.[28,29]

Its main structural features are (i) a separation of 2.5885(4) Å in **1** and 2.5804(5) Å in **2** between a pair of molybdenum atoms, consistent with a single metal−metal bond, and (ii) a nonplanar $Mo(\mu_2\text{-}O)_2Mo$ bridging unit. The puckering of the $Mo(\mu_2\text{-}O)_2Mo$ unit is presumably a means of allowing a close approach of the metal atoms.[30] The six coordination sites of the $\{Mo_2O_4\}^{2+}$ core, three per each metal center, are occupied with four halides and glycolato ligand $Hglyc^-$ with a preserved hydroxylic group. The $Hglyc^-$ ion is coordinated through the carboxylate function in a bidentate bridging manner. Its presence has a distorting influence over geometry of the $Mo(\mu_2\text{-}O)_2Mo$ rhombus which flattens out by approximately 10°, as shown by the comparison with $\{Mo_2O_4\}^{2+}$ species without a third bridging ligand.[31] Large

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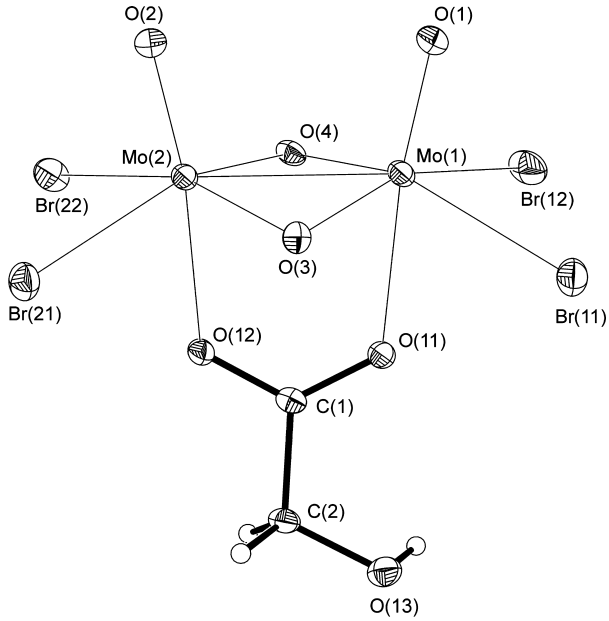


Figure 1. Drawing of $[Mo_2O_4Br_4(Hglyc)]^{3-}$, the anionic part of **2**. Atoms are represented by displacement ellipsoids at the 30% probability level. Hydrogen atoms are shown as spheres of arbitrary radii. Analogous labeling scheme pertains to **1**.

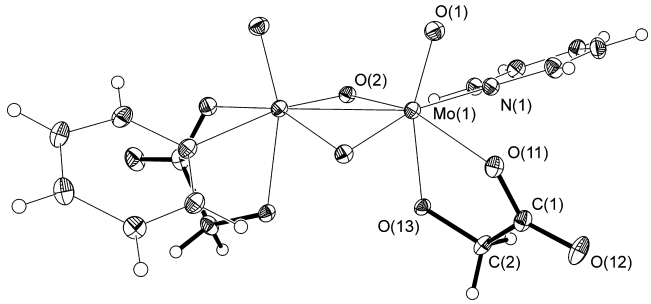


Figure 2. Drawing of $[Mo_2O_4(glyc)_2Py_2]^{2-}$, the anionic part of **3**. Atoms are represented by displacement ellipsoids at the 30% probability level.

deviations from the ideal octahedral geometry have their origin in the strong, multiple bond between molybdenum and the terminal oxide.[16] The ligand in its trans position, a carboxylate oxygen in **1** and **2**, is subject to its labilizing influence. As a consequence, the molybdenum-to-glycolate bond distances are rather long.

The crystal structure of $(PyH)_2[Mo_2O_4(glyc)_2Py_2]$ (**3**) consists of $[Mo_2O_4(glyc)_2Py_2]^{2-}$ anions (depicted in Figure 2) and protonated pyridine molecules as countercations.

Only one half of the anion belongs to the asymmetric unit; the other half is generated by a crystallographic 2-fold rotation axis, which passes along the Mo=O vectors through the center of the Mo(μ_2-O)$_2$Mo rhombus. The geometric parameters of the $\{Mo_2O_4\}^{2+}$ core are unexceptional.[32] A distorted octahedral environment of each molybdenum atom is completed with a pyridine ligand and a fully deprotonated glycolato ligand, $glyc^{2-}$. Glycolate is coordinated in a bidentate chelating manner through a carboxylate oxygen

(32) The shorter metal−metal bond length in **3** (2.5593(4) Å) as compared to **1** and **2** is due to the presence of pyridine ligands whose nature is electron-donating. As a rule, longer metal−metal bonds occur in complexes with the electron-withdrawing ligands such as chlorides and bromides.

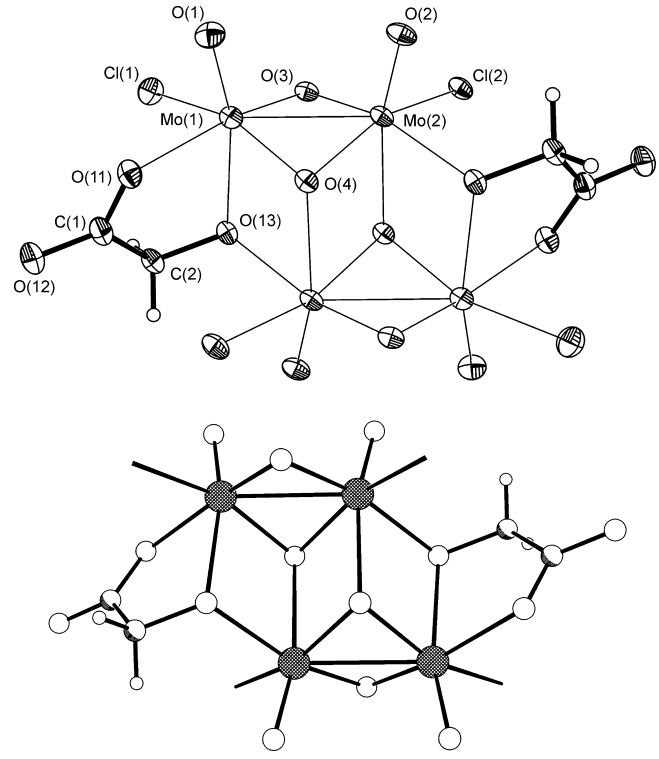


Figure 3. Drawings of $[Mo_4O_8Cl_4(glyc)_2]^{4-}$, the anionic part of **4** (top), and a tetranuclear core common to both **4** and **5** (down). Atoms are represented by displacement ellipsoids at the 30% probability level.

O(11) and an alkoxyl oxygen O(13) with two distinct bond distances, 2.092(2) vs. 2.183(2) Å, and with the formation of a five-membered chelate ring. The angle subtended at the metal by the bidentate glycolate is 73.15(7)°. This value compares well with the bite angles of the structurally similar ligand, the oxalate ion.[33] Compound **3** has a structural analogue of a very similar composition, i.e., the oxalato complex $(PyH)_2[Mo_2O_4(C_2O_4)_2Py_2]$ (see the Supporting Information).[34]

The anionic part of $(PyH)_4[Mo_4O_8Cl_4(glyc)_2]\cdot 2EtOH$ (**4**) and the neutral molecule $[Mo_4O_8(glyc)_2Py_4]$ (**5**) have a common structural feature: a tetranuclear core $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(glyc)_2\}$, which may be regarded as a compact assembly of two $\{Mo_2O_4\}^{2+}$ units assisted by two doubly ionized glycolates (Figure 3 and the Supporting Information, Figure S2).[35] The tetranuclear core is centrosymmetric with the center of symmetry located at the midpoint of the vector connecting the triply bridging oxide O(4) and its symmetry-related counterpart. There are four sites on the periphery of the core which serve as anchor points of additional ligands. These sites are occupied with chlorides in **4** and with pyridine ligands in **5**.

(33) Bernalte, A.; Barros, F. J. G.; Cavaco, I.; Costa Pessoa, J.; Gillard, R. D.; Higes, F. J.; Tomaz, I. *Polyhedron* **1998**, *17*, 3269–3274.

(34) Modec, B.; Dolenc, D.; Brenčič, J. V.; Koller, J.; Zubieta, J. *Eur. J. Inorg. Chem.* **2005**, 3224–3237.

(35) The $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(glyc)_2\}$ core of **4** and **5** is a structural analogue of the alkoxide-containing $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OR)_2\}^{2+}$ (R = Me, Et) core, in which a monodentate alkoxide serves a role of the alkoxyl oxygen in **4** and **5** (see refs 28 and 29). The rhomboid arrangement of metal atoms in **4**, **5**, and the alkoxide tetranuclear clusters is a motif often found in various contexts of molybdenum(V) coordination chemistry.

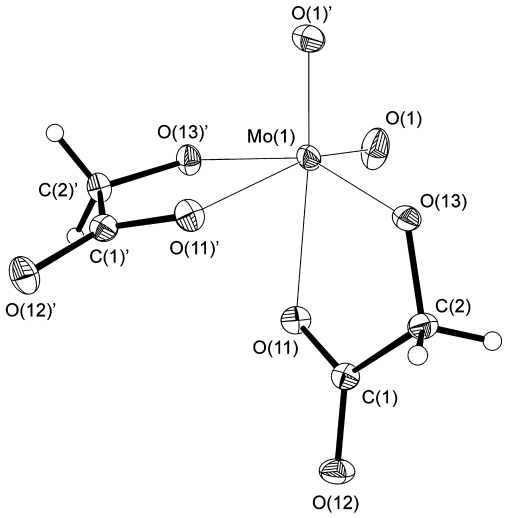


Figure 4. View of a mononuclear anion in **6** with displacement ellipsoids drawn at the 30% probability level. Primed and unprimed atoms are related by a C_2 axis.

The tetranuclear species of **4** thus carries a negative charge of 4−, whereas compound **5** is neutral. The glycolates are bonded through two oxygens, one belongs to the monodentate carboxylate and another to the deprotonated alcoholic group. The latter donor behaves as a monatomic bridge and binds to two metal atoms. The Mo−O(carboxylate) bond lengths are 2.117(3) (complex **4**) and 2.046(3) Å (**5**), whereas the corresponding Mo−O(alkoxyl) bonds are longer, 2.115(2) and 2.245(3) Å for **4** and 2.097(3) and 2.183(3) Å for **5**. The molybdenum-to-glycolate bonds in **4** are on the whole longer than in **5**. The lengthening may be attributed to the anionic nature of the tetranuclear species of **4**.

The crystal structure of $\{(C_6H_5)_4P\}[MoO_2(glyc)(Hglyc)]$ (**6**) contains formally mononuclear anions (Figure 4). With molybdenum atom residing on a 2-fold rotation axis in the *Pbcm* space group, the $[MoO_2(glyc)(Hglyc)]^-$ ion possesses C_2 point group symmetry.

A highly distorted octahedral environment of molybdenum atom consists of two oxido ligands at 1.703(2) Å in the conventional cis disposition and two glycolates coordinated through O(13) of the deprotonated hydroxyl group and O(11) of the carboxylate group. The molybdenum-to-glycolate bond distances, as a result of an operating trans influence, are distinctly different: the Mo−O(11) bond is 2.271(1) Å, whereas the Mo−O(13) bond is 1.945(1) Å. Molybdenum is not located at the center of the coordination octahedron, but is shifted toward the multiply bonded oxido ligands. The O−Mo−O angle (105.7(1)°) within the cis-$\{MoO_2\}^{2+}$ structural unit displays the usual deviation from the nominal 90° angle.[16] To maintain charge balance, one of the two glycolates is protonated. Although the protonation site could not be located from the electron density map, a very short contact with the length of 2.446(3) Å between O(12), a nonbonded carboxylate oxygen, and its symmetry equivalent from a neighboring anion, related through $1 - x, -y, 1 - z$, strongly suggests its position in-between these two oxygen

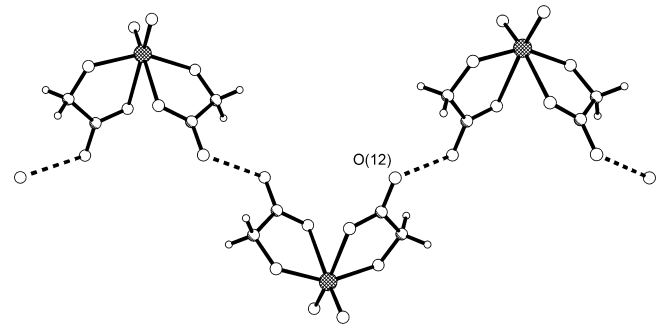


Figure 5. Section of the $[MoO_2(glyc)(Hglyc)]_n^{n-}$ chain found in **6**.

atoms.[36] A strong intermolecular hydrogen bond is substantiated by the absence of characteristic bands for nonionized COOH group between 1740 and 1700 cm^{-1} in the infrared spectrum of **6**.[37] It is to be noted that no conclusion about the location of proton can be drawn from the carboxylate C−O bonds which are of almost the same length (Table S4). As such, they speak more of delocalized bond characters than a localized single or double bond. In view of the previously demonstrated capacity of molybdenum(VI) to promote the proton release from hydroxylic groups,[38] a complete deprotonation of the hydroxyl group rather than the more acidic carboxylic entity does not appear unusual. The above-described hydrogen bonds connect the formally mononuclear anions into infinite chains (Figure 5), which run along the crystallographic *b* axis.

Their conformation is sinusoidal with a period corresponding to the length of the *b* lattice constant. The chains may be alternatively viewed as an alternating array of cis-$\{MoO_2\}^{2+}$ moieties and $glyc_2H^{3-}$ groupings, with the latter consisting of two glycolates linked by a proton.

Infrared Spectroscopy. A full list of IR peaks and assignments for all compounds studied is contained in the Supporting Information. The assignments are based on the reported values for compounds with terminal molybdenum−oxygen double bonds,[39] carboxylato,[40,41] or α-hydroxycarboxylato complexes.[8,37,42,43]

(36) The sum of the corresponding van der Waals radii is significantly longer, 3.04 Å. Data were taken from: Douglas, B.; McDaniel, D.; Alexander, J. *Concepts and Models of Inorganic Chemistry*, 3rd ed.; John Wiley and Sons: New York, 1994; p 102.
(37) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1964; pp 257–262 and 273–274.
(38) (a) Schröder, F. A.; Scherle, J.; Hazell, R. G. *Acta Crystallogr., Sect. B* **1975**, *31*, 531–536. (b) Knobler, C.; Penfold, B. R.; Robinson, W. T.; Wilkins, C. J.; Yong, S. H. *J. Chem. Soc., Dalton Trans.* **1980**, 248–252. (c) Litos, C.; Terzis, A.; Raptopoulou, C.; Rontoyianni, A.; Karaliota, A. *Polyhedron* **2006**, *25*, 1337–1347.
(39) (a) Young, C. G. In. *Comprehensive Coordination Chemistry II*; McCleverty, J. A.; Meyer, T. J., Eds.; Elsevier Pergamon: Amsterdam, 2004; Vol. *4*, Chapter 4.7, pp 415–527. (b) Doonan, C. J.; Millar, A. J.; Nielsen, D. J.; Young, C. G. *Inorg. Chem.* **2005**, *44*, 4506–4514.
(40) Nakamoto, K. *Infrared and Raman spectra of Inorganic and Coordination Compounds. Part B: Applications in Coordination, Organometallic and Bioinorganic Chemistry*, 5th ed.; John Wiley and Sons: New York, 1997.
(41) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227–250.
(42) Cotton, F. A.; Barnard, T. S.; Daniels, L. M.; Murillo, C. A. *Inorg. Chem. Commun.* **2002**, *5*, 527–532.
(43) Biagioli, M.; Strinna-Erre, L.; Micera, G.; Panzanelli, A.; Zema, M. *Inorg. Chim. Acta* **2000**, *310*, 1–9.

Table 2. Mo(VI)−L Bond Lengths (Å) in $[Mo^{VI}O_2L_2]^{2-}$ Ions[a]

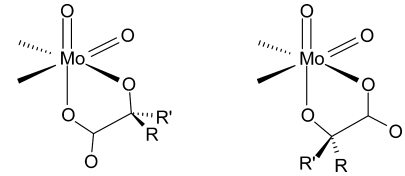
L	Mo−O(alkoxyl)	Mo−O(carboxylate)	ref
glycolate in **6**[b]	1.945(1)	2.271(1)	this work
glycolate	1.929(3), 1.953(2)	2.202(2), 2.204(2)	8
S-lactate	1.947(4), 1.969(5)	2.181(4), 2.201(5)	8
R-mandelate	1.932(3), 1.954(3)	2.187(4), 2.228(3)	12
benzilate	1.977(2)	2.166(3)	13
S-malate	1.939(8)	2.243(9)	10
R,R-tartrate	1.921(9), 1.941(10)	2.226(8), 2.227(9)	11
citrate	1.953(6), 1.960(7)	2.190(7), 2.247(6)	14

[a] L = α-Hydroxycarboxylate. [b] The glycolate ions in **6** are partially protonated.

Synthetic Considerations. As far as the synthetic procedures are concerned, there are two points of interest. The title complexes were prepared from the molybdenum(V) starting materials. The oxidation to molybdenum(VI) took place in one instance. Neither the content of the reaction mixture nor the reaction conditions reveal an obvious reason for that. Previous work suggests that the formation of $\{Mo_2O_4\}^{2+}$ species from $[Mo^{V}OCl_4(H_2O)]^-$ or $[Mo^{V}OBr_4]_n^{n-}$ is almost instantaneous.[29] In view of the relatively good stability of the $\{Mo_2O_4\}^{2+}$-containing species, the oxidation is rather surprising. Second, with the preparations of **1** and **2** excepted, a deprotonation of the carboxylic group of glycolic acid was accompanied by the release of proton from the hydroxyl group. The extent of ionization of glycolic acid depends primarily on the basicity of the reaction mixture. The complexes **1** and **2** with singly ionized $Hglyc^-$ ions were isolated from the relatively acidic solutions containing pyridinium or triethylammonium glycolate. Under these conditions, dinuclear $\{Mo_2O_4\}^{2+}$ species with a high halide content are formed. Such species favor the coordination to a pair of sites which lie opposite the Mo═O bonds. As demonstrated in our previous work,[31] the carboxylate is a perfect ligand for binding to these two sites in a bidentate bridging manner. On the other hand, complexes **3** and **5** with doubly ionized $glyc^{2-}$ ions were formed when the reaction mixtures contained an excess of pyridine. The syntheses of **4** and **6**, despite the absence of free pyridine, also yielded products containing the $glyc^{2-}$ ions. The likely explanation in the latter case is that the oxidation with atmospheric oxygen is coupled with the increased basicity of the medium, whereas the formation of **4** remains unclear. It is to be noted that the presence of $glyc^{2-}$ ions in reaction mixtures directs the substitution and aggregation reactions toward the formation of molybdenum species which allow a bidentate chelating coordination of $glyc^{2-}$ ions.

Comments on the Glycolate Ligation. As will be shown presently, the coordination demands of Mo(VI) and Mo(V) differ and only certain types of bonding seem to be preferred within each class. The glycolato ligands in $[MoO_2(glyc)(Hglyc)]^-$ (**6**) are bonded in a chelating manner. This type of coordination is employed by all α-hydroxycarboxylates L in the $[Mo^{VI}O_2L_2]^{2-}$ series.[8−14] The rather unusual feature of **6** is only partial deprotonation of the more acidic carboxylic group. The literature reports on a complex of an almost the same composition, $[MoO_2(glyc)_2]^{2-}$, where both glycolates are fully deprotonated.[8] The bond lengths within the $[Mo^{VI}O_2L_2]^{2-}$ series, shown in Table 2, are within a narrow interval and practically independent of ligand L. The Mo−O(carboxylate) bonds (2.166(3)–2.271(1) Å) are significantly longer than the Mo−O(alkoxyl) bonds (1.921(9)–1.977(2) Å). The arrangement of glycolate ions in **6** within the metal's coordination sphere relative to the Mo═O bonds merits further comment. Herein after, a coordination site that is trans (or cis) with respect to the multiply bonded oxide will be referred to as a trans (or cis) site. The ligand can be oriented in one of the two possible ways (illustrated in Scheme 2): either with a carboxylate or with an alkoxyl oxygen occupying the trans site.

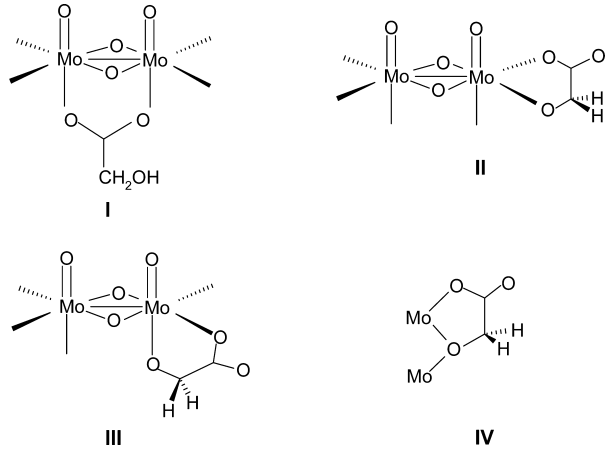
Scheme 2. Two Orientations of α-Hydroxycarboxylate in Dioxomolybdate(VI) Ion



The adopted arrangement in **6**, $[Mo^{VI}O_2L_2]^{2-}$ ions,[8−14] analogous W(VI) complexes,[14,44] and all other Mo(VI) complexes,[6,7,45,46] is the one with the carboxylate oxygen located at the trans site. The preference of this ligand's orientation over the other was ascribed to a powerful trans influence of the terminal oxido ligand which favors in its trans position ligands with the weaker π-bonding ability, the carboxylate group with a delocalized four-electron π-system being such a ligand.[47] On the other hand, the stronger π-bonding ligands, i.e. the alkoxyl groups, arrange cis to the multiply bonded oxides and trans to one another. The alkoxyl oxygen is also capable of stronger bonding because it provides a more concentrated anionic charge.[9] The only instance with the alkoxyl oxygen located at the trans site, proved by the X-ray structure analysis, is a mononuclear $[MoO_3(cit)]^{4-}$ ion with three terminal oxides and a citrato ligand coordinated in a tridentate manner.[46,48]

(44) Zhou, Z.-H.; Wang, G.-F.; Hou, S.-Y.; Wan, H.-L.; Tsai, K.-R. *Inorg. Chem. Acta* **2001**, *314*, 184–188.
(45) (a) Zhou, Z.-H.; Hou, S.-Y.; Wan, H.-L. *Dalton Trans.* **2004**, 1393–1399. (b) Bayot, D.; Tinant, B.; Devillers, M. *Inorg. Chim. Acta* **2004**, *357*, 809–816.
(46) Zhou, Z.-H.; Wan, H.-L.; Tsai, K.-R. *Inorg. Chem.* **2000**, *39*, 59–64.
(47) Freeman, M. A.; Schultz, F. A.; Reilley, C. N. *Inorg. Chem.* **1982**, *21*, 567–576.
(48) Binding with the alkoxyl oxygen to trans site was proposed also for dianion of D-(−)quinic acid in its dioxomolybdate(VI) or dioxotungstate(VI) complexes. The existence of both isomers of $[M^{VI}O_2L_2]^{2-}$ was assumed in order to provide a plausible explanation of the solution NMR spectra. Nevertheless, the X-ray structure analysis of a potassium salt of dioxotungstate(VI) which crystallized from such a solution revealed the usual disposition of ligands, i.e., the one with the carboxylate oxygen atoms occupying the trans sites. See: Ramos, M. L.; Pereira, M. M.; Beja, A. M.; Silva, M. R.; Paixao, J. A.; Gil, V. M. S. *J. Chem. Soc., Dalton Trans.* **2002**, 2126–2131.
(49) (a) Xu, J.-Q.; Zhou, X.-H.; Zhou, L.-M.; Wang, T.-G.; Huang, X.-Y.; Averill, B. A. *Inorg. Chim. Acta* **1999**, *285*, 152–154. (b) Li, D.-M.; Xing, Y.-H.; Li, Z.-C.; Xu, J.-Q.; Song, W.-B.; Wang, T.-G.; Yang, G.-D.; Hu, N.-H.; Jia, H.-Q.; Zhang, H.-M. *J. Inorg. Biochem.* **2005**, *99*, 1602–1610. (c) Xing, Y.-H.; Xu, H.-Q.; Sun, H.-R.; Li, D.-M.; Xing, Y.; Lin, Y.-H.; Jia, H.-Q. *Eur. J. Solid State Inorg. Chem.* **1998**, *35*, 745–756. (d) Zhou, Z.-H.; Deng, Y.-F.; Cao, Z.-X.; Zhang, R.-H.; Chow, Y.-L. *Inorg. Chem.* **2005**, *44*, 6912–6914.

Scheme 3. Coordination of Hglyc$^-$ (**I**) and glyc^{2-} (**II–IV**) in $\{Mo_2O_4\}^{2+}$ Species; See Text for Detailed Descriptions



The α-hydroxycarboxylato complexes of Mo(V) are very rare: there is only one structurally characterized complex with glycolate[8] and a few with citrate.[49] The binding modes observed in complexes **1–5** and in the only other known glycolato complex, $[Mo_8O_{16}(glyc)_6(Hglyc)_2]^{6-}$, are illustrated in Scheme 3. The cluster ion $[Mo_8O_{16}(glyc)_6(Hglyc)_2]^{6-}$ possesses both types of glycolato ligands, engaged in several different binding roles.[8] A detailed structure analysis of the octanuclear ion reveals a striking resemblance to **4** and **5**, which becomes apparent upon recognizing a central tetranuclear core $\{Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(glyc)_2\}$ that is identical to that in **4** and **5**. Although the Hglyc$^-$ ion is known to engage in binding the hydroxyl group,[50] it does not do so in the present case. Instead, it coordinates to the $\{Mo_2O_4\}^{2+}$ moiety through the carboxylate end in a bidentate bridging manner, depicted as **I** in Scheme 3. Conversely, a fully deprotonated glyc^{2-} ion engages in its coordination to the $\{Mo_2O_4\}^{2+}$ moiety both functional groups. It binds through the alkoxyl and one of the two carboxylate oxygen atoms to either one metal atom, i.e., chelating binding modes **II** and **III**, or to two metal atoms which belong to different $\{Mo_2O_4\}^{2+}$ units, i.e., a bridging binding mode **IV**. When the glyc^{2-} ion acts as a bridging ligand, it is the alkoxyl oxygen which serves as a bridge, whereas the carboxylate oxygen binds in a terminal manner. In coordination type **II**, the glycolate occupies a pair of cis sites relative to the multiply bonded oxide, whereas in **III**, a cis and a trans site. In the latter case, there are in principle two options: the glycolate could attach to the trans site either with its carboxylate or alkoxyl oxygen atom. Surprisingly, in complex **3**, as the only example of coordination type **III**, the glycolate is oriented in such a way that the trans site is occupied with the alkoxyl oxygen. Interestingly, even with glyc^{2-} adopting a bridging role as in **4** and **5**, its orientation is such that the alkoxyl and not the carboxylate oxygen occupies the trans site (see Figure 3). The disposition of glycolate with respect to the multiply bonded oxide influences the bonding pattern in an anticipated manner (Table 3): the Mo−O(alkoxyl) bond lengths (2.089(5)–2.245(3) Å) are on the whole longer than the corresponding Mo−O(carboxylate) bond lengths (2.046(3)–2.117(3) Å). Exceptions are the glyc^{2-} ligands in $[Mo_8O_{16}(glyc)_6(Hglyc)_2]^{6-}$ which are engaged in a type **II** coordination with neither the alkoxyl nor the carboxylate oxygen atom subject to the trans influence of the Mo=O entity. As such, they provide a reference of what bond lengths are in the absence of the trans influence. The emerging bonding pattern for $\{Mo^V_2O_4\}^{2+}$-containing complexes is the reverse of the situation observed for Mo(VI) complexes. The explanation of the preferential orientation of α-hydroxycarboxylato ligands based solely on the trans influence[47] appears to have no validity for $\{Mo^V_2O_4\}^{2+}$ complexes. The inspection of the $\{Mo^V_2O_2(\mu_2\text{-}S)_2\}^{2+}$- and $\{Mo^V_2O_4\}^{2+}$-containing complexes with citrate reveals an even more intricate picture.[49] Contrary to the expectations, a random distribution of α-carboxylate, β-carboxylate and alcoholate oxygen atoms over a trans and two cis sites is displayed. With the citrate possessing a carboxylate group on each β-carbon atom in addition to the basic C(O)-COO structural fragment, and therefore being capable of binding in several other ways, the citrato complexes might not be the best choice for comparison. The particularly favorable type of coordination in dinuclear $\{Mo_2O_2(\mu_2\text{-}S)_2\}^{2+}$ and $\{Mo_2O_4\}^{2+}$ species is a tridentate chelating one that counterweighs any destabilization caused by the supposedly less stable binding to the trans site.

To assess the relative stabilities of binding of glycolate to the trans site with each of its functional groups, we carried out DFT calculations on the $[Mo^{VI}O_2(glyc)_2]^{2-}$ and $[Mo^V_2O_4(glyc)_2Py_2]^{2-}$ ions. Geometry optimization for the isomer of the $[Mo^{VI}O_2(glyc)_2]^{2-}$ ion with the carboxylate oxygen atoms bonded to trans sites, abbreviated as **6c**, was done using the data from the crystal structure of **6** as a starting point. The trial geometry of **6a**, the isomer with the alkoxyl oxygen atoms located at trans sites, was derived by reversing the orientation of glycolate ions in **6** (see Figure 6). The calculations confirmed the **6c** species to be more favored by 46.3 kJ/mol. The optimized bond lengths for **6c**, shown in Table 4, agree fairly well with the X-ray data. The bonding pattern in the model **6a** species follows the anticipated trend: with a reversed orientation of glycolate, the Mo−O(alkoxyl) bonds lengthen, whereas the Mo−O(carboxylate) bonds shorten. The calculations on molybdenum(V) complexes, i.e., isomers of the $[Mo^V_2O_4(glyc)_2Py_2]^{2-}$ ion with the alkoxyl (**3a**) or the carboxylate (**3c**) oxygen atoms bonded to trans sites, reveal the **3a** isomer to be more stable by 21.3 kJ/mol.[51] The calculated molybdenum-to-glycolate bond lengths in **3a** show deviations from the experimental X-ray data. Intriguingly, the corresponding bonds in the model **3c** species are almost the same. An orbital

(50) Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153.

(51) Geometry optimization for the **3a** isomer was done using the data from the crystal structure of **3** as a starting point. The trial geometry of **3c** was derived by reversing the orientation of glycolato ligands in **3**.

Table 3. Mo(V)−Glycolate Bond Lengths (Å)

compd	ligand	type of coordination[a]	Mo−O(alkoxyl)	Mo−O(carboxylate)
1	$Hglyc^-$	I		2.307(2), 2.389(2)
2	$Hglyc^-$	I		2.314(3), 2.373(3)
3	$glyc^{2-}$	III	2.183(2)	2.092(2)
4	$glyc^{2-}$	IV	2.115(2), 2.245(3)	2.117(3)
5	$glyc^{2-}$	IV	2.097(3), 2.183(3)	2.046(3)
$K_6[Mo_8O_{16}(glyc)_6(Hglyc)_2]$[b]	$Hglyc^-$	I		2.298(5), 2.318(6)
	$glyc^{2-}$	II	1.984(7)	2.075(6)
	$glyc^{2-}$	IV	2.089(5), 2.130(5)	2.061(5)

[a] Same labels as in Scheme 3. See text for detailed discussion. [b] Bond lengths are taken from ref 8.

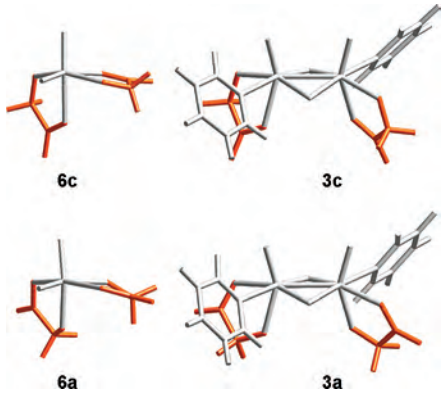


Figure 6. DFT-optimized geometries for $[Mo^{VI}O_2(glyc)_2]^{2-}$ and $[Mo^{V}_2O_4(glyc)_2Py_2]^{2-}$ ions. Glycolate's function bound to the trans site is indicated by the letter in the label, c for carboxylate and a for alkoxyl.

Table 4. Relevant Structural Parameters (Å, deg) in the Experimental and Computed Energy Minima

$[Mo^{VI}O_2(glyc)_2]^{2-}$	exp.[a]	6c	6a
Mo═O	1.703(2)	1.716	1.718
O═Mo═O	105.7(1)	103.2	102.6
Mo−O(carboxylate)	2.271(1)	2.257	2.124
Mo−O(alkoxyl)	1.945(1)	1.971	2.072
$[Mo^{V}_2O_4(glyc)_2Py_2]^{2-}$	exp.[b]	3a	3c
Mo═O	1.694(2)	1.710	1.701
Mo−Mo	2.5593(4)	2.549	2.568
Mo−O(μ_2)	1.930(2), 1.944(2)	1.930, 1.958	1.916, 1.972
Mo−O(carboxylate)	2.092(2)	2.163	2.176
Mo−O(alkoxyl)	2.183(2)	2.043	2.053

[a] X-ray data for **6**. [b] X-ray data for **3**.

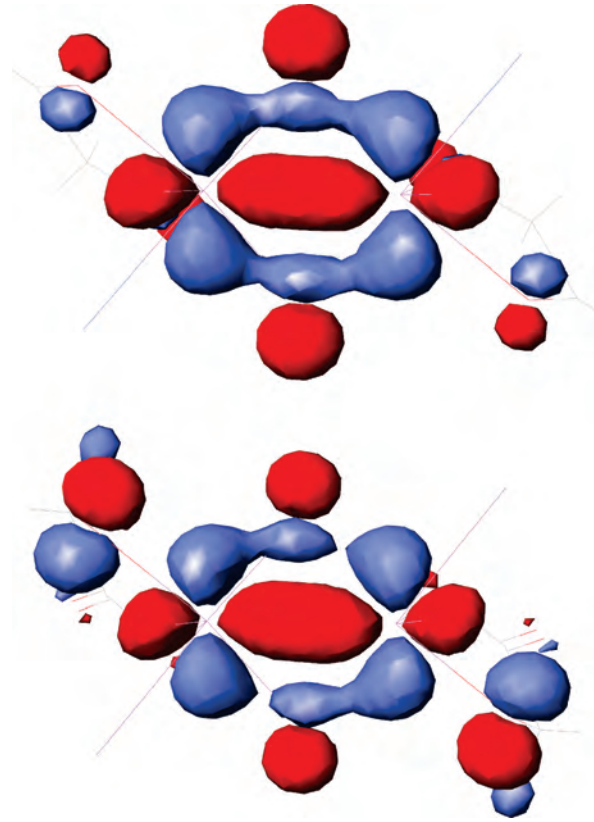


Figure 7. HOMO orbitals of **3a** (top) and **3c** (down). A view along the *z* axis.

analysis of bonding in **3a** and **3c** reveals an antibonding interaction of a lone electron pair of the glycolate's oxygen atom with the Mo d_{xy} part of the HOMO of the complex anion (Figure 7). This interaction is particularly strong when the alkoxyl oxygen occupies the equatorial (cis) position (**3c**). When the carboxylate is located at this position (**3a**), the interaction is weaker because the oxygen lone pairs are attracted by the carbonyl group and thereby delocalized away from the Mo−O bond. Consequently, the coordination of the alkoxyl oxygen to cis site is not favored and the **3a** species, the one with the carboxylate oxygen atom occupying this site, is more stable. The orientation of glycolate in the $[Mo^{VI}O_2(glyc)_2]^{2-}$ ion or α-hydroxycarboxylates in Mo(VI) complexes in general is governed exclusively by the trans influence of the Mo═O bond.[47] In $\{Mo^{V}_2O_4\}^{2+}$ species, where the trans influence is also present, the above-described destabilizing interaction prevails.

Concluding Remarks

Facile substitution chemistry of $[Mo^{V}OCl_4(H_2O)]^-$ and $[Mo^{V}OBr_4]_n^{n-}$ has afforded a series of novel glycolato molybdenum(V) species, important additions to the rare α-hydroxycarboxylato molybdenum(V) complexes. A complete deprotonation of glycolic acid is invariably coupled with a chelating binding of the $glyc^{2-}$ ion to molybdenum through a deprotonated hydroxyl group and a monodentate carboxylate. Molybdenum(V) complexes addressed in this work feature a reversed orientation of α-hydroxycarboxylate with respect to the multiply bonded oxide as compared to that observed in Mo(VI) complexes. Theoretical DFT investigations on $[Mo^{V}_2O_4(glyc)_2Py_2]^{2-}$ and $[Mo^{VI}O_2(glyc)_2]^{2-}$ ions in the gas phase yielded conformations whose symmetries proved consistent with the X-ray results. Studies to discern the generality of our observations to other α-hydroxycarboxylates are under way.

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Supporting Information Available: X-ray crystallographic data in standard CIF format for compounds **1**–**6**; tables of bond lengths and angles for **1**–**6**; drawings of analogous $[Mo_2O_4(glyc)_2Py_2]^{2-}$ and $[Mo_2O_4(C_2O_4)_2Py_2]^{2-}$ complexes (Figure S1) and an ORTEP drawing of **5** (Figure S2); complete listings of IR data for **1**–**6** and assignations; thermochemical data for **3a**, **3c**, **6a**, and **6c** with the calculated coordinates (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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