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Article

Polyoxomolybdates Functionalized with Phosphonocarboxylates[†]

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The novel, functionalized heteropolymolybdate $[(O_2CCH_2PO_3)_2Mo_5O_{15}]^{6-}$ (**1**) has been synthesized and characterized by IR and ^{31}P NMR spectroscopy and elemental analysis. Single-crystal X-ray analysis was carried out on $Rb_4KNa[(O_2CCH_2PO_3)_2Mo_5O_{15}]\cdot H_2O$, which crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 10.146(2)$ Å, $b = 13.704(3)$ Å, $c = 20.577(4)$ Å, $\beta = 94.88(3)°$, and $Z = 4$. The title polyanion consists of a ring of five MoO_6 octahedra with four edge junctions and one corner junction. This nonplanar arrangement is stabilized by two phosphonocarboxylate groups that are bound via their phosphonate functionalities on opposite sides of the ring. As a result the two dangling arms with their terminal carboxylate groups protrude away from the molybdenum–oxo framework in diametrically opposed directions. The solid-state structure of **1** is preserved in solution on the basis of NMR. We also report on the synthesis and characterization of the isostructural derivative $[(O_2CC_2H_4PO_3)_2Mo_5O_{15}]^{6-}$ (**2**).

Introduction

Polyoxoanions are a unique class of metal−oxygen clusters with a multitude of structures and many properties that are of interest in different fields including catalysis, medicine, and materials science.[1−5] Although the first polyoxometalates were reported almost two centuries ago, the majority of species have been structurally characterized fairly recently. Many novel polyoxoanions have completely unexpected shapes and sizes, but some consist of subunits or fragments of known species. The mechanism of formation of polyoxoanions is still not well understood and mostly described as self-assembly. Therefore, rational synthesis of novel polyoxoanion architectures is a major challenge. Nevertheless, during the recent past some very large polyoxoanions have been isolated.[6−9]

During the last two decades it has been well established that the dimensions and charge density of many polyoxoan-

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ions are appropriate for pharmaceutical applications. However, a general problem of many polyoxoanions has been the lack in selectivity toward the biological target. Often it seems desirable to just modify the surface properties of a polyoxoanion structure slightly, but most of the time this is impossible. Frequently such attempts result in the discovery of a novel polyoxoanion framework. Therefore, it is highly desirable to discover a family of polyoxoanions that can be surface-modified in a controlled fashion. It seems that attachment of organic groups to the surface of polyoxoanions is the most elegant route.

Different synthetic approaches have been used to incorporate organic or organometallic moieties in polyoxoanion frameworks.[10] Interaction of carboxylate-containing, organic compounds with polyoxoanions has led to a number of products, but with an emphasis on polyoxovanadates.[11] The reactivity of amino acids with polyoxovanadates has also been investigated as a model study for polyoxometalate–protein interactions.[12] Only very few examples of structurally characterized polyoxoanions with covalently bound amino acids are known.[13] Very recently Kortz et al. reported on a family of 18 lone-pair-containing heteropolymolybdates functionalized by five different amino acids including chiral ones.[14]

In 1975 Kwak et al. reported on the heteropolymolybdate family $[(RP)_2Mo_5O_{21}]^{4-}$ (R = H, CH_3, C_2H_5, C_6H_5, $C_2H_4NH_3^+$, p-$CH_2C_6H_4NH_3^+$).[15] In the following year Stalick and Quicksall determined the structures of the derivatives with R = CH_3 and $C_2H_4NH_3^+$.[16] They were shown to be isostructural with the pentamolybdophosphate ions $[P_2Mo_5O_{23}]^{6-}$, $[HP_2Mo_5O_{23}]^{5-}$, and $[H_2P_2Mo_5O_{23}]^{4-}$.[17] Pettersson et al. studied the speciation properties of the molybdophosphate and molybdophenylphosphonate systems in solution.[18] Then the structures of the phosphite derivative $[H_2P_2Mo_5O_{21}]^{4-}$ and the phenylphosphonate derivative $[(C_6H_5P)_2Mo_5O_{21}]^{4-}$ were determined by Ozeki et al. and Lyxell and Strandberg, respectively.[19,20] Recently Lyxell et al. isolated $[H(HP)PMo_5O_{22}]^{4-}$, which represents the first example of the pentamolybdate type containing two different heterogroups (phosphate and phosphite).[21]

We have been interested in the synthesis of functionalized polyoxoanions for some time, with an emphasis on medicinal applications. Our work on diphosphate and diphosphonate complexes of polyoxotungstates and polyoxomolybdates resulted in a number of interesting architectures.[22] One of these structural types exhibited very promising antiviral properties, but there was a lack of selectivity.[23] We were not able to modify the electrostatic and/or steric surface properties of this polyanion. Therefore, we decided to undergo a search for novel polyoxoanions with tightly bound organic groups that are accessible for additional modification of the heteropoly surface (drug design).[14]

Here we report on the first examples of polyoxomolybdates functionalized with phosphonocarboxylates.

Experimental Section

Synthesis. All reagents were used as purchased without further purification.

$Rb_4KNa[(O_2CCH_2PO_3)_2Mo_5O_{15}]\cdot H_2O$. A 0.14 g (1 mmol) sample of phosphonoacetic acid ($H_2O_3PCH_2COOH$) was added to 30 mL of H_2O with stirring. Then 0.605 g (2.5 mmol) of $Na_2MoO_4\cdot 2H_2O$ was added followed by addition of 0.224 g (3 mmol) of KCl. The pH of the clear and colorless solution was adjusted to 3 by addition of 12 M HCl. Then the solution was refluxed for 1 h, and after about 20 min a color change to blue was observed. The solution was cooled to room temperature, and 2 g of RbCl was added with stirring. Then the solution was filtered and placed in a closed container with ethanol. After about 2 weeks small, colorless crystals were formed (0.29 g, yield 41%). It is also possible to isolate an amorphous product in almost quantitative yield by addition of 30 mL of ethanol to the above solution, resulting in immediate precipitation of the product. The identity of both products was demonstrated by IR and NMR. IR for $Rb_4KNa[(O_2CCH_2PO_3)_2Mo_5O_{15}]\cdot H_2O$: 1717(s), 1636(m), 1390(w), 1274(m), 1240(m), 1213(m), 1159(s), 1136(s), 1113(s), 1049(s), 1025(m), 983(s), 928(vs), 907(vs), 807(w), 683(vs), 614(w), 596(w), 537(m), 504(w), 491(w), 415(w), 377(w), 351(w), 321(w) cm^{-1}. Anal. Calcd (Found) for $Rb_4KNa[(O_2CCH_2PO_3)_2Mo_5O_{15}]\cdot H_2O$: P, 4.4 (4.6); Mo, 33.9

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(34.3); C, 3.4 (3.7); H, 0.4 (0.3); Rb, 24.2 (24.3); K, 2.8 (2.7); Na, 1.6 (1.7). ^{31}P NMR (D_2O, 293 K): [$[(O_2CCH_2PO_3)_2Mo_5O_{15}]^{6-}$ at pH 3] δ 22.0 ppm (triplet, 2P), $^2J_{PH} = 22$ Hz; [phosphonoacetic acid ($H_2O_3PCH_2COOH$) at pH 3] δ 13.6 ppm (triplet), $^2J_{PH} = 19$ Hz; (at pH 6) δ 17.3 ppm (triplet), $^2J_{PH} = 21$ Hz.

$Rb_4KNa[(O_2CC_2H_4PO_3)_2Mo_5O_{15}]$. A 0.154 g (1 mmol) sample of phosphonopropionic acid ($H_2O_3PC_2H_4COOH$) was added to 30 mL of H_2O with stirring. Then 0.605 g (2.5 mmol) of $Na_2MoO_4 \cdot 2H_2O$ was added followed by addition of 0.224 g (3 mmol) of KCl. The pH of the clear and colorless solution was adjusted to 3 by addition of 12 M HCl. Then the solution was refluxed for 1 h, and after about 20 min a color change to blue was observed. The solution was cooled to room temperature, and 1 g of RbCl was added with stirring. Then the solution was filtered and placed in a closed container with ethanol. After about 2 weeks small, colorless crystals were formed (0.1 g, yield 14%). It is also possible to isolate an amorphous product in significantly higher yield by addition of 30 mL of ethanol to the above solution, resulting in immediate precipitation of the product. The identity of both products was demonstrated by IR and NMR. IR for $Rb_4KNa[(O_2CC_2H_4PO_3)_2Mo_5O_{15}]$: 1609(s), 1546(m), 1498(m), 1451(m), 1416(s), 1347(m), 1327(m), 1220(w), 1151(w), 1110(w), 1061(s), 1050(s), 993(s), 931(vs), 899(vs), 875(vs), 789(m), 776(m), 676(vs), 535(m), 444(w), 377(w), 338(w) cm^{-1}. Anal. Calcd (Found) for $Rb_4KNa[(O_2CC_2H_4PO_3)_2Mo_5O_{15}]$: P, 4.3 (4.5); Mo, 33.6 (33.3); C, 5.1 (4.9); H, 0.6 (0.4); Rb, 24.0 (23.6); K, 2.7 (2.8); Na, 1.6 (1.9). ^{31}P NMR (D_2O, 293 K): [$[(O_2CC_2H_4PO_3)_2Mo_5O_{15}]^{6-}$ at pH 3] δ 32.6 ppm (multiplet, 2P), $J_{PH} = 9$ Hz; [phosphonopropionic acid ($H_2O_3PC_2H_4COOH$) at pH 3] δ 24.4 ppm (multiplet), $J_{PH} = 8$ Hz; (at pH 6) δ 24.9 ppm (multiplet), $J_{PH} = 9$ Hz.

Elemental analysis was performed by Kanti Labs Ltd. in Mississauga, Canada. The FTIR spectra were recorded on a Bio-Rad FTS 165 spectrophotometer using KBr pellets. ^{31}P NMR spectra were obtained on a Bruker AC300 spectrometer at 121.5 MHz using D_2O as a solvent in 5 mm tubes. Chemical shifts are reported with respect to the peak of external 85% H_3PO_4 as a standard.

X-ray Crystallography. A colorless needle of $Rb_4KNa[(O_2CCH_2PO_3)_2Mo_5O_{15}] \cdot H_2O$ with dimensions $0.12 \times 0.05 \times 0.05$ mm^3 was mounted on a glass fiber for indexing and intensity data collection at 123 K on a Nonius Kappa CCD single-crystal diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). Of the 4783 unique reflections ($R_{int} = 0.057$, $2\theta_{max} = 49.42°$), 4095 reflections were considered observed ($I > 2\sigma(I)$). Direct methods were used to solve the structure and to locate the heavy atoms Mo, Rb, and K (SHELXS-86). Then the remaining atoms were found from successive difference maps (SHELXL-93). The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (Mo, P, Rb, and K atoms), and isotropic thermal parameters (O and C atoms) converged at $R = 0.054$ and $R_w = 0.138$ ($I > 2\sigma(I)$). In the final difference map the highest peak was 4.425 e Å^{-3} and the deepest hole -3.297 e Å^{-3}. Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the MULABS program.[24] Crystallographic data are summarized in Table 1.

All the rubidium and potassium counterions in $Rb_4KNa[(O_2CCH_2PO_3)_2Mo_5O_{15}] \cdot H_2O$ could be identified, but not the sodium ion. However, its existence is clearly demonstrated by elemental analysis. Bond-valence sum calculations confirm that protonation of polyanion **1** can be ruled out.[25] Therefore, all six required counterions are accounted for. The remaining electron density is centered around Rb2, indicating modest disorder and/or poor absorption correction. The disorder of Rb4 is more pronounced, and we could refine it by assignment of partial occupancies.

Table 1. Crystal Data and Structure Refinement for $Rb_4KNa[(O_2CCH_2PO_3)_2Mo_5O_{15}] \cdot H_2O$

empirical formula	$C_4H_6KMo_5NaO_{26}P_2Rb_4$	Z	4
fw	1415.8	temp (°C)	−150
space group	$P2_1/n$	wavelength (Å)	0.71073
a (Å)	10.146(2)	d_{calcd} (Mg m^{-3})	3.240
b (Å)	13.704(3)	abs coeff. (mm^{-1})	9.284
c (Å)	20.577(4)	R [$I > 2\sigma(I)$]^a	0.054
β (deg)	94.88(3)	R_w (all data)^b	0.138
vol (Å^3)	2850.7(10)		

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

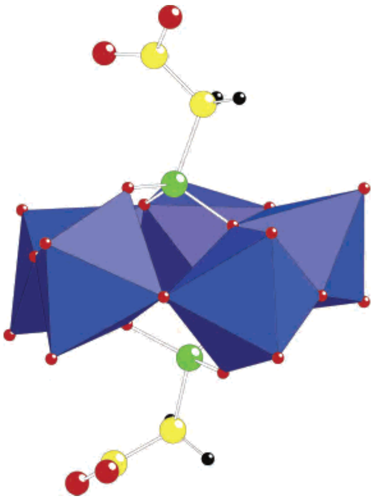

Figure 1. Combined polyhedral/ball-and-stick representation of **1**. The MoO_6 octahedra are shown in blue, oxygen in red, phosphorus in green, carbon in yellow, and hydrogen in black.

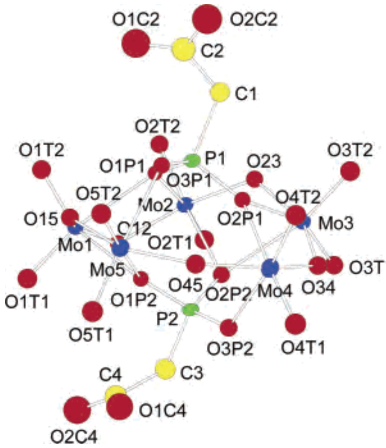

Figure 2. Ball-and-stick representation of the asymmetric unit of **1** showing 50% probability ellipsoids and the labeling scheme.

Results and Discussion

The novel polyoxoanion $[(O_2CCH_2PO_3)_2Mo_5O_{15}]^{6-}$ (**1**) consists of a ring of five MoO_6 octahedra with four edge junctions and one corner junction (see Figures 1 and 2). This nonplanar arrangement is stabilized by two phosphonocarboxylate groups that are bound via their phosphonate

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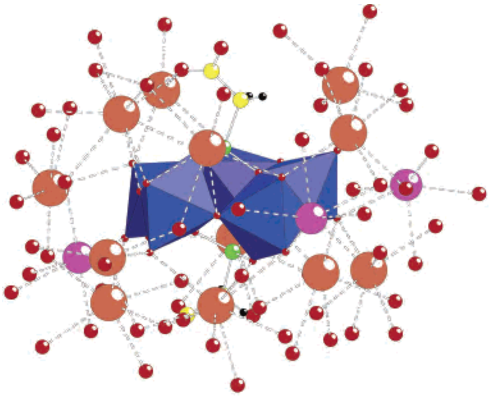

Figure 3. Representation of the solid-state lattice of $Rb_4KNa[(O_2CCH_2PO_3)_2Mo_5O_{15}]\cdot H_2O$ showing polyanion **1** and the surrounding rubidium (orange) and potassium (purple) counterions and their coordinated water molecules of hydration (red). The color code for polyanion **1** is the same as in Figure 1.

functionalities on opposite sides of the ring. As a result the two dangling arms with their terminal carboxylate groups protrude away from the molybdenum−oxo framework in diametrically opposed directions. Polyanion **1** is a rather small and highly unsymmetrical (C_1 symmetry) species, even if free rotation of the organic arms in solution is considered. All molybdenum centers in **1** are coordinated in a distorted octahedral fashion, and three pairs of Mo−O bonds can be identified: (a) short terminal bonds ($Mo-O_{term}$, 1.693−1.732(8) Å), (b) long bonds trans to the terminal bonds ($Mo-O_P$, 2.201−2.408(7) Å), and (c) bonds of intermediate length ($Mo-O_{Mo}$, 1.899−1.927(7) Å). Therefore, **1** may be described as a ring of five corner-shared MoO_4 tetrahedra, stabilized by the presence of two tetrahedral heterogroups.[26]

The pentamolybdate core was first observed in the solid state by Strandberg and Hedman for the molydophosphate $[P_2Mo_5O_{23}]^{6-}$ and its mono- and diprotonated derivatives.[17] Later it was shown that this structural motif is preserved in the large pentamolybdophosphonate family $[(RP)_2P_2Mo_5O_{21}]^{4-}$ (R = H, CH_3, C_2H_5, C_6H_5, $C_2H_4NH_3^+$, *p*-$CH_2C_6H_4NH_3^+$).[15,16,18−21] Polyanion **1** is an additional member of this structural class, and it represents the first polyoxoanion with incorporated phosphonocarboxylate groups.

The title polyanion **1** was synthesized by stoichiometric interaction of phosphonoacetic acid ($H_2O_3PCH_2CO_2H$) with sodium molybdate in aqueous solution at pH 3. We discovered that the presence of KCl during the synthesis of **1** is helpful. This indicates that the structure of **1** is stabilized by potassium counterions, but not by sodium ions. It appears that rubidium ions also play a stabilizing role and perhaps even better than potassium ions. We obtained the best quality single crystals of **1** usually in the presence of rubidium ions. Close inspection of the solid-state lattice indicates that each polyanion **1** is virtually wrapped by 12 rubidium and 3 potassium counterions all around (see Figure 3). Most likely the sodium ion is also located in the vicinity of **1**, but we could not determine its precise location by XRD (see the Experimental Section). All counterions are coordinated to bridging and terminal oxygens of **1** and to water molecules of hydration. We conclude that the role of the cations extends from charge balance to a significant stabilizing effect. The presence of 15 counterions in the immediate proximity of each title polyanion overcompensates its negative charge by more than a factor of 2, which explains that the cations also act as linkers to neighboring polyanions. This extended lattice breaks apart after redissolution in water, but most likely some counterions remain loosely associated with the polyanion in solution. Therefore, the title compound presents another example in polyoxoanion chemistry demonstrating the important role of countercations in solution and in the solid state.

By using ^{31}P NMR, we showed that the solid-state structure of **1** is preserved in solution. A solution of synthesized **1** at pH 3 and a solution of the redissolved salt of **1** at the same pH result in identical NMR spectra, a triplet with a chemical shift of 22.0 ppm ($^2J_{PH}$ = 22 Hz). Also at pH 3 free phosphonoacetic acid appears as a triplet at δ = 13.6 ppm ($^2J_{PH}$ = 19 Hz).

The above observations were helpful in the synthesis of the phosphonopropionate derivative $[(O_2CC_2H_4PO_3)_2Mo_5O_{15}]^{6-}$ (**2**). Interaction of ($H_2O_3PC_2H_4CO_2H$) with sodium molybdate in stoichiometric amounts and in the presence of potassium chloride at pH 3 resulted in the desired product. The ^{31}P NMR spectrum of this solution showed a multiplet at δ = 32.6 ppm (J_{PH} = 9 Hz). Free phosphonopropionic acid shows a multiplet with a chemical shift of 24.4 ppm (J_{PH} = 8 Hz) at pH 3. These results indicated very strongly that the isostructural derivative of **1** was present. We were also able to obtain a pure solid of **2**, and the combination of IR, elemental analysis, and NMR was conclusive. Unfortunately we could not grow single crystals of **2** suitable for X-ray diffraction, but the identity of this title polyanion is unequivocally established with the data in hand.

Synthesis of the hypothetical phosphonoformate derivative $[(O_2CPO_3)_2Mo_5O_{15}]^{6-}$ was unsuccessful, because phosphonoformic acid quickly hydrolyzes in an acidic, aqueous medium, resulting in phosphite (HPO_3^{2-}), CO_2, and water. This reaction led to the well-known pentamolybdophosphite derivative $[(HPO_3)_2Mo_5O_{15}]^{4-}$ with the same metal−oxo framework as the title compounds.[15,19] This observation emphasizes again the fact that in polyoxometalate chemistry the reaction conditions are in general more important than the precursors used.

During the synthesis of **1** and **2** a color change to blue was observed, indicating heteropoly blue formation by reduction of some molybdenum centers to Mo(V). However, when the solutions were left standing open to the air during crystallization, they slowly turned colorless again. Most likely the contact with atmospheric dioxygen results in complete reoxidation of all Mo(V) centers. All solid products obtained were white in color, and our analyses (NMR, XRD, elemental analysis) confirmed that fully oxidized materials were present.

The title polyanions **1** and **2** have dangling arms with terminal carboxylate groups on each side of the polyanion. This allows for additional functionalization via attachment

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(26) Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 952.

of a large variety of organic or organometallic fragments. It could therefore be envisioned to bind chiral amino acids to **1** and **2**. This could lead to a large reservoir of water-soluble, chiral polyoxomolybdates with potentially very interesting biological and catalytic activity. This work is currently under way.

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Supporting Information Available: One X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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