Inorg. Chem. **2003**, *42*, 1135–1139

Heteropolymolybdates of Phosphate, Phosphonate, and Phosphite Functionalized by Glycine

Ulrich Kortz,*,† Jacqueline Vaissermann,‡ René Thouvenot,‡ and Pierre Gouzerh‡

School of Engineering and Science, International University Bremen, P.O. Box 750 561, 28725 Bremen, Germany, and Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UMR 7071, Case Courrier 42, Université Pierre et Marie Curie, 4, Place Jussieu, 75252 Paris Cedex 05, France

Received October 29, 2002

The novel, functionalized heteropolymolybdates $[RPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (R = OH, CH_3, C_2H_5, H) have been synthesized and characterized by IR, ^{31}P NMR spectroscopy, and elemental analysis. Single-crystal X-ray analysis was carried out on $K_2[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$, which crystallizes in the orthorhombic system, space group *Pnma*, with $a = 14.118(2)$ Å, $b = 20.660(3)$ Å, $c = 12.191(2)$ Å, and $Z = 4$; $K_2[H_3CPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$, which crystallizes in the orthorhombic system, space group *Pnma*, with $a = 14.1643(6)$ Å, $b = 20.8658(8)$ Å, $c = 12.2235(5)$ Å, and $Z = 4$; and $K_2[HPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8H_2O$, which crystallizes in the orthorhombic system, space group *Pnma*, with $a = 14.092(3)$ Å, $b = 20.696(2)$ Å, $c = 12.199(4)$ Å, and $Z = 4$. We also report on the synthesis and characterization of the isostructural derivative $K_2[H_5C_2PMo_6O_{21}(O_2CCH_2NH_3)_3]$. The four title polyanions consist of an RP (R = OH, CH_3, C_2H_5, H) hetero group surrounded by a ring of six MoO_6 octahedra sharing edges and corners alternatingly. Three glycine molecules are each bound to two edge-sharing Mo centers via their carboxylate functionality on the same side of the ring. The central phosphorus atom is located slightly above the plane of the six molybdenums, and its terminal R group is on the same side of the ring as the glycines. NMR studies show that the solid state structures of the title compounds are preserved in solution.

Introduction

Polyoxometalates are metal−oxygen clusters with a tremendous structural variety and interesting properties in different fields including catalysis, medicine, and materials science.[1−5] The multitude of potential applications has led to significant interest in polyoxometalates over the recent past. The first polyoxoanions were reported almost two centuries ago, but they could only be characterized structurally more than 100 years later.[6] Especially the availability of single-crystal X-ray diffraction has led to the discovery of a large number of novel polyoxoanions with different shapes and sizes.

During the last 20 years it has been well established that the size, shape, and charge density of many polyoxoanions are of interest for pharmaceutical applications (e.g., antiviral, -cancer, -tumor).[1−3] However, the mechanism of action of many polyoxoanions has not been selective toward a specific target. In order to improve selectivity it appears often desirable to modify a given polyoxoanion core structure slightly. However, such attempts result frequently in a different polyoxoanion framework. The main reason is probably the fact that the mechanism of formation of polyoxoanions is still not well understood and commonly described as self-assembly. Therefore the most straightforward and promising approach toward systematic derivatization of polyoxoanions involves attachment of organic groups to the surface of the metal−oxo framework. In order to be attractive for pharmaceutical applications the functionalized polyoxoanions should be water-soluble and fairly stable at physiological pH.

* Author to whom correspondence should be addressed. E-mail: u.kortz@iu-bremen.de. Fax: +49-(0)421-200 3229.
† International University Bremen.
‡ Université Pierre et Marie Curie.

(1) *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*; Pope, M. T., Müller, A., Eds.; Kluwer: Dordrecht, 2001.
(2) Hill, C. L., Guest Ed. Polyoxometalates. *Chem. Rev.* **1998**, *98*, 1−390.
(3) *Polyoxometalates: from Platonic Solids to Anti Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer: Dordrecht, 1994.
(4) Pope, M. T.; Müller, A. *Angew. Chem.* **1991**, *103*, 56; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34.
(5) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer: Berlin, 1983.
(6) Berzelius, *J. Pogg. Ann.* **1826**, *6*, 369.

10.1021/ic0261427 CCC: $25.00 © 2003 American Chemical Society
Published on Web 01/17/2003

A variety of approaches have been used in order to incorporate organic or organometallic moieties in polyoxoanions. Many different compounds have been synthesized and characterized over the years, and this work has recently been reviewed.[7] Interaction of polyoxovanadates with carboxylate functionalities has led to a large number of functionalized species, but only a few analogues of polyoxomolybdates and -tungstates with nuclearities > 3 are known.[8] The reactivity of amino acids with polyoxovanadates has also been investigated as model studies for polyoxometalate−protein interactions.[9] The 20 natural amino acids with their variety of side chains represent a rich reservoir toward the synthesis of functionalized polyoxoanions. However, to date the only examples of structurally characterized polyoxoanions with covalently bound amino acids are $[Mo_8O_{26}(L\text{-}lysH_2)_2]^{2-}$, $[HMo_6VO_{22}(NH_3CH_2COO)_3]^{2-}$, and $[Mo_{154}O_{462}H_{14}(H_2O)_{48}(HO_2C-(NH_3^+)HC-CH_2-S-S-CH_2-CH(NH_3^+)-COO^-)_{11}]^{3-}$.[10−12] Very recently Kortz et al. reported on a large family of lone-pair-containing heteropolymolybdates functionalized by five different amino acids: $[XMo_6O_{21}(O_2CRNH_3)_3]^{n-}$ ($n = 2$, X = Se^{IV}, Te^{IV}; $n = 3$, X = As^{III}, Sb^{III}, Bi^{III}; R = CH_2, C_2H_4, C_3H_6, $CHCH_3$, $CH(CH_2)_4NH_2$).[13] Three of these polyanions were the first examples of chiral, functionalized heteropolymolybdates.

Here we report on phosphorus-containing derivatives of the same structural type.

Experimental Section

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

$K_2[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$. The synthesis of $[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**1**) was accomplished by dissolving 0.138 g (1 mmol) of $NaH_2PO_4\cdot H_2O$, 1.452 g (6.0 mmol) of $Na_2MoO_4\cdot 2H_2O$, 0.451 g (6.0 mmol) of $HOOCCH_2NH_2$, and 0.224 g (3.0 mmol) of KCl in 30 mL of water upon stirring. The pH of the solution was adjusted to 3 by addition of 4 M HCl. Then the solution was refluxed for 1 h, and after about 20 min a color change to blue was observed. After cooling to room temperature the solution was filtered into a 100 mL beaker. Slow evaporation of the solvent at room temperature led to pink crystals of $K_2[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$ suitable for X-ray diffraction after 1 week. Evaporation was allowed to continue for 3−4 weeks until the solvent level had approached the solid product, which was filtered off and dried in an oven (70 °C) overnight. Yield: 0.68 g (52%). $K_2[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]$: elemental analysis (%) calcd (found), K 6.2 (6.4), P 2.5 (2.5), Mo 45.6 (45.1), C 5.7 (5.4), H 1.3 (1.5), N 3.3 (3.3). IR of $K_2[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$ (KBr): 1646, 1610, 1592, 1501, 1458, 1422, 1335, 1313, 1114, 1079, 1046, 1022, 936, 912, 896, 690, 628, 553, 524, 451 cm^{-1}. Phosphorus-31 NMR (D_2O, 293 K): $[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ at pH 3, δ 1.9 ppm (singlet, 1P); sodium phosphate (NaH_2PO_4) at pH 3, δ 0.7 ppm (singlet, 1P); at pH 6, δ 1.6 ppm (singlet, 1P).

$K_2[H_3CPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$. The synthesis of $[H_3CPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**2**) was accomplished by dissolving 0.113 g (1 mmol) of H_3CPOCl_2, 1.452 g (6.0 mmol) of $Na_2MoO_4\cdot 2H_2O$, 0.451 g (6.0 mmol) of $HOOCCH_2NH_2$, and 0.224 g (3.0 mmol) of KCl in 30 mL of water upon stirring. The pH of the solution was adjusted to 3 by addition of 4 M HCl. Then the solution was refluxed for 1 h, and after about 20 min a color change to blue was observed. After cooling to room temperature the solution was filtered into a 100 mL beaker. Slow evaporation of the solvent at room temperature led to pink crystals of $K_2[H_3CPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$ suitable for X-ray diffraction after 1 day. Evaporation was allowed to continue for 3−4 weeks until the solvent level had approached the solid product, which was filtered off and dried in an oven (70 °C) overnight. Yield: 0.98 g (78%). $K_2[H_3CPMo_6O_{21}(O_2CCH_2NH_3)_3]$: elemental analysis (%) calcd (found), K 6.2 (6.8), P 2.5 (2.9), Mo 45.7 (45.8), C 6.7 (6.3), H 1.4 (1.7), N 3.3 (3.2). IR of $K_2[H_3CPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$ (KBr): 1645, 1607, 1506, 1459, 1423, 1348, 1335, 1299, 1118, 1102, 1050, 997, 933, 909, 893, 774, 686, 629, 555, 504, 452 cm^{-1}. Phosphorus-31 NMR (D_2O, 293 K): $[H_3CPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ at pH 3, δ 33.9 ppm (quartet, 1P), $^2J_{PH} = 18$ Hz; methylphosphonic acid ($H_3CPO_3H_2$) at pH 3, δ 26.3 ppm (quartet, 1P), $^2J_{PH} = 17$ Hz; at pH 6, δ 24.8 ppm (quartet, 1P), $^2J_{PH} = 16$ Hz.

$K_2[H_5C_2PMo_6O_{21}(O_2CCH_2NH_3)_3]$. The synthesis of $[H_5C_2PMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**3**) was accomplished by dissolving 0.110 g (1 mmol) of $H_5C_2PO_3H_2$, 1.452 g (6.0 mmol) of $Na_2MoO_4\cdot 2H_2O$, 0.451 g (6.0 mmol) of $HOOCCH_2NH_2$, and 0.224 g (3.0 mmol) of KCl in 30 mL of water upon stirring. The pH of the solution was adjusted to 3 by addition of 4 M HCl. Then the solution was refluxed for 1 h, and after about 20 min a color change to blue was observed. After cooling to room temperature the solution was filtered into a 100 mL beaker. Slow evaporation of the solvent at room temperature led to pink crystals of $K_2[H_5C_2PMo_6O_{21}(O_2CCH_2NH_3)_3]$ that were too small for single-crystal X-ray analysis. Evaporation was allowed to continue for 3−4 weeks until the solvent level had approached the solid product, which was filtered off and dried in an oven (70 °C) overnight. Yield: 0.83 g (65%). $K_2[H_5C_2PMo_6O_{21}(O_2CCH_2NH_3)_3]$: elemental analysis (%) calcd (found), K 6.1 (6.3), P 2.4 (2.6), Mo 45.1 (45.2), C 7.5 (7.0), H 1.6 (1.5), N 3.3 (3.5). IR of $K_2[H_3CPMo_6O_{21}(O_2CCH_2NH_3)_3]$ (KBr): 1614, 1493, 1451, 1416, 1344, 1277, 1234, 1127, 1043, 1010, 984, 927, 891, 878, 778, 745, 669, 549, 521, 449 cm^{-1}. Phosphorus-31 NMR (D_2O, 293 K): $[H_5C_2PMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ at pH 3, δ 37.0 ppm (multiplet, 1P), $J_{PH} = 19$ Hz; ethylphosphonic acid ($H_5C_2PO_3H_2$) at pH 3, δ 29.7 ppm (multiplet, 1P), $J_{PH} = 18$ Hz; at pH 6, δ 28.9 ppm (multiplet, 1P), $J_{PH} = 18$ Hz.

(7) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77−111.

(8) (a) Reference 7, p 97 and references therein. (b) *Vanadium Compounds: Chemistry, Biochemistry, and Therapeutic Applications*; Tracey, A. S., Crans, D. C., Eds.; ACS Symposium Series 711; American Chemical Society: Washington, DC, 1998. (c) Müller, A.; Sarkar, S.; Shah, S. Q. N.; Bögge, H.; Schmidtmann, M.; Sarkar, S.; Kögerler, P.; Hauptfleisch, B.; Trautwein, A. X.; Schünemann, V. *Angew. Chem.* **1999**, *111*, 3435; *Angew. Chem., Int. Ed.* **1999**, *38*, 3238. (d) Müller, A.; Polarz, S.; Das, S. K.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Hauptfleisch, B. *Angew. Chem.* **1999**, *111*, 3439; *Angew. Chem., Int. Ed.* **1999**, *38*, 3241. (e) Wei, X.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **1997**, *36*, 130. (f) Wassermann, K.; Lunk, H.-J.; Palm, R.; Fuchs, J.; Steinfeldt, N.; Stoesser, R.; Pope, M. T. *Inorg. Chem.* **1996**, *35*, 3273. (g) Yamase, T.; Inoue, M.; Naruke, H.; Fukaya, K. *Chem. Lett.* **1999**, *7*, 563.

(9) (a) Crans, D. C.; Mohammad, M.-T.; Anderson, O. P.; Miller, M. M. *Inorg. Chem.* **1994**, *33*, 5586. (b) Fritzsche, M.; Elvingson, K.; Rehder, D.; Pettersson, L. *Acta Chem. Scand.* **1997**, *51*, 483.

(10) Inoue, M.; Yamase, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 3055.

(11) Cindrić, M.; Strukan, N.; Devčić, M.; Kamenar, B. *Inorg. Chem. Commun.* **1999**, *2*, 558.

(12) Müller, A.; Das, S. K.; Kuhlmann, C.; Bögge, H.; Schmidtmann, M.; Diemann, E.; Krickemeyer, E.; Hormes, J.; Modrow, H.; Schindler, M. *Chem. Commun.* **2001**, 655.

(13) Kortz, U.; Savelieff, M. G.; Abou Ghali, F. Y.; Khalil, L. M.; Maalouf, S. A.; Sinno, D. I. *Angew. Chem.* **2002**, *114*, 4246; *Angew. Chem., Int. Ed.* **2002**, *41*, 4070.

$K_2[HPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8H_2O$. The synthesis of $[HPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**4**) was accomplished by dissolving 0.216 g (1 mmol) of $Na_2HPO_3\cdot 5H_2O$,[14] 1.452 g (6.0 mmol) of $Na_2MoO_4\cdot 2H_2O$, 0.451 g (6.0 mmol) of $HOOCCH_2NH_2$, and 0.224 g (3.0 mmol) of KCl in 30 mL of water upon stirring. The pH of the solution was adjusted to 3 by addition of 4 M HCl. Then the solution was refluxed for 1 h, and after about 20 min a color change to blue was observed. After cooling to room temperature the solution was filtered into a 100 mL beaker. Slow evaporation of the solvent at room temperature led to pink crystals of $K_2[HPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8H_2O$ suitable for X-ray diffraction after 1 day. Evaporation was allowed to continue for 3−4 weeks until the solvent level had approached the solid product, which was filtered off and dried in an oven (70 °C) overnight. Yield: 1.1 g (88%). $K_2[HPMo_6O_{21}(O_2CCH_2NH_3)_3]$: elemental analysis (%) calcd (found), K 6.3 (6.3), P 2.5 (2.2), Mo 46.2 (45.7), C 5.8 (5.4), H 1.3 (1.0), N 3.4 (3.4). IR of $K_2[HPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8H_2O$ (KBr): 1646, 1607, 1505, 1459, 1421, 1349, 1335, 1315, 1263, 1201, 1120, 1105, 1077, 1011, 934, 911, 895, 694, 634, 552, 514, 448 cm^{-1}. Phosphorus-31 NMR (D_2O, 293 K): $[HPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ at pH 3, δ 8.4 ppm (doublet, 1P), $^1J_{PH} = 684$ Hz; sodium phosphite (Na_2HPO_3) at pH 3, δ 0.7 ppm (doublet, 1P), $^1J_{PH} = 628$ Hz; at pH 6, δ 1.2 ppm (doublet, 1P), $^1J_{PH} = 581$ 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. Phosphorus-31 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 external 85% H_3PO_4 as a standard.

X-ray Crystallography. A pink block of $K_2[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$ with dimensions 0.20 × 0.18 × 0.16 mm^3 was mounted on a glass fiber for indexing and intensity data collection at 173 K on a Bruker SMART CCD single-crystal diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). Of the 4511 unique reflections ($R_{int} = 0.133$, $2\theta_{max} = 56.66°$), 3745 reflections were considered observed ($I > 2\sigma(I)$). Direct methods were used to solve the structure and to locate the heavy atoms Mo 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, and K atoms), and isotropic thermal parameters (O, N, C atoms), converged at $R = 0.072$ and $R_w = 0.149$ ($I > 2\sigma(I)$). In the final difference map the highest peak was 1.980 e $Å^{-3}$ and the deepest hole −2.794 e $Å^{-3}$. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program.[15]

A pink needle of $K_2[H_3CPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$ with dimensions 0.30 × 0.05 × 0.05 mm^3 was mounted on a glass fiber for indexing and intensity data collection at 293 K on a Bruker Apex CCD single-crystal diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). Of the 4606 unique reflections ($R_{int} = 0.045$, $2\theta_{max} = 56.60°$), 4233 reflections were considered observed ($I > 2\sigma(I)$). Direct methods were used to solve the structure and to locate the heavy atoms Mo and K (SHELXS-97). Then the remaining atoms were found from successive difference maps (SHELXL-97). The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (Mo, P, and K atoms), and isotropic thermal parameters (O, N, C atoms), converged at $R = 0.049$ and $R_w = 0.107$ ($I > 2\sigma(I)$). In the final difference map the highest peak was 1.379 e $Å^{-3}$ and the deepest hole −0.997 e $Å^{-3}$. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program.[15]

A pink rhombic prism of $K_2[HPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8H_2O$ with dimensions 0.20 × 0.20 × 0.15 mm^3 was mounted on a glass fiber for indexing and intensity data collection at 191 K on an Enraf Nonius CAD4 single-crystal diffractometer using Mo Kα radiation ($\lambda = 0.71069$ Å). Of the 4392 unique reflections ($2\theta_{max} = 56.0°$), 3715 reflections were considered observed ($I > 3\sigma(I)$). Direct methods were used to solve the structure and to locate the heavy atoms Mo and K (SHELXS-86). Then the remaining atoms were found from successive difference maps (CRYSTALS). The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (Mo, P, and K atoms) and isotropic thermal parameters (O, N, C atoms) converged at $R = 0.040$ and $R_w = 0.047$ ($I > 3\sigma(I)$). In the final difference map the highest peak was 1.38 e$Å^{-3}$ and the deepest hole −1.22 e$Å^{-3}$. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the DIFABS program.[16]

Crystallographic data are summarized in Table 1.

Table 1. Crystal Data and Structure Refinement for $K_2[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$, $K_2[H_3CPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$, and $K_2[HPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8H_2O$

emp formula	$C_6H_{33}K_2Mo_6N_3O_{36.5}P$	$C_7H_{35}K_2Mo_6N_3O_{35.5}P$	$C_6H_{32}K_2Mo_6N_3O_{35}P$
fw	1416.2	1414.3	1391.2
space group (No.)	*Pnma* (62)	*Pnma* (62)	*Pnma* (62)
a (Å)	14.118(2)	14.1643(6)	14.092(3)
b (Å)	20.660(3)	20.8658(8)	20.696(2)
c (Å)	12.191(1)	12.2235(5)	12.199(4)
vol ($Å^3$)	3555.9(7)	3612.6(3)	3558(1)
Z	4	4	4
temp (°C)	−100	20	−82
wavelength (Å)	0.71073	0.71073	0.71069
d_{calc} (Mg m^{-3})	2.60	2.56	2.56
abs coeff (mm^{-1})	2.46	2.42	2.40
R	0.072[a,b]	0.049[a,b]	0.040[a,d]
R_w (all data)	0.149[c]	0.107[c]	0.047[e]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $[I > 2\sigma(I)]$. [c] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. [d] $[I > 3\sigma(I)]$. [e] $R_w = [\sum w(F_o - F_c)/\sum w(F_o)]$.

Results and Discussion

The novel polyoxoanions $[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**1**), $[H_3CPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**2**), $[H_5C_2PMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**3**), and $[HPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**4**) are isostructural. They consist of a central hetero group surrounded by a ring of six MoO_6 octahedra sharing edges and corners alternatingly. Three glycine molecules are each bound to two edge-sharing Mo centers via their carboxylate functionality on the same side of the ring leading to a structure with idealized C_{3v} symmetry (see Figures 1−4). The four title compounds differ only in the terminal function R of the phosphorus heteroatom (R = OH, H, CH_3, C_2H_5). The phosphorus atom is located slightly above the plane of six molybdenums and in addition to the terminal rest it is coordinated to three μ_3-oxo groups leading to a distorted tetrahedral coordination geometry.

Some other polyoxometalates are known that also contain the hexamolybdate ring of the title compounds. Robl et al.

(14) Phosphonoformic acid ($H_2O_3PCO_2H$) can also be used instead of sodium phosphite. Phosphonoformic acid quickly hydrolyzes in acidic, aqueous medium, resulting in phosphite (HPO_3^{2-}), CO_2, and water.

(15) Sheldrick, G. M. *SADABS*; Siemens Analytical X-ray Instrument Division: Madison, WI, 1995.

(16) Walker, N.; Stuart, D. *Acta Crystallogr. A* **1983**, *39*, 158.

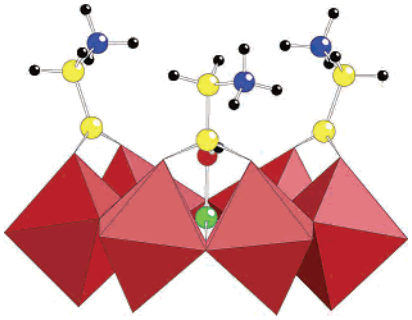

Figure 1. Combined polyhedral/ball and stick representation of $[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**1**). Color code: MoO_6 octahedra (red), phosphorus (green), oxygen (red), carbon (yellow), nitrogen (blue), and hydrogen (black).

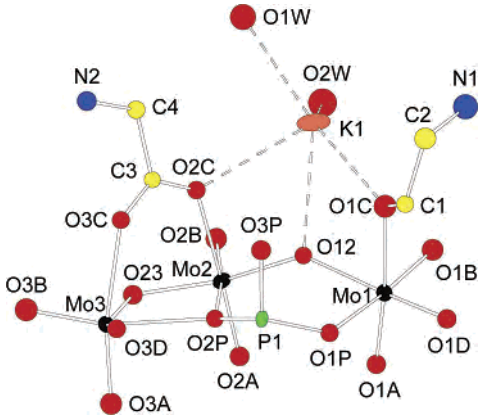

Figure 2. Ball and stick representation of the asymmetric unit of $K_2[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8.5H_2O$ showing 50% probability ellipsoids and the labeling scheme. Only the water molecules associated with the potassium ion are shown.

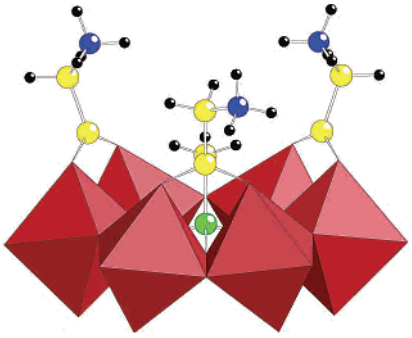

Figure 3. Combined polyhedral/ball and stick representation of $[H_3CPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**2**). The color code is the same as in Figure 1.

synthesized monomeric species based on the $Se^{IV}Mo_6$ core that are stabilized by XO_4 (X = SVI, SeVI) fragments or carboxylate units.[17] The same authors also obtained dimeric and polymeric polyanions by linking different $Se^{IV}Mo_6$ units with dicarboxylate functions. Matsumoto's ion $[CH_3AsO_3Mo_6O_{18}(H_2O)_6]^{2-}$ contains a methylarsenate hetero group, and the six terminal water molecules of the molybdenum centers are alternating above and below the ring.[18] Kortz's diphosph(on)ate complexes $[(O_3PCH_2OPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$

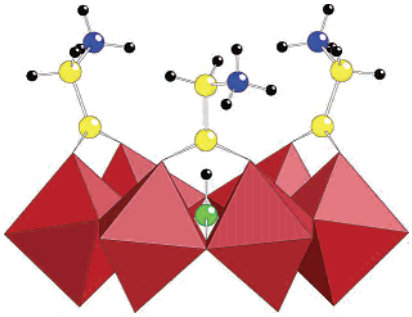

Figure 4. Combined polyhedral/ball and stick representation of $[HPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**4**). The color code is the same as in Figure 1.

and $[(O_3POPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ contain ditetrahedral hetero groups, and the four terminal water molecules are all on the same side of the hetero group.[19,20] Cindrić's molybdovanadate $[HMo_6VO_{22}(NH_3CH_2COO)_3]^{2-}$ was the first example of a polyoxoanion functionalized by glycine.[11] The glycine molecules are all bound on the same side of the Mo_6 ring. Recently Kortz et al. reported that the same structure can be formed with lone-pair-containing heteroatoms and for a variety of amino acids, as seen in $[XMo_6O_{21}(O_2CRNH_3)_3]^{n-}$ (n = 2, X = Se^{IV}, Te^{IV}; n = 3, X = As^{III}, Sb^{III}, Bi^{III}; R = CH_2, C_2H_4, C_3H_6, $CHCH_3$, $CH(CH_2)_4NH_2$).[13]

The title polyanions **1**−**4** are the first phosphorus-containing examples of the family of amino acid substituted heteropolymolybdates. We were able to incorporate hydrogenphosphate ($HOPO_3^{2-}$), methylphosphonate ($H_3CPO_3^{2-}$), ethylphosphonate ($H_5C_2PO_3^{2-}$), and phosphite (HPO_3^{2-}) in **1**−**4**, indicating the steric and electronic flexibility of this structural type with respect to the hetero group. The four hetero groups contain phosphorus in two different oxidation states: +V (**1**−**3**) and +III (**4**). Nevertheless, all hetero groups have the same charge (−2) and this charge corresponds to the total charge of the respective polyanion. This is in complete agreement with X-ray diffraction and elemental analysis, which indicated the presence of two potassium counterions in all cases. Protonation of the terminal oxygen atom of the phosphate hetero group in **1** was identified by bond-valence sum calculations.[21] The glycine molecules are bound via their carboxylate functions, and all three terminal amino groups are protonated. This is not surprising because the title polyanions were synthesized at pH 3.[13]

Attempts to obtain derivatives of **1**−**4** with other amino acids besides glycine (e.g., L-alanine, β-alanine) were unsuccessful. It appears that steric effects of the terminal rest on the hetero group could be the sole reason for **2** and **3** (R = CH_3, C_2H_5), but probably not for **1** and **4** (R = OH, H). It must be remembered that Kortz et al. were able to synthesize a large number of derivatives (with five different amino acids) for the isostructural, lone-pair-containing family $[XMo_6O_{21}(O_2CRNH_3)_3]^{n-}$ (n = 2, X = Se^{IV}, Te^{IV}; n = 3, X = As^{III}, Sb^{III}, Bi^{III}; R = CH_2, C_2H_4, C_3H_6, $CHCH_3$, $CH(CH_2)_4NH_2$).[13] Therefore it seems that the lone pair of electrons on

(17) Robl, C. *Chemistry at the Beginning of the Third Millennium*; Fabbrizzi, L., Poggi, A., Eds.; Springer: Berlin, Heidelberg, Germany, 2000 and references therein.
(18) Matsumoto, K. Y. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3284.
(19) Kortz, U.; Pope, M. T. *Inorg. Chem.* **1995**, *34*, 2160.
(20) Kortz, U. *Inorg. Chem.* **2000**, *39*, 625.
(21) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

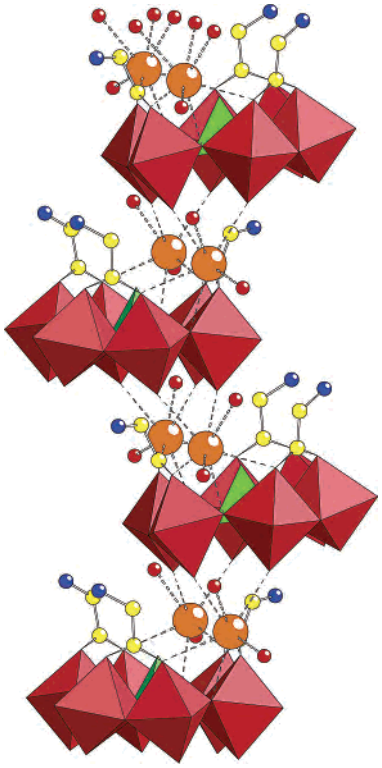

Figure 5. Combined polyhedral/ball and stick representation of $[HOPMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**1**) showing the solid state lattice structure. The color code is the same as in Figure 1, and potassium ions are shown in orange. Hydrogen atoms are omitted for clarity. The crystal structures of polyanions **1**, **2**, and **4** are isomorphous.

the heteroatom plays an important role leading to a stabilization of the entire polyoxoanion.

The title polyanions were synthesized by refluxing an aqueous solution containing hetero group/molybdate/glycine/potassium chloride in the mole ratio 1/6/6/3 at pH 3 for 1 h. We discovered that the presence of KCl during the synthesis is helpful, indicating that **1**−**4** are stabilized by potassium counterions in solution. In all cases the solutions turned blue during reflux, which is a sign for heteropoly blue formation by reduction of some molybdenum centers to Mo(V).[5] However, when the solutions were left standing open to the air during crystallization, they slowly turned lighter blue in color. Most likely the contact with atmospheric dioxygen resulted in partial oxidation of the Mo(V) centers. All solid products obtained were pink in color, and our analyses (NMR, XRD, elemental analysis) confirmed that fully oxidized materials were present.

On the basis of ^{31}P NMR it can be concluded that the solid state structures of **1**, **2**, and **4** are preserved in solution (see Experimental Section). These observations (together with IR and elemental analysis) were helpful in the synthesis of the ethylphosphonate derivative $[H_5C_2PMo_6O_{21}(O_2CCH_2NH_3)_3]^{2-}$ (**3**), which we could not characterize by single-crystal XRD.

Close inspection of the X-ray data in Table 1 indicates that the crystal structures of polyanions **1**, **2**, and **4** are all potassium salts and that they are isomorphous. The solid state structures are based on a chainlike arrangement of the title polyanions, which are connected via potassium ions (see Figure 5). Every polyanion has both of its potassium counterions closely associated with it, being located in between adjacent glycine molecules. Most likely the potassium ions remain in these positions even after redissolution of the solid, which would explain why the presence of potassium ions in solution stabilizes the title polyanions. Interestingly the molybdoselenite ($K_2[Se^{IV}Mo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8H_2O$) and molybdotellurite ($K_2[Te^{IV}Mo_6O_{21}(O_2CCH_2NH_3)_3]\cdot 8H_2O$) of Kortz et al. and the molybdovanadate ($K_2[OVMo_6O_{20}OH(O_2CCH_2NH_3)_3]\cdot 8H_2O$) of Cindrić et al. are also isomorphous with the title compounds.[11,13]

Polyanions **1**−**4** have three glycine molecules bound via their carboxylate functions, and the terminal amino groups are all protonated. It seems that additional functionalization of the title compounds should be possible, e.g., via attachment of organic or organometallic fragments. The biological properties of **1**−**4** will also be investigated.

Acknowledgment. Figures 1−5 were generated by Diamond, version 2.1b (copyright Crystal Impact GbR). This work was performed during a temporary appointment of U.K. at the Université Pierre et Marie Curie, Paris. X-ray measurements for polyanions **1** and **3** were performed by U.K. during visits in the laboratories of Prof. M. T. Pope (Georgetown University) and Prof. N. Dalal (Florida State University), respectively. U.K. thanks both Chemistry Departments for allowing use of the X-ray diffractometer.

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

IC0261427