Synthesis and Characterization of [Mo$_7$O$_{16}$(O$_3$PCH$_2$PO$_3$)$_3$]:$^{8-}$ A Mixed-Valent Polyoxomolybdenum Diphosphonate Anion with Octahedrally and Tetrahedrally Coordinated Molybdenum

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Two new compounds containing the title diphosphono-polyoxometalate anion and diprotonated ethylenediamine (enH$_2$) or piperazine (ppzH$_2$) countercations have been hydrothermally synthesized and structurally characterized ((enH$_2$)$_4$[Mo$_7$O$_{16}$(O$_3$PCH$_2$PO$_3$)$_3$]·7H$_2$O, triclinic, $P\bar{1}$, $Z = 2$, $a = 10.3455(7)$ Å, $b = 13.136(1)$ Å, and $c = 20.216(3)$ Å, $\alpha = 93.247(6)°$, $\beta = 96.434(6)°$, and $\gamma = 111.900(6)°$; (ppzH$_2$)$_4$[Mo$_7$O$_{16}$(O$_3$PCH$_2$PO$_3$)$_3$]·8H$_2$O, triclinic, $P\bar{1}$, $Z = 2$, $a = 13.255(2)$ Å, $b = 13.638(2)$ Å, and $c = 16.874(4)$ Å, $\alpha = 93.20(2)°$, $\beta = 101.27(2)°$, and $\gamma = 105.87(1)°$). The anion is a ring of three pairs of edge-sharing octahedra of Mo^{V}O$_6$ (with Mo^V–Mo^V bonds) that share corners with each other. The diphosphonate groups connect the pairs at the periphery. The ring is "capped" by a tetrahedron of Mo^{VI}O$_4$. According to magnetic measurements, the compounds are diamagnetic.

Introduction

One of the currently dynamic areas of materials chemistry concerns the development of new inorganic−organic hybrid materials with open-framework structures where the organic fragments are not just counterions or templates but are rather part of the structure as covalently bonded linkers. The potential for useful physical and chemical properties of such compounds makes them promising materials for eventual applications as catalysts, molecular sieves, nonlinear optical materials, and so forth.[1−4] Numerous multifunctional linkers such as organophosphonates,[1,2] organoarsonates,[2] and organo-diamines[3] have been used for the construction of structures that range from zero-dimensional molecular species to three-dimensional frameworks. Among these systems, the diphos-phonates of vanadium have attracted most attention.[2,5−6] This can be easily understood when taking into account the versatility of the vanadium coordination and the resulting multitude of structures and properties that are accessible with different linkers. Comparatively, the molybdenum organo-

diphosphonate systems have remained somewhat underde-veloped. Only a few compounds have been reported before, all of them molecular anions of molybdenum(VI).[7] Here, we describe the hydrothermal synthesis and characterization of two new compounds, (enH$_2$)$_4$[Mo$_7$O$_{16}$(O$_3$PCH$_2$PO$_3$)$_3$]·7H$_2$O (**1**) and (ppzH$_2$)$_4$[Mo$_7$O$_{16}$(O$_3$PCH$_2$PO$_3$)$_3$]·8H$_2$O (**2**), which contain the first mixed-valent Mo^V/Mo^{VI} diphosphonate molecular anion, [Mo$_7$O$_{16}$(O$_3$PCH$_2$PO$_3$)$_3$]$^{8-}$, with molybde-num in both tetrahedral and octahedral coordination.

Experimental Section

(enH$_2$)$_4$[Mo$_7$O$_{16}$(O$_3$PCH$_2$PO$_3$)$_3$]·7H$_2$O (1). This compound was initially synthesized in an attempt to prepare the diphosphonate analogue of the recently reported polyoxomolybdenum borophos-phate anion [Mo^V$_5$Mo^{VI}$_7$O$_{22}$(BO$_4$)$_2$(PO$_4$)$_5$(HPO$_4$)$_3$]$^{8-}$.[8] Later, the synthesis was carried out in a rational way from a mixture of Na$_2$-MoO$_4$·2H$_2$O, elemental Mo, methylenediphosphonic acid, ethyl-

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enediamine, and H$_2$O in a molar ratio of 1:0.25:1:1:140, respectively. The mixture was loaded in a Teflon-lined autoclave (23 mL capacity) and was heated at 160 °C for 5 days under autogenous pressure. The solid product was collected by filtration, washed with water, and dried at room temperature. Red polyhedral crystals of compound **1** (50% yield, based on Mo) and black, unidentified solid were isolated. The IR spectrum of selected crystals of **1** was obtained on a Perkin-Elmer Paragon 1000 FT-spectrometer (KBr pellet, cm^{-1}): 3445vs, br; 1634m, br; 1519w; 1452w; 1386w; 1327w; 1184s; 1158s; 1117s; 1067vs; 1026vs; 957vs; 889s; 828m; 795m; 760s; 726sh; 611w; 550m; 507m; 459m, 342s. Thermogravimetric analysis was carried out on a Perkin-Elmer TGA7 thermogravimetric analyzer in a flow of oxygen (60 mL/min) up to 800 °C. It showed one weight-loss step of 6.15% between room temperature and 190 °C, and this was attributed to the release of crystallization water (theoretical = 6.94%). A second step of abrupt weight loss was observed at about 310 °C, and this was followed by a continuous lesser weight loss which was not completed up to 800 °C. The total weight lost in the last two steps was 14.92%, and this was attributed to the partial calcination of the organic part of the compound (theoretical = 15.98%).

(ppzH$_2$)$_4$[Mo$_7$O$_{16}$(O$_3$PCH$_2$PO$_3$)$_3$]·8H$_2$O (2). The identical synthetic conditions and molar ratio as for **1**, but with piperazine instead of ethylenediamine, were used to make this compound. It was isolated as a pure phase (30% yield, based on Mo) of red polyhedral crystals. Magnetic measurements carried out on a Quantum Design MPMS SQUID magnetometer at different temperatures showed negative magnetic susceptibility which is consistent with a diamagnetic compound. IR: 3446vs, br; 3246vs; 3004vs; 2819s; 2414m; 1619m, br; 1560m; 1439m; 1380w; 1317w; 1195s; 1153s; 1118s; 1067vs; 1028vs; 954vs; 894m; 866m; 831m; 796m; 760s; 741s; 582m; 571m; 550m; 515m; 459m, 347s.

Structure Determination. X-ray diffraction data sets were collected at room temperature from single crystals of **1** (0.52 × 0.16 × 0.12 mm) and **2** (0.40 × 0.26 × 0.13 mm) on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å, $\omega-2\theta$ scans, $2\theta_{max}$ = 50°). The data sets were corrected for absorption with the aid of ψ-scans of a few appropriate reflections at different θ-angles. The structures were solved by direct methods and refined on F^2 using the SHELXTL-V5.1 software package. All non-hydrogen atoms, except one water oxygen atom and one disordered ethylenediamine in **1**, were refined with anisotropic thermal parameters. The final reliability factors were R1/wR2 = 0.0248/0.0682 for 8469 observed reflections ($I >$ $2\sigma_I$) for **1** and R1/wR2 = 0.0263/0.0654 for 8841 observed reflections for **2**. Details of the data collection and refinement of the compounds and selected bond distances for the anion in compound **1** are given in Tables 1 and 2, respectively.

Results and Discussion

The structures of the two new compounds contain a novel polyoxometalate anion, a polyoxomolybdenum diphosphonate, [Mo$_7$O$_{16}$(O$_3$PCH$_2$PO$_3$)$_3$]$^{8-}$ (denoted P$_6$Mo$_7$). Because there are only minor differences between the anions in the two compounds, only the structure of the anion in compound **1** will be discussed in detail. It is a ring-like anion made of three pairs of edge-sharing octahedra of Mo^{V}O$_6$ (Figure 1). The two molybdenum(V) atoms within a pair are bonded to each other by a single bond according to the average Mo—Mo distance of 2.563 Å (2.571 Å in compound **2**). This is confirmed further by the observed diamagnetic behavior of the compound. Similar molybdenum dinuclear fragments of
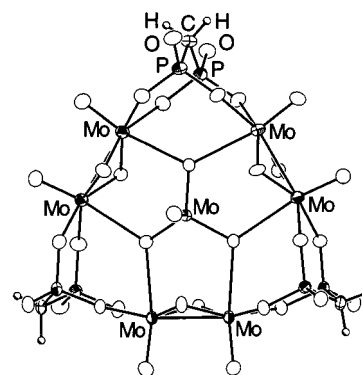

Figure 1. ORTEP view (thermal ellipsoids at the 50% probability level) of the molecular anion [Mo$^V_6$Mo^{VI}O$_{16}$(O$_3$PCH$_2$PO$_3$)$_3$]$^{8-}$. Oxygen, carbon, and both phosphorus and molybdenum are shown with open, crossed, and full thermal ellipsoids, respectively.

Table 1. Crystallographic Data for
(H$_3$N(CH$_2$)$_2$NH$_3$)$_4$[(O$_3$PCH$_2$PO$_3$)$_3$Mo$_7$O$_{16}$]·7H$_2$O (**1**) and
(N$_2$C$_4$H$_{12}$)$_4$[(O$_3$PCH$_2$PO$_3$)$_3$Mo$_7$O$_{16}$]·8H$_2$O (**2**)

formula	C$_{11}$H$_{60}$Mo$_7$N$_8$O$_{41}$P$_6$	C$_{19}$H$_{54}$Mo$_7$N$_8$O$_{42}$P$_6$
fw	1818.07	1924.10
space group, Z	$P\bar{1}$ (No. 2), 2	$P\bar{1}$ (No. 2), 2
lattice parameters		
a	10.3455(7) Å	13.255(2) Å
b	13.136(1) Å	13.638(2) Å
c	20.216(3) Å	16.874(4) Å
α	93.247(6)°	93.20(2)°
β	96.434(6)°	101.27(2)°
γ	111.900(6)°	105.87(1)°
V	2518.4(5) Å^3	2858.1(9) Å^3
radiation, λ	Mo Kα, 0.710 73 Å	Mo Kα, 0.710 73 Å
temp	20 °C	20 °C
abs coeff	19.94 cm^{-1}	17.66 cm^{-1}
density (calcd)	2.397 g/cm^3	2.236 g/cm^3
R1/wR2 ($I > 2\sigma_I$)^a	0.0248/0.0682	0.0263/0.0654
R1/wR2 (all data)^a	0.0261/0.0696	0.0325/0.0695

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ and wR2 = $\{[\Sigma w(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F^2_o)^2]\}^{1/2}$ where $w = [\sigma^2(F_o)^2 + (0.0351P)^2 + 7.0348P]^{-1}$ for **1** and $w = [\sigma^2(F_o)^2 + (0.028P)^2 + 4.5202P]^{-1}$ for **2**, and $P = [(F_o)^2 + 2(F_c)^2]/3$.

Table 2. Selected Bond Distances in
(H$_3$NCH$_2$CH$_2$NH$_3$)$_4$[Mo$_7$O$_{16}$(O$_3$PCH$_2$PO$_3$)$_3$]·7H$_2$O (**1**)

Mo(1)−O(22)	1.674(3)	Mo(5)−O(26)	1.676(3)	P(1)−O(29)	1.497(3)
Mo(1)−O(2)	1.939(2)	Mo(5)−O(14)	1.931(2)	P(1)−O(5)	1.535(3)
Mo(1)−O(1)	1.939(2)	Mo(5)−O(13)	1.938(2)	P(1)−O(3)	1.541(2)
Mo(1)−O(18)	2.062(2)	Mo(5)−O(12)	2.054(3)	P(1)−C(12)	1.802(4)
Mo(1)−O(17)	2.080(2)	Mo(5)−O(11)	2.078(3)	P(2)−O(30)	1.496(3)
Mo(1)−O(21)	2.472(2)	Mo(5)−O(20)	2.536(2)	P(2)−O(4)	1.535(3)
Mo(2)−O(23)	1.690(3)	Mo(6)−O(27)	1.680(3)	P(2)−O(6)	1.536(3)
Mo(2)−O(2)	1.921(2)	Mo(6)−O(14)	1.921(2)	P(2)−C(12)	1.805(4)
Mo(2)−O(1)	1.932(2)	Mo(6)−O(13)	1.942(3)	P(3)−O(31)	1.505(3)
Mo(2)−O(3)	2.068(2)	Mo(6)−O(16)	2.060(2)	P(3)−O(11)	1.535(3)
Mo(2)−O(4)	2.085(2)	Mo(6)−O(15)	2.077(2)	P(3)−C(34)	1.800(4)
Mo(2)−O(19)	2.470(2)	Mo(6)−O(21)	2.530(2)	P(4)−O(32)	1.489(3)
Mo(3)−O(24)	1.682(3)	Mo(7)−O(28)	1.731(2)	P(4)−O(12)	1.537(3)
Mo(3)−O(8)	1.929(2)	Mo(7)−O(20)	1.784(2)	P(4)−O(10)	1.543(3)
Mo(3)−O(6)	1.939(3)	Mo(7)−O(21)	1.787(2)	P(4)−C(34)	1.804(4)
Mo(3)−O(6)	2.052(3)	Mo(7)−O(19)	1.795(2)	P(5)−O(33)	1.506(3)
Mo(3)−O(5)	2.069(3)	Mo(1)−Mo(2)	2.5535(4)	P(5)−O(15)	1.535(3)
Mo(3)−O(19)	2.564(2)	Mo(3)−Mo(4)	2.5725(5)	P(5)−O(17)	1.536(2)
Mo(4)−O(25)	1.680(3)	Mo(5)−Mo(6)	2.5621(5)	P(5)−C(56)	1.806(4)
Mo(4)−O(7)	1.939(2)			P(6)−O(34)	1.501(3)
Mo(4)−O(8)	1.939(2)			P(6)−O(18)	1.531(2)
Mo(4)−O(10)	2.056(3)			P(6)−O(16)	1.539(3)
Mo(4)−O(9)	2.062(3)			P(6)−C(56)	1.806(4)
Mo(4)−O(20)	2.482(2)				

edge-sharing octahedra are well-known as the fundamental building units in other reduced (hetero)polyoxomolybdate-(V) anions.[9] The three pairs in P$_6$Mo$_7$ share corners with

each other and form a triangular ring with a semi 3-fold axis of symmetry. The shared corners are additionally shared with a tetrahedron of $Mo^{VI}O_4$ that caps the ring on one side.

The dimolybdenum pairs are also linked by methylene-diphosphonate groups which are positioned at the periphery of the ring (Figure 1). One such group connects two dimers by coordinating two oxygen atoms of each phosphonate functionality to two different dimolybdenum units. Thus, the methylenediphosphonate provides two bridges per a pair of dimers (Figure 1). The third oxygen of each phosphonate group is terminal and not protonated which makes the diphosphonate linker a tetradentate ligand. The formula of the ring, therefore, can be written as $\{Mo_2O_5(O_3PCH_2PO_3)\}_3$. The six molybdenum atoms of the ring are nearly coplanar with a maximum deviation of 0.02 Å from the least-squares plane (0.06 Å in **2**). The octahedra around the molybdenum atoms are quite distorted with one short (1.674(3)−1.690-(3) Å), four intermediate (1.921(2)−2.085(2) Å), and one long (2.470(2)−2.564(2) Å) Mo−O distances (Table 2). The short distance is to the peripheral terminal oxygen (Figure 1) and is trans to the long distance. The latter is to the oxygen atom which is three-bonded to two molybdenum(V) and one molybdenum(VI) atoms. The four intermediate Mo−O distances can be split in two categories: two of them are to oxygen atoms of the shared edge between the octahedra (1.921(2)−1.942(3) Å) and two are to the phosphonate oxygen atoms (2.052(3)−2.085(2) Å).

The tetrahedrally coordinated molybdenum(VI) capping the center of the ring bonds to the three oxygen atoms that are shared between the dinuclear units, thus making them three-bonded. The fourth oxygen atom of the tetrahedral coordination is a terminal oxygen positioned along the semi 3-fold axis of the anion. Therefore, the formula of the anion can be written as $[Mo^{VI}O\{Mo^V_2O_5(O_3PCH_2PO_3)\}_3]^{8-}$. The distance to the terminal oxygen, 1.731(2) Å, is quite shorter than the other three distances, 1.784(2)−1.795(2) Å. This molybdenum atom is 0.73 Å above the least-squares plane of the six molybdenum(V) atoms.

At first glance, the new polyoxomolybdenum diphosphonate anion, P_6Mo_7, seems very similar to the well-known polyoxomolybdenum phosphate anion $[PO\{Mo_2O_7(O_3-POH)\}_3]^{9-}$ (denoted P_4Mo_6, Figure 2). A closer look, however, reveals that the similarity is only in the overall triangular geometry of the two species and that they differ significantly in the bonding between the building units.[10] Thus, although the building units of molybdenum(V) in both anions are dimers of edge-sharing octahedra, these dimers in P_4Mo_6 are bonded to each other by sharing edges while they share corners in P_6Mo_7. Despite the edge-sharing between the dimers in P_4Mo_6, however, there are no Mo−Mo interactions between molybdenum atoms of different dimers ($d_{Mo-Mo} \approx 3.5$ Å) but only within them ($d_{Mo-Mo} \approx 2.6$ Å). The major result of the different connectivities of the two anions is that the edge-sharing between the dimers in P_4Mo_6 leads to smaller opening in the middle of the ring compared to that in P_6Mo_7 (Figure 2). Thus, a "capping"
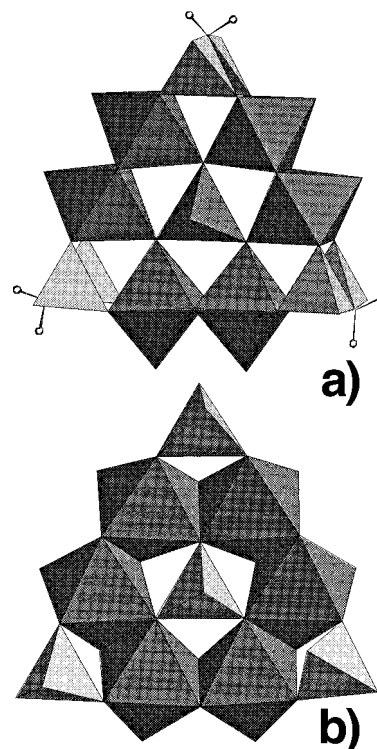
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Figure 2. Polyhedral representation of the molecular anions of (a) $[Mo^V_6Mo^{VI}O_{16}(O_3PCH_2PO_3)_3]^{8-}$ (denoted P_6Mo_7) and (b) $[P_4Mo_6O_{28}(OH)_3]^{9-}$ (denoted P_4Mo_6).

phosphorus atom fits well in the smaller void of P_4Mo_6 (average $d_{P-O} = 1.52$ Å) but is too small for P_6Mo_7 where it is replaced by molybdenum (average $d_{Mo-O} = 1.79$ Å).

The two anions differ substantially also in the bonding at the periphery of the ring. The three peripheral phosphate groups in P_4Mo_6 are bidentate and connect the units by single O−P−O bridges. In P_6Mo_7, on the other hand, the phosphates are "replaced" by methylenediphosphonate groups which coordinate as tetradentate ligands with two oxygen atoms per phosphonate functionality. This, again, is possible only because the edge-sharing mode between the dimers of P_4Mo_6 is replaced with corner-sharing in P_6Mo_7 which provides two more octahedral corners available for coordination by the peripheral group. The methylene linkers in the methylenediphosphonate provide also some degree of hydrophobicity which can potentially lead to different behavior

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of these anions when used for building structures of higher dimensionality.

The P_6Mo_7 anions in the structures are well separated by diprotonated ethylenediamine or piperazine cations as well as water molecules (see the figures in Supporting Information). They are involved also in a vast net of hydrogen bonding with both the cations and the water molecules. The IR spectra display a common general pattern of five bands in the $1000-1200$ cm^{-1} region that are attributed to the P−O stretching vibrations and a sharp and intense band at 957 and 954 cm^{-1} for **1** and **2**, respectively, from the asymmetric Mo−O vibration for the terminal oxygen atoms.[11] They also show similar features for the skeletal vibrations in the region between 300 and 900 cm^{-1}. The main differences between the two spectra occur in the $1300-1600$ and $2000-3500$ cm^{-1} regions that correspond to the vibrations of the diamine cations.

The new mixed-valent molecular anion $[Mo^{VI}Mo^{V}_6O_{16}(O_3PCH_2PO_3)_3]^{8-}$ is another example of a large class of compounds of general formula "$X_4Mo_6E_6$" (E = O, S) in which a flexible oxo(or thio)hexamolybdenum(V) ring can accommodate various central and peripheral X groups. The prototype of this family, first isolated by Haushalter et al., contains phosphate groups in both central and peripheral positions of the molybdenum ring.[10a] The flexibility of the latter was then confirmed with the insertion of a large variety of X groups such as $\{PO_4\}$,[10] $\{C_6H_5PO_3\}$,[12] $\{C_6H_5AsO_3\}$,[13] and $\{CO_3\}$[14] as well as the synthesis of the first reduced sulfate anion with a central $\{As^{III}O_3\}$ and three peripheral $\{SO_4\}$ groups where a lone pair at the arsenic atom replaces the terminal oxygen atom.[15] The system was later extended to the oxo*thio* chemistry by the synthesis of the anions $[X_4Mo_6S_6O_6(OH)_3]^{5-}$ (X = HPO$_4$, HAsO$_4$) where six sulfur atoms were inserted in the bridging positions of the dimolybdenum pairs.[16,17] Successive substitution of the peripheralphosphate groups by arsenate or acetate groups has been illustrated by NMR studies,[16] as well as regioselective partial S/O substitution allowing the characterization of "$P_4Mo_6S_{6-x}O_x$" ($0 \leq x \leq 3$) species.[17] In the solid state, these species are often found as dimers of parallel rings positioned with the capping groups pointing outward and interacting via an alkali- or transition-metal cation which is in octahedral coordination between them.[10,12,13,15−17] The existence of the title anion proves further that the ring is not only flexible in bonding to different central groups but is also flexible in the modes of sharing the molybdenum dimers and in the Mo−O distances. The three peripheral diphosphonate groups induce different bonding and an overall widening of the ring, and the latter accommodates these changes by simply incorporating a larger central capping $\{Mo^{VI}O_4\}$ tetrahedron. The title anion offers new perspectives and ideas on how eventual three-dimensional networks of such building units and multifunctional linkers might be designed.

Supporting Information Available: Figure of the anion in **1** with all atoms labeled, two figures showing the packing of the anions, cations, and water molecules in **1**, and an X-ray crystallographic file for the two structures in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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