Inorg. Chem. **2003**, *42*, 7304–7308

Inorganic Chemistry

Article

Novel Mixed-Valence Heteropolyoxometalates: A Molybdenum Diphosphonate Anion $[\mathrm{Mo^{V}{}_7Mo^{VI}O_{16}(O_3PPhPO_3H)_4}]^{3-}$ and Its One- and Two-Dimensional Assemblies

Nathalie Calin and Slavi C. Sevov*

Department of Chemistry and Biochemistry, University of Notre Dame,
Notre Dame, Indiana 46556

Received May 12, 2003

A novel mixed-valence polyoxomolybdenum anion, $[\mathrm{Mo^{V}{}_7Mo^{VI}O_{16}(O_3PPhPO_3H)_4}]^{3-}$, was synthesized hydrothermally from molybdenum oxide, molybdenum metal, boric and phosphoric acids, 1,2-phenyldiphosphonic acid, and imidazole (ImH) and was structurally characterized as an imidazolium salt (orthorhombic, *Aba*2; $a = 16.674(4)$, $b = 17.238(1)$, and $c = 24.81(2)$ Å). One- and two-dimensional structures of this anion and additional molybdenum diphosphonate linkers were assembled as well. They were structurally characterized as their pyridinium (pyH) salts $\mathrm{(pyH)_4[\{Mo^{V}{}_7Mo^{VI}O_{16}(O_3PPhPO_3)_2(O_3PPhPO_3H)_2\}\{Mo_2O_4(OH)(HO_3PPhPO_3H)\}]\cdot 5H_2O}$ (monoclinic, $P2_1/c$; $a = 20.8506(9)$, $b = 22.866(1)$, and $c = 21.1403(9)$ Å; $\beta = 118.7087(8)°$) and $\mathrm{(pyH)_3[\{Mo^{V}{}_7Mo^{VI}O_{16}(O_3PPhPO_3)_4\}\{Mo_2O_2(OH)_2(HO_3PPhPO_3H)\}]\cdot 3H_2O}$ (orthorhombic, $Pca2_1$; $a = 19.057(1)$, $b = 20.402(2)$, and $c = 20.660(2)$ Å). The compounds were also characterized by IR spectroscopy and magnetic measurements.

Introduction

The heteropolyoxometalates as a class of compounds have been studied very extensively for their potential applications in the fields of catalysis, medicine, and various applied sciences.[1] Various approaches for their synthesis and postsynthetic modifications are available.[2] On the other hand, several strategies for systematic construction of frameworks from variety of molecular building blocks are also known.[3] Perhaps the oldest of these strategies is the hydrothermal synthesis in the presence of structure-directing templates. Its success has been demonstrated by both the enormous diversity of systems for which it can be applied and by the huge number of compounds with various dimensionalities that can be achieved only by this technique. One of the syntheses for which this method has been successful is the synthesis of reduced or mixed-valence heteropolyoxometalates.[4] Hydrothermal synthesis provides also the capability of using elemental transition metals as the reducing agents in the reaction mixture. Recently, we reported the hydrothermal synthesis and structure of a mixed-valence polyoxomolybdenum anion with two different heterogroups, borate and phosphate, $[\mathrm{Mo^{V}{}_5Mo^{VI}{}_7O_{22}(BO_4)_2(PO_4)_5(HPO_4)_3}]^{8-}$, where one of the starting materials was elemental molybdenum.[5] Six of the phosphate groups are part of the outer shell of the species and have terminal oxygen or hydroxyl groups that can be “replaced” by phenyl groups, and the same anion was later synthesized with six phenylphosphonate groups at these positions, $[\mathrm{Mo^{V}{}_5Mo^{VI}{}_7O_{22}(BO_4)_2(PO_4)_2(PhPO_3)_6}]$.[6] This novel borophosphonate is one step closer to building a covalently bonded extended structure of polyoxometalates as it is easy to envision the use of phenyldiphosphonate as the linker between them. Although there are many compounds that claim to be extended structures of polyoxometalates, only very few of them are actually connected by covalently bonded linkers.[7] In the majority cases the anions are assembled via either hydrogen bonds or coordination to transition-metal or rare-earth cations. Here we report the hydrothermal synthesis and characterization of a novel

---

* To whom correspondence should be addressed. E-mail: ssevov@nd.edu.

(1) See the articles in issue 1: Hill, C. L., Guest Ed. *Chem. Rev.* **1998**, *98*, 8.

(2) Pope, M. T. *Heteropoly and isopoly oxometalates*; Spring-Verlag: Berlin, 1983.

(3) (a) Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3052. (b) Ferey, G. J. *J. Solid State Chem.* **2000**, *152*, 37. (c) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem. Mater.* **1999**, *11*, 2633. (d) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638.

(4) Haushalter, R.; Mundi, L. *Chem. Mater.* **1992**, *4*, 31 and references therein.

(5) Dumas, E.; Sevov, S. C. *J. Am. Chem. Soc.* **2002**, *124*, 908.

(6) Sassoye, C.; Norton, K.; Sevov, S. C. *Inorg. Chem.* **2003**, *42*, 1652.

(7) (a) Finn, R. C.; Burkholder, E.; Zubieta, J. *Chem. Commun.* **2001**, *18*, 1852. (b) Finn, R. C.; Zubieta, J. *Inorg. Chem.* **2001**, *40*, 2466.

10.1021/ic034505c CCC: $25.00

© 2003 American Chemical Society
Published on Web 10/02/2003

Table 1. Crystallographic Data for $(ImH_2)_3(\mathbf{1})$, $(pyH)_4(\mathbf{2})$, and $(pyH)_3(\mathbf{3})$

param	$(ImH_2)_3(\mathbf{1})$	$(pyH)_4(\mathbf{2})$	$(pyH)_3(\mathbf{3})$
fw	2170.93	2882.75	2747.98
space group, Z	$Aba2$, 4	$P2_1/c$, 4	$Pca2_1$, 4
a (Å)	16.675(4)	20.8506(9)	19.057(1)
b (Å)	17.238(1)	22.866(1)	20.402(2)
c (Å)	24.881(2)	21.1403(9)	20.660(2)
		118.7087(8)	
V (Å^3)	7152(2)	8839	8032
ρ_{calc} (g/cm^3)	2.014	2.139	2.252
radiation, λ (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
temp (K)	293	100	100
μ (cm^{-1})	16.27	16.56	18.13
R1/wR2 for $I \geq 2\sigma_I$ (%)[a]	4.65/11.67	7.26/18.63	5.11/11.49
R1/wR2 for all data (%)[a]	5.85/12.37	8.72/19.80	6.20/12.08

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{[\Sigma w[(F_o)^2 - (F_c)^2]^2]/[\Sigma w(F^2o)^2]\}^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$, where $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$ and $P = [(F_o)^2 + 2(F_c)^2]/3$: $A = 0.0792$ and $B = 0$ for $(ImH_2)_3(\mathbf{1})$; $A = 0.0825$ and $B = 179.3759$ for $(pyH)_4(\mathbf{2})$; $A = 0.0503$ and $B = 21.1447$ for $(pyH)_3(\mathbf{3})$.

mixed-valence polyoxomolybdenum diphosphonate anion $[Mo^{V}_7Mo^{VI}O_{16}(O_3PPhPO_3H)_4]^{3-}$ (**1**) and its one- and two-dimensional derivatives, $[\{Mo^{V}_7Mo^{VI}O_{16}(O_3PPhPO_3)_2(O_3PPhPO_3H)_2\}\{Mo^{VI}_2O_4(OH)(HO_3PPhPO_3\ H)\}]^{4-}$ (**2**) and $[\{Mo^{V}_7Mo^{VI}O_{16}(O_3PPhPO_3)_4\}\{Mo^{VI}_2O_2(OH)_2(HO_3PPhPO_3H)\}]^{3-}$ (**3**), respectively, assembled via additional molybdenum diphosphonate groups.

Experimental Section

Synthesis. The imidazolium $(ImH_2)^+$ salt of **1** was prepared by the hydrothermal reaction of MoO_3 (Baker, 99.9%), elemental Mo (Acros, 99.99%), boric acid (Acros, 99.5%), imidazole (Alfa-Aesar, 99%), 1,2-bis(dimethoxyphosphoryl)benzene (Alfa-Aesar, 99%), phosphoric acid (Fisher, 85%), and deionized water in a molar ratio of 1:0.25:5:3.3:0.8:1.2:445. The mixture was stirred, and the pH was adjusted to 2.0 with hydrochloric acid (Fisher). Initially, the pyridinium $(pyH)^+$ salts of **1**−**3** were synthesized from similar mixtures with the same molar ratios but using pyridine (Fisher) instead of imidazole and pH of 1.5 (adjusted with HCl). This synthesis was later optimized by leaving out the boric and phosphoric acids. In a typical reaction 2 mL of the reaction mixture is loaded in a 23 mL Teflon-lined acid digestion bomb, and it is then heated for 5 days at 175 °C (final pH = 1.5). The solid products were collected by filtration, washed with water, and dried at room temperature. All compounds are dark purple, almost blue, and while $(ImH_2)_3(\mathbf{1})$ was synthesized as a single-phase product, the reactions with pyridine always provided the three compounds $(pyH)_3(\mathbf{1})$, $(pyH)_4(\mathbf{2})$, and $(pyH)_3(\mathbf{3})$. Apparently, the amount of reaction mixture inside the Teflon containers and the pH values are very important for whether the compounds form and whether other impurities will form. Variations of these often lead to formation of unknown brown powder as an impurity.

Structure Determination. Single-crystal X-ray diffraction data were collected with Mo Kα radiation on single crystals of $(ImH_2)_3(\mathbf{1})$ (0.20 × 0.20 × 0.15 mm) on an Enraf-Nonius CAD4 diffractometer and of $(pyH)_3(\mathbf{1})$ (0.20 × 0.20 × 0.16 mm), $(pyH)_4(\mathbf{2})$ (0.28 × 0.24 × 0.05 mm), and $(pyH)_3(\mathbf{3})$ (0.11 × 0.09 × 0.03 mm) on a Bruker APEX diffractometer with a CCD area detector. The structures were solved by direct methods and were refined (on F^2) using the SHELXTL V5.1 package. Details of the data collections and refinements are summarized in Table 1. The structure of $(pyH)_3(\mathbf{1})$ is clearly similar to $(ImH_2)_3(\mathbf{1})$ but could not be refined satisfactory and is not presented here.

Properties. The magnetizations of 28 mg of $(ImH_2)_3(\mathbf{1})$, 4 mg of $(pyH)_4(\mathbf{2})$, and 3 mg of $(pyH)_3(\mathbf{3})$ were measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T for the first one and of 6 T for the latter two over the temperature range of 10−250 K. The temperature dependencies of the molar magnetic susceptibilities of the compounds showed Curie−Weiss behavior. They were fitted with $\chi = C/(T - \Theta) + \chi_0$, where χ_0 is a temperature-independent contribution to the paramagnetism. The accuracies of the fits were better than 99.99%, and the following parameters were obtained from these fits: $C = 0.229(1)$ (emu·K)/mol, $\Theta = -0.48(6)$ K, and $\chi_0 = 98(1) \times 10^{-5}$ emu/mol for $(ImH_2)_3(\mathbf{1})$; $C = 0.130(1)$ (emu·K)/mol, $\Theta = 0.70(9)$ K, and $\chi_0 = 40(1) \times 10^{-5}$ emu/mol for $(pyH)_4(\mathbf{2})$; $C = 0.561(7)$ (emu·K)/mol, $\Theta = -1.8(2)$ K, and $\chi_0 = 200(7) \times 10^{-5}$ emu/mol for $(pyH)_3(\mathbf{3})$. EPR spectra of the three compounds were taken on a Bruker EMX EPR spectrometer at 77 K. All three compounds showed nice isotropic and strong signals with g values of 1.9252, 1.9212, and 1.9194 for **1**−**3**, respectively. IR (pellets with KBr) spectra were obtained on an Perkin-Elmer Paragon 1000 FT spectrometer.

Results and Discussion

The isolated anion **1** is characterized as its imidazolium and pyridinium salts, $(ImH_2)_3(\mathbf{1})$ and $(pyH)_3(\mathbf{1})$, respectively. It is a novel ring made of eight MoO_6 octahedra that share alternatingly corners and edges (Figure 1). This mode of fusion of octahedra in small rings is quite rare. The only other example is a hexameric ring of octahedra that is capped on one side by MoO_4 tetrahedron, $[MoMo_6O_{16}(O_3PCH_2PO_3)_3]^{8-}$ (Figure 2a).[8] Other modes of fusion are more typical for most of the known small rings of octahedra. Some examples are rings of six edge-sharing octahedra, $[PMo_6O_{22}(O_3POH)_3]^{9-}$ (Figure 2b),[9] and rings of eight octahedra that share alternatingly faces and edges, $[WMo_8S_8O_{11}(OH)_{11}]^{3-}$ (Figure 2c).[10] The higher degree of fusion observed in the last two examples is needed most likely because of the small number of MoO_6 oxygen atoms that are shared with other groups, i.e., only six with the phosphate groups in $[PMo_6O_{22}(O_3POH)_3]^{9-}$ and none in $[WMo_8S_8O_{11}(OH)_{11}]^{3-}$. On the

---

(8) Dumas, E.; Sassoye, C.; Smith, K. D.; Sevov, S. C. *Inorg. Chem.* **2002**, *41*, 4029.

(9) (a) Haushalter, R. C.; Lai, F. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 743. (b) Haushalter, R. C.; Lai, F. W. *Inorg. Chem.* **1989**, *28*, 2904. (c) Mundi, L. A.; Haushalter, R. C. *Inorg. Chem.* **1992**, *31*, 3050. (d) Meyer, L. A.; Haushalter, R. C. *Inorg. Chem.* **1993**, *32*, 1579. (e) Guesdon, A.; Borel, M. M.; Leclaire, A.; Raveau, B. *Chem.−Eur. J.* **1997**, *3*, 1797. (f) Du Peloux, C.; Mialane, P.; Dolbecq, A.; Marrot, J.; Rivière, E.; Sécheresse, F. *J. Mater. Chem.* **2001**, *11*, 3392.

(10) Dollbecq, A.; du Peloux, C.; Auberty, A. L.; Mason, S. A.; Barboux, P.; Marrot, J.; Cadot, E.; Sécheresse, F. *Chem.−Eur. J.* **2002**, *8*, 350.

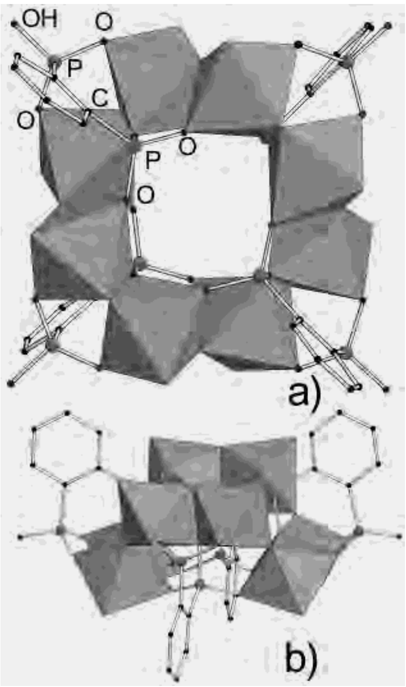

Figure 1. Two views of the isolated ring **1** made of eight MoO_6 octahedra that alternatingly share corners and edges and four phenyldiphosphonate groups: (a) the center of the ring is open; (b) the ring is puckered with approximate symmetry of D_{2d}.

other hand, the diphosphonates are multidentate ligands that can coordinate and share all of their six oxygen atoms. As it can be seen in Figure 2a, each methylenediphosphonate coordinates with four oxygen atoms in $[MoMo_6O_{16}(O_3PCH_2PO_3)_3]^{8-}$. Similarly, each phenyldiphosphonate molecule in **1** (Figure 1) uses five oxygen atoms for coordination to molybdenum atoms from the ring. The sixth phosphonic oxygen atom in **1** is protonated giving the overall formula $[Mo_8O_{16}(O_3PPhPO_3H)_4]^{3-}$.

While the known rings discussed above are flat and either capped along the ring axis or centered (Figure 2),[8−10] the novel ring **1** is puckered and empty (Figure 1). This geometry for **1** is simply a result of the specific connectivity within the ring. The only way for four dimers of edge-fused octahedra to form a ring via corner-sharing is to share corners of the edges that are parallel to the fused edge. This leads ultimately to puckering and the observed shape of approximate symmetry D_{2d}. The pentadentate phenyldiphosphonate coordinates to three dimers with one phosphonate group while the second such group coordinates two of its oxygens to one dimer (Figure 1). The geometry of the ring and this particular coordination of the diphosphonates provide four terminal P−OH functionalities positioned at the corners of a square (Figure 1a). These groups are available and can participate in additional bonding by coordinating to other available metal centers to form extended structures. The charge of the anion, 3−, the measured Curie−Weiss magnetic behavior that corresponds approximately to one unpaired electron, the EPR results, and the calculated low valence sums for the terminal phosphonate oxygen atoms indicate that (a) the latter are protonated and (b) one of the eight molybdenum atoms is Mo(VI) while the other seven are Mo(V). The available d-electrons from the latter are apparently delocalized, and six of them are paired. The formula of **1** can be therefore written as $[Mo^{V}_{7}Mo^{VI}O_{16}(O_3PPhPO_3H)_4]^{3-}$. Supporting this description are the Mo−Mo distances in the rings compared with those in the known hexameric $[MoMo_6O_{16}(O_3PCH_2PO_3)_3]^{8-}$ (Figure 2a) with similar connectivity between the Mo octahedra, i.e., alternating edge- and corner-sharing.[8] All six Mo atoms of the ring in the latter are Mo^{V} (the central atom is Mo^{VI}) and form single Mo−Mo (d^1−d^1) bonds of 2.55−2.70 Å within the pairs of edge-sharing octahedra while the distances between the corner-sharing centers are nonbonding, ca. 4.5 Å. In contrast, the Mo−Mo distances within the edge- and corner-sharing pairs of octahedra in compound **1** are quite similar, 3.35−3.40 and 3.70−3.75 Å, respectively. This indicates that, first, there are no single Mo−Mo bonds and therefore some of the molybdenum atoms are Mo^{VI} and, second, the Mo−Mo interactions, as weak as they might be, are distributed more or less evenly over the ring. These observations are consistent with delocalized electrons and mixed-valent molybdenum. The latter is also supported by the color of the compounds, deep purple to deep blue.

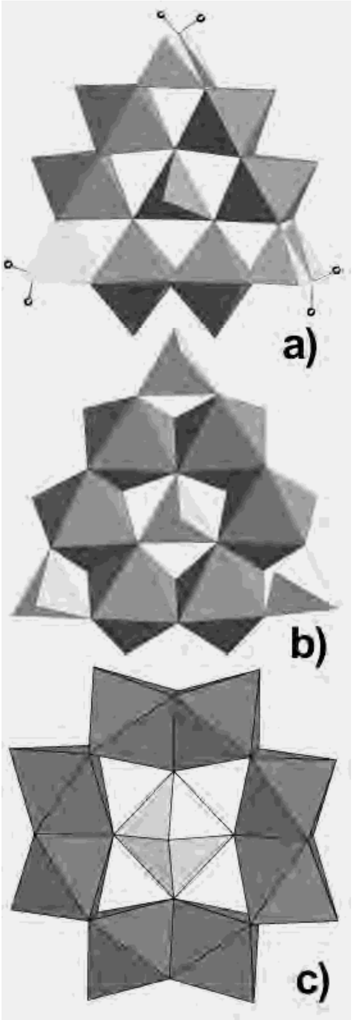

Figure 2. Various small rings with different connectivity between the octahedra: (a) $[MoMo_6O_{16}(O_3PCH_2PO_3)_3]^{8-}$ with alternatingly shared corners and edges;[8] (b) $[PMo_6O_{22}(O_3POH)_3]^{9-}$ with shared edges only;[9] (c) $[WMo_8S_8O_{11}(OH)_{11}]^{3-}$ with alternatingly shared edges and faces.[10]

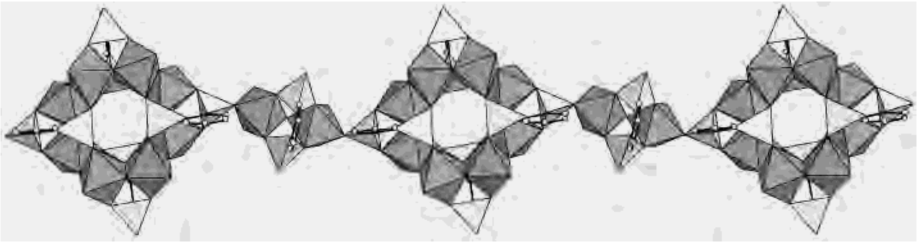

Figure 3. Chain of **2** made of rings **1** connected to each other via a linker made of two corner-sharing MoO_6 octahedra and a phenylphosphonate group.

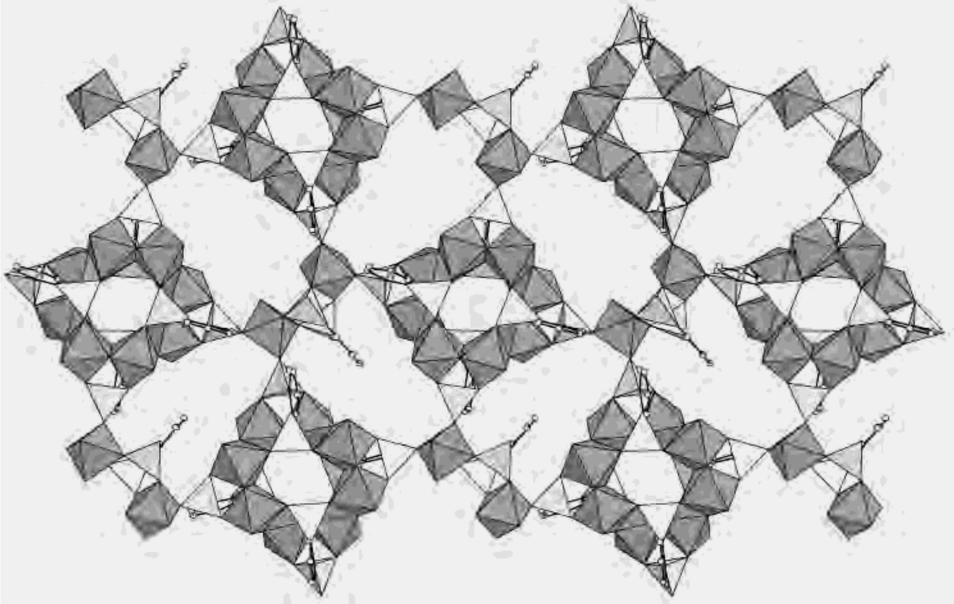

Figure 4. Layer of **3** made of rings of **1** connected to four rings of the same kind via linkers made of two MoO_6 octahedra and a phenyldiophosphonate group.

Compounds of Mo^V only or localized bonding are typically red, while molybdenum mixed-valence compounds with delocalized electrons are typically blue.

The IR spectrum of $(ImH_2)_3$(**1**) displays the bands typical for imidazolium, aromatic C−C vibrations, phosphonate group, and various skeletal vibrations below 800 cm^{-1}. The compound is soluble in a mixture of pyridine and 1 M HCl in equal volumes. The IR of the solid after evaporation of the solvent is virtually unchanged in the anionic part. The only differences are that bands due to the pyridinium cation have appeared while those of the imidazolium cation have either disappeared or have been significantly reduced. Unfortunately, the solid material could not be crystallized well enough for characterization by X-ray diffraction. Nevertheless, the existence of the corresponding compound $(pyH)_3$(**1**) was proven by its direct synthesis at the same conditions as for the imidazolium analogue but using pyridine. It contains the same isolated ringlike anions, and the only difference are the countercations.

Anion **2**, $[\{Mo^V{}_7Mo^{VI}O_{16}(O_3PPhPO_3)_2(O_3PPhPO_3H)_2\}\{Mo^{VI}{}_2O_4(OH)(HO_3PPhPO_3\,H)\}]^{4-}$, is the repeating unit of a chain formed when two opposite P−OH groups of the monomer **1** connect to linking groups made of two corner-sharing MoO_6 octahedra and a diphosphonate molecule (Figure 3). The phosphonate terminal oxygen atoms of the other two corners of the ring remain protonated giving the formula of the ring as $\{Mo^V{}_7Mo^{VI}O_{16}(O_3PPhPO_3)_2(O_3PPhPO_3H)_2\}$. The distances within the ring and the corresponding valence sums of the atoms are virtually the same as for the isolated monomer and indicate that the oxidation state of molybdenum remains the same. This is confirmed with the observed Curie−Weiss behavior of the magnetic susceptibility.

The two MoO_6 octahedra of the group linking the rings share an oxygen corner (Figure 3). The phenylphosphonic group coordinates to these two octahedra with four of its oxygen atoms, two of each phosphonic end to one molybdenum atom. The remaining two phosphonic and one MoO_6 oxygen atoms are protonated giving a formula of $\{Mo_2O_4(OH)(HO_3PPhPO_3H)\}$ for the linker. The latter shares oxygen atoms, one per MoO_6 octahedron, with two rings to form the chain. These connections are very likely achieved by dehydration of Mo−OH and P−OH groups from the linker and the ring, respectively; i.e., monomers such as $\{Mo_2O_4(OH)_3(HO_3PPhPO_3H)\}^-$ and $\{Mo^V{}_7Mo^{VI}O_{16}(O_3PPhPO_3H)_4\}^{3-}$ couple to produce H_2O and $[\{Mo^V{}_7Mo^{VI}O_{16}(O_3PPhPO_3)_2(O_3PPhPO_3H)_2\}\{Mo_2O_4(OH)(HO_3PPhPO_3H)\}]^{4-}$.

Anion **3**, $[\{Mo^V{}_7Mo^{VI}O_{16}(O_3PPhPO_3)_4\}\{Mo^{VI}{}_2O_2(OH)_2(HO_3PPhPO_3H)\}]^{3-}$, is the repeating unit of a layer formed by linking the rings of **1** to four other rings of the same kind (Figure 4). Each ring uses all four P−OH groups to connect to the same linking groups as those in **2** made of two MoO_6 octahedra and a diphosphonate group. The difference in the linkers is that the octahedra in **3** are not directly connected

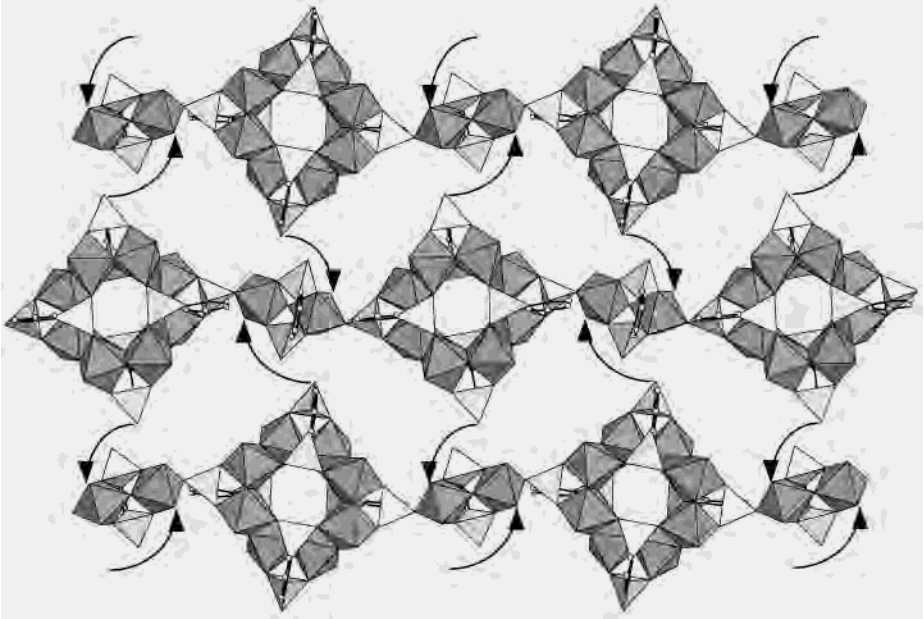

Figure 5. Part of the structure of $(pyH)_4(\mathbf{2})$ showing how the chains are positioned with respect to each other and how close this order is to the structure of the layer (Figure 4). The arrows show how phosphonic OH groups and corners of the linkers should be connected to achieve the layer structure of **3**.

to each other as in **2** but only via the diphosphonate. The latter is coordinated and protonated in the same way as in **2**. Each MoO_6 octahedron shares two oxygen atoms with rings, and therefore, the linker connects to four rings (Figure 4). The connections between the rings and the linkers can be viewed again as achieved via dehydration of Mo−OH and P−OH groups, i.e., as made of monomers of $\{Mo_2O_2(OH)_6(HO_3PPhPO_3H)\}$ and $\{Mo^{V}_7Mo^{VI}O_{16}(O_3PPhPO_3H)_4\}^{3-}$ that couple via dehydration to a layer with repeating unit of $[\{Mo^{V}_7Mo^{VI}O_{16}(O_3PPhPO_3)_4\}\{Mo^{VI}_2O_2(OH)_2(HO_3PPhPO_3H)\}]^{3-}$. The IR spectra of $(pyH)_4(\mathbf{2})$ and $(pyH)_3(\mathbf{3})$ display bands characteristic for pyridinium cations in addition to the same bands for aromatic C−C, phosphonate groups, and various skeletal vibrations as for $(ImH_2)_3(\mathbf{1})$.

A closer look at a layer of $(pyH)_3(\mathbf{3})$ and the positioning of the chains with respect to each other in $(pyH)_4(\mathbf{2})$ reveals that the chains of **2** can be easily recognized in **3** and that they form the same pattern (Figure 5). In both structures each chain is shifted by half of the repeating unit with respect to the neighboring chains. Thus, for the structure of $(pyH)_4(\mathbf{2})$ each linker is already surrounded by four rings but only two of them are connected to it. Going from this structure to that of $(pyH)_3(\mathbf{3})$ takes a very small step that couples two more oxygen atoms of the linker in **2** with the two nearby groups of P−OH as shown with arrows in Figure 5. This coupling evidently requires some twisting of the linker (Figures 4 and 5) which cannot be accomplished with two corner-sharing octahedra, and as a result of this, the link is severed. The apparent ease of the “transformation” from **2** to **3** is most likely the reason it has been impossible to synthesize the two compounds as pure phases.

The novel ring of eight MoO_6 octahedra and four 1,2-phenyldiphosphonic groups appears to be quite a stable formation judging from the four different compounds with three different dimensionalities in which it has been found. Therefore, it can be reasonably assumed that these species are perhaps also stable and predominant in the starting solutions under hydrothermal conditions. It seems that very minute differences in the local environment direct the crystallization to monomers, chains, or layers. The availability of four phosphonic OH groups of the monomer can be exploited further for formation of better defined structures with various dimensionality if linkers that can bond better to these groups can be found. Among the candidates are transition metals that coordinate easily to such phosphonic oxygens.

Acknowledgment. We thank the National Science Foundation (Grant DMR-0139565) for the financial support of this research.

Supporting Information Available: X-ray crystallographic files for the three structures in CIF format, plots of the temperature dependence of the magnetic susceptibilities of the three compounds, and a table with the calculated bond-valence sums for the oxygen atoms. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034505C