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Hydrothermal Synthesis of a Three-Dimensional Organic–Inorganic Hybrid Network Formed by Poly(oxomolybdophosphate) Anions and Nickel Coordination Cations

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A novel organic–inorganic hybrid nickel molybdenum(V) phosphate has been synthesized hydrothermally and characterized by single-crystal X-ray diffraction, thermogravimetric analysis, and magnetic susceptibility. The structure consists of poly(oxomolybdophosphate) anions linked by both Ni^{II} cations and 4,4-bipyridine bridging ligands to form a three-dimensional open-framework structure with large cavities where the uncoordinated 4,4′-bipyridinium cations and lattice water molecules are located. This is the first example of an extended framework solid containing poly(oxomolybdophosphate) anions interconnected by both transition-metal complexes and organic moieties. Crystal data: $(4,4'\text{-}H_2bpy)[Ni(4,4'\text{-}bpy)(H_2O)_2Ni_{0.5}Mo_6(OH)_3O_{12}(HPO_4)_4]\cdot 2H_2O$, orthorhombic, space group *Pccn* (No. 56), $a = 27.745(2)$ Å, $b = 16.158(1)$ Å, $c = 22.819(2)$ Å, $V = 10230.3(1)$ Å^3, and $Z = 8$.

Recently, many research activities have focused on the synthesis of open-framework metal phosphates with organic ligands because of their interesting structural chemistry and potential applications.[1−3] The underlying idea is to combine the robustness of inorganic phosphate frameworks with the versatility and chemical flexibility of organic ligands. Such organic−inorganic hybrid compounds can also combine the characteristics of each component to produce novel structural types. It has been established that oxalate readily substitutes for phosphate in the skeletons of inorganic phosphates, forming a large number of oxalate−phosphate hybrid compounds.[4] Another class of organic−inorganic hybrid compounds is based on 4,4′-bipyridine and phosphate, in which the metal atoms are coordinated by both types of ligands.[5]

A large number of reduced molybdenum phosphates containing Mo−Mo bonds have been synthesized under hydrothermal conditions in the presence of organic cationic templates.[1] These compounds include molecular ionic aggregates, one-dimensional (1D) polymers, 2D layer structures, and 3D microporous solids. Under the reaction conditions, the structural unit is commonly the poly(oxomolybdophosphate) cluster $[Mo_6P_4O_{28}(OH)_3]^{9-}$, denoted as Mo_6P_4, a very stable species often encountered in the chemistry of molybdenum(V) phosphates. A lot of research efforts have been focused on the assembly of the poly(oxomolybdophosphate) anions into larger clusters or to 1D, 2D, and 3D extended frameworks. d-block elements have been widely used as the linker atoms to bridge cluster anions.[6] To our knowledge, extended framework solids containing poly(oxomolybdophosphate) anions interconnected by both transition-metal complexes and organic moieties have not been reported. This work presents a novel

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organic–inorganic hybrid nickel molybdenum(V) phosphate, $(4,4'\text{-}H_2bpy)[Ni(4,4'\text{-}bpy)(H_2O)_2Ni_{0.5}Mo_6(OH)_3O_{12}(HPO_4)_4]\cdot 2H_2O$ (denoted as **1**), which is the first example of a 3D framework constructed by poly(oxomolybdophosphate) anions and nickel aromatic amine components linked via covalent bonds. In this structure, the 4,4′-bpy unit is incorporated in two distinct forms: one is in the free state as a countercation, and the other one is a bridging ligand linked to two metal atoms.

Hydrothermal reaction of $NiSO_4\cdot 6H_2O$, MoO_3, Mo, $(NH_4)H_2PO_4$, H_3PO_4, 4,4′-bipyridine, H_2O, and butan-1-ol in the molar ratio of 0.3:1:0.2:4:2:4:333:65.6 in a 23-mL Teflon-lined acid digestion bomb at 160 °C for 3 days yielded red-brown block crystals of **1** as the major product and a small amount of unidentified orange plate crystals. A suitable red-brown crystal was selected for structure determination by single-crystal X-ray diffraction.[7] The crystals were easily separated by hand sorting, and the yield of **1** was 55% based on Ni. The purity of the sample for property measurements was confirmed by powder X-ray diffraction (Figure S1 in the Supporting Information). Anal. Calcd: C, 14.39; H, 1.98; N, 3.36. Found: C, 14.44; H, 2.07; N, 3.47. A thermogravimetric analysis (TGA) was performed by heating the sample in flowing O_2 from 50 to 900 °C. The TGA curve shows a step of weight loss in the temperature range 50–200 °C and several overlapping steps of weight loss in 200–900 °C (see Figure S2 in the Supporting Information). The first (50–200 °C) corresponds to the release of lattice water molecules (obsd 2.3%, $2H_2O$ calcd 2.14%). The final decomposition products were not identified. Powder X-ray diffraction studies of a sample of **1** that had been heated at 200, 250, 275, and 300 °C for several hours in air and then cooled to room temperature revealed that the compound is stable up to 200 °C, changes to a different crystalline product at 250 °C, and decomposes at 275 °C. Variable-temperature magnetic susceptibility data were obtained on 26.1 mg of a polycrystalline sample of **1** in a magnetic field of 5 kG after zero-field cooling. The data from 2 to 300 K were described well by a Curie–Weiss equation: $\chi_M = C/(T - \theta)$, where $C = 2.11\ \text{cm}^3\cdot\text{K/mol}$ and $\theta = -0.31$ K (Figure S3 in the Supporting Information). From the equation $C = N\mu_{\text{eff}}/3k_B$, the effective magnetic moment μ_{eff} per Ni atom is 3.36 μ_B, which is consistent with the observation that the magnetic moments of Ni^{II} complexes are generally in the range from 2.8 to 4.0 μ_B.

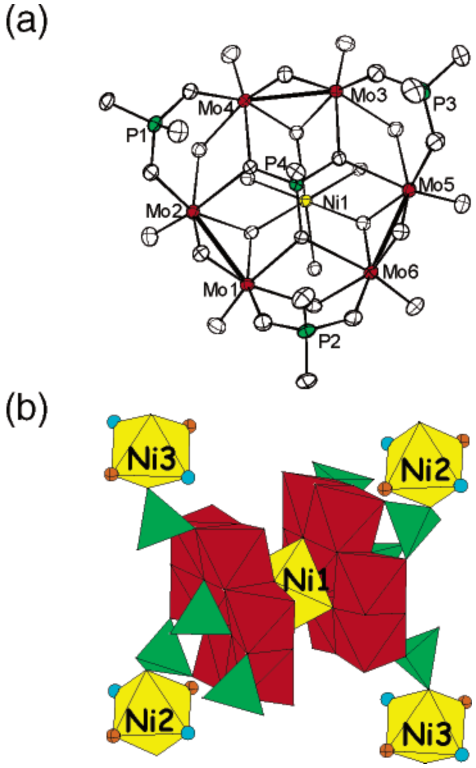

Figure 1. (a) Ball-and-stick representation of an anionic hexamer $[Mo_6O_{12}(OH)_3(HPO_4)_4]$ in **1**. Thermal ellipsoids are shown at 50% probability. The H atoms are not shown. (b) Polyhedral representation of a $Ni[Mo_6O_{12}(OH)_3(HPO_4)_4]_2$ cluster.

The structure of **1** consists of $Ni[Mo_6O_{12}(OH)_3(HPO_4)_4]_2$ (denoted as $Ni[Mo_6P_4]_2$) clusters, $[Ni(4,4'\text{-}bpy)(H_2O)_2]$ structural units, bipyridinium cations, and lattice water molecules. As shown in Figure 1, the Mo_6P_4 cluster has a ring of six edge-sharing MoO_6 octahedra with alternating three long Mo···Mo contacts (3.52 Å) and three short Mo–Mo single bonds (2.60 Å). A central phosphate group bridges the ring internally, and each one of the other three phosphate groups bridges one long Mo···Mo contact externally. Bond-valence calculation results indicate that the Mo atoms are pentavalent, each phosphate has a hydroxyl group, and the three μ_2-O atoms that bridge long Mo···Mo contacts are hydroxyl O atoms.[8]

There are three crystallographically different Ni atoms, which can be divided into two types. Ni1 bridges two Mo_6P_4 clusters via six μ_3-O atoms, which link the metal–metal-bonded Mo atoms together to produce $[Ni(Mo_6P_4)_2]$ dimers with a local symmetry of C_i (Figure 1). Note that the Mo–Mo bonds and the central phosphate groups on the two rings are staggered relative to each other. The $M[Mo_6P_4]_2$ (M = alkali or transition metals) dimers have been observed in a great number of reduced molybdenum phosphate derivatives. The second type of Ni atoms, Ni2 and Ni3, is coordinated by two phosphate O atoms from two $Ni[Mo_6P_4]_2$ clusters, two water molecules, and two N atoms from two 4,4′-bpy ligands at trans positions, forming $[Ni(4,4'\text{-}bpy)_{2/2}(H_2O)_{2/1}]$ structural units with a local symmetry of C_2 (Figure 2). The fractional numbers in the chemical formula denote that each 4,4′-bpy ligand is coordinated to two Ni atoms and the

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(7) Crystal data for $(4,4'\text{-}H_2bpy)[Ni(4,4'\text{-}bpy)(H_2O)_2Ni_{0.5}Mo_6(OH)_3O_{12}(HPO_4)_4]\cdot 2H_2O$: orthorhombic, space group *Pccn* (No. 56) with $a = 27.745(2)$ Å, $b = 16.158(1)$ Å, $c = 22.819(2)$ Å, $V = 10230.3(1)$ Å^3, and $Z = 8$, 10 191 absorption corrected reflections with $F_o > 4\sigma(F_o)$ out of 12 655 unique reflections [$R_{\text{int}} = 0.0476$; $2\theta_{\text{max}} = 56.6°$] measured at 21 °C for a red-brown crystal of dimensions 0.30 × 0.175 × 0.10 mm on a Siemens Apex CCD diffractometer on convergence gave final values of R1 = 0.0414, wR2(F^2) = 0.1568, GOF = 1.098, residual electron density between +3.00 and −0.87 e·Å^{-3}. The H atoms in the hydroxyl groups are not located. O32 and O33, which are coordinated to Ni2 and Ni3, respectively, are water O atoms. Only one lattice water O atom was located in the difference Fourier maps. All non-H atoms were refined with anisotropic thermal parameters, and the H atoms that are bonded to C atoms were positioned geometrically and were refined using a riding model.

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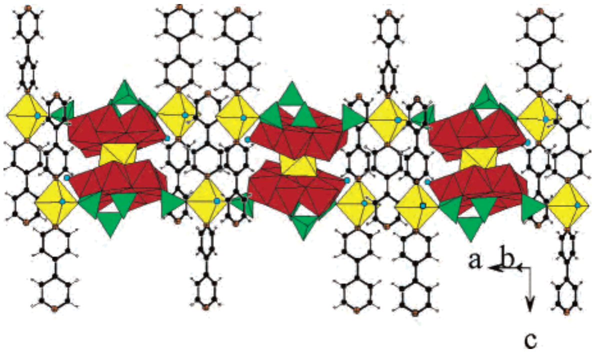

Figure 2. Section of a layer in **1** viewed in a direction perpendicular to the *c* axis showing the connectivity between the $Ni[Mo_6O_{12}(OH)_3(HPO_4)_4]_2$ clusters and $[Ni(4,4'\text{-bpy})(H_2O)_2]$ complexes. Key: red octahedra, MoO_6; yellow octahedra, NiO_6 or NiN_2O_4; green tetrahedra, HPO_4; black circles, C atoms; orange circles, N atoms; cyan circles, H_2O molecules; small open circles, H atoms.

coordination number for the water O atoms is 1. Each $Ni[Mo_6P_4]_2$ cluster is connected to four $[Ni(4,4'\text{-bpy})(H_2O)_2]$ units to form layers in the *ab* plane with large rectangular windows formed by four $[Ni(Mo_6P_4)_2]$ clusters and four $[Ni(4,4'\text{-bpy})(H_2O)_2]$ units (Figure 3). Each 4,4′-bpy ligand coordinates to two Ni atoms, acting as pillars between adjacent layers to produce the extended 3D network. The layer stacking sequence along the *c* axis is ABAB... such that the rectangular windows are not aligned to form straight tunnels and large cavities are created between adjacent layers where the 4,4′-bipyridinium cations and lattice water molecules are located.

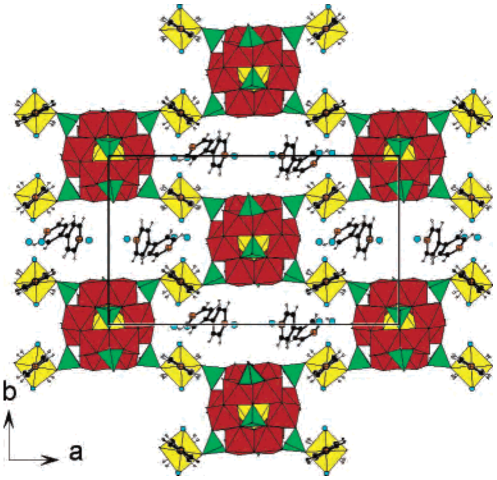

Figure 3. Section of a layer in **1** viewed in a direction parallel to the *c* axis. The layer stacking sequence along the *c* axis is ABAB... such that the rectangular windows are not aligned to form straight tunnels.

In conclusion, an organic−inorganic hybrid molybdenum phosphate with covalently bonded transition-metal coordination complexes has been synthesized by the hydrothermal method. Few analogous systems have been reported: a 3D framework with $[Mo_8O_{26}]^{4-}$ clusters incorporated within the polymeric $\{Ni(H_2O)_2(4,4'\text{-bpy})_2\}_n^{2n+}$ backbone[9] and a 3D framework based on a $\{Ni(4,4'\text{-bpy})_2\}_n^{2n+}$ subunit and entrapped V_{16} clusters $[V^{IV}_7V^{V}_9O_{38}Cl]^{4-}$.[10] Although a good number of compounds containing anionic $M[Mo_6P_4]_2$ dimers connected by transition-metal complexes have been reported, compound **1** is the first example of an extended framework solid containing the poly(oxomolybdophosphate) clusters interconnected by both transition-metal complexes and organic moieties. Linkages of the $M[Mo_6P_4]_2$ building blocks by other metal cations and multidentate organic ligands can be envisaged. Further work on this theme is in progress.

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Supporting Information Available: Crystal data for $(4,4'\text{-}H_2\text{-bpy})[Ni(4,4'\text{-bpy})(H_2O)_2Ni_{0.5}Mo_6(OH)_3O_{12}(HPO_4)_4]\cdot 2H_2O$ in CIF format, X-ray powder diffraction patterns, a TGA curve, and magnetic susceptibility measurement results. The material is available free of charge via the Internet at http://pubs.acs.org.

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