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A New Class of Organic−Inorganic Hybrid Materials: Hydrothermal Synthesis and Structural Characterization of Bimetallic Organophosphonate Oxide Phases of the Mo/Cu/O/RPO_3^{2-} Family

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The incorporation of organic substructures into inorganic oxide phases provides a powerful method for structural modification and synthesis of novel organic−inorganic hybrid materials, which combine the unique features of both the organic and inorganic substructures.[1] Organic components have been introduced not only as structure-directing cations in a wide range of materials including zeolites, mesoporous materials of the MCM-41 class, and transition metal phosphate and oxides, but also as ligands directly coordinated to the inorganic scaffolding of the material.[2] Metal organophosphonate phases are representative hybrid materials which have been extensively studied with respect to the structural consequences of steric demands of the organic subunit, spacer length modifications, and additional functionality.[3,4] Metal organophosphonate oxide phases, $[M_xO_y(RPO_3)_z]$, constitute a subclass of these hybrid materials which conflates the structural versatility of metal oxides with that of organophosphonate architectures. Curiously, while numerous soluble oxide clusters of the type $[Mo_xO_y(O_3PR)_3]^{n-}$ have been described, the only structurally characterized examples of solids are provided by the isomorphous two-dimensional phases $[M_2(MoO_3)_3(O_3PR)]$.[5] In an attempt to extend the chemistry of oxomolybdenum organophosphonate materials, we exploited a strategy previously successful in the preparation of bimetallic phosphonate networks of the oxovanadium family,[6] that is, the introduction of a secondary metal−ligand component as a charge-compensating unit and, more significantly, as a structure-directing component. This communication describes the structural consequences on oxomolybdenum−organodiphosphonate phases of secondary metal−organic subunits, an approach which combines the spatial transmission of structural information by the diphosphonate ligand and surface modification of the oxide material by a bidentate organodiimine ligand. The prototypical materials of a new family of oxomolybdenum organophosphonates $[Cu(o\text{-}phen)(Mo_2O_5)(O_3PCH_2PO_3)(H_2O)]$ **(1)**, $[\{Cu(o\text{-}phen)\}_2(Mo_4O_{12})(H_2O)_2(O_3PCH_2CH_2PO_3)]\cdot 2H_2O$ (**2**$\cdot 2H_2O$), and $[\{Cu(H_2O)_2(o\text{-}phen)\}\{Cu(o\text{-}phen)_2\}(Mo_5O_{15})(O_3PCH_2CH_2CH_2PO_3)]\cdot 2.5H_2O$ (**3**$\cdot 2.5H_2O$) are described.

In a typical reaction, a mixture of $Cu(SO_4)\cdot 5H_2O$, MoO_2, 1,-10-phenanthroline (o-phen), methylenediphosphonic acid, and water in the mole ratio 1.0:2.1:1.4:2.0:3500 was heated at 170 °C for 74 h to give blue plates of **1** in 30% yield.[7] Compounds **2** and **3** were prepared under analogous conditions.

The structure of **1,** shown in Figure 1,[8] consists of one-dimensional chains constructed from corner-sharing Cu(II) square pyramids and phosphorus tetrahedra, and corner- and edge-sharing Mo(VI) octahedra. The coordination sphere of the Cu(II) site is defined by the nitrogen donors of the chelating o-phen ligand, an oxygen donor from each $\{PO_3\}$ group of the chelating methylenediphosphonate ligand, and an oxo group bridging to a molybdenum site. Binuclear Mo sites constructed from edge-sharing octahedra are embedded in the chain, each bonding to three diphosphonate ligands. The diphosphonate units, in turn, chelate a Cu site and employ the remaining four oxygen donors to link three adjacent binuclear molybdenum units.

The profound structural consequences of increasing the diphosphonate tether length by one methylene group are evident in the two-dimensional structure of **2**$\cdot 2H_2O$, shown in Figure 2.[9] The structure may be described as bimetallic oxide phosphate chains linked through ethylene bridges of the diphosphonate ligands into a layer structure. The $\{Cu(o\text{-}phen)(Mo_2O_6)(H_2O)(O_3P-)\}_n$ chains are constructed from noncyclic $\{Mo_4O_{16}\}$ clusters linked through diphosphonate ligands and square pyramidal Cu(II) sites. The copper centers bond to two nitrogen donors from a chelating phenanthroline ligand, two oxygen donors from two different diphosphonate ligands, and an oxo group bridging to a molybdenum site. Each $\{-PO_3\}$ unit of the diphosphonate provides two oxygen donors to adjacent copper sites in a μ^2-O,O′-type bridge while the third oxygen bonds to an octahedral molybdenum center. The ethylene groups of the diphosphonate ligands serve to bridge adjacent inorganic chains. The tetranuclear molybdate cluster embedded in the chain of **2** exhibits several unusual features. The molybdenum centers are arranged in a nonlinear chain of edge-sharing polyhedra with octahedra at the termini and square pyramids in the interior locations.

Somewhat suprisingly, the structure of the propylene derivative, **3**$\cdot 2.5H_2O$, shown in Figure 3, is one-dimensional.[10] The structure may be described as $\{Mo_5O_{21}\}$ cyclic clusters, linked through diphosphonate ligands into a chain which is decorated by {Cu-

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(7) All reactions were carried out in Teflon-lined 23 mL Parr acid digestion bombs. **1**: $Cu(SO_4)\cdot 5H_2O$ (0.54 g, 0216 mmol), MoO_2 (0.059 g, 0.461 mmol), 1,10-phenanthroline (0.062 g, 0.313 mmol), methylenediphosphonic acid (0.078 g, 0.426 mmol), and water (10.04 g, 557 mmol) were heated at 170 °C for 74 h to give blue crystals in 40% yield. **2**: $Cu(SO_4)\cdot 5H_2O$ (0.055 g, 0.220 mmol), MoO_2 (0.106 g, 0.825 mmol), 1,-10-phenanthroline (0.065 g, 0.33 mmol), ethylenediphosphonic acid (0.039 g, 0.220 mmol), and water (8.64 g, 480 mmol) were heated at 180 °C for 44 h to give blue plates in 30% yield. **3**: $Cu(SO_4)\cdot 5H_2O$ (0.0578, 0.228 mmol), $Na_2MoO_4\cdot 2H_2O$ (0.0448, 0.182 mmol), 1,2-propylenediphosphonic acid (0.0478, 0.230 mmol), 1,10-phenanthroline (0.060 g, 0.303 mmol), and water (10.31 g, 572 mmol) were heated at 140 °C for 21 h, and the temperature was subsequently ramped at 10 °C/min to 175 °C, whereupon the reaction mixture was heated for an additional 3 h. Green crystals of **3** were recovered in 25% yield.

(8) Crystal data for **1**: $C_{13}H_{12}N_2CuMo_2P_2O_{12}$, monoclinic $P2_1/c$, $a = 11.867(1)$ Å, $b = 10.398(1)$ Å, $c = 15.695(1)$ Å, $\beta = 107.937(2)°$, $V = 1842.6(3)$ Å^3, $Z = 4$, $D_{calc} = 2.536$ g cm^{-3}; 4418 reflections, R1 = 0.0485, wR2 = 0.1163.

(9) Crystal data for **2**$\cdot 2H_2O$: $C_{13}H_{14}N_2CuMo_2PO_{11}$, triclinic $P\bar{1}$, $a = 7.9401(7)$ Å, $b = 10.4771(9)$ Å, $c = 12.895(1)$ Å, $\alpha = 101.137(1)°$, $\beta = 104.176(2)°$, $\gamma = 110.066(1)°$, $V = 930.6(1)$ Å^3, $Z = 2$, $D_{calc} = 2.351$ g cm^{-3}; 4314 reflections, R1 = 0.0480, wR2 = 0.1104.

(10) Crystal data for **3**$\cdot 2.5H_2O$: $C_{39}H_{39}Cu_2Mo_5P_2N_6O_{25.5}$, triclinic $P\bar{1}$, $a = 8.8623(3)$ Å, $b = 16.9880(5)$ Å, $c = 17.1166(5)$ Å, $\alpha = 91.286(1)°$, $\beta = 95.399(1)°$, $\gamma = 102.754(1)°$, $V = 2\,499.7(1)$ Å^3, $Z = 2$, $D_{calc} = 2.205$ g cm^{-3}; 11549 reflections, R1 = 0.0360, wR2 = 0.0851.

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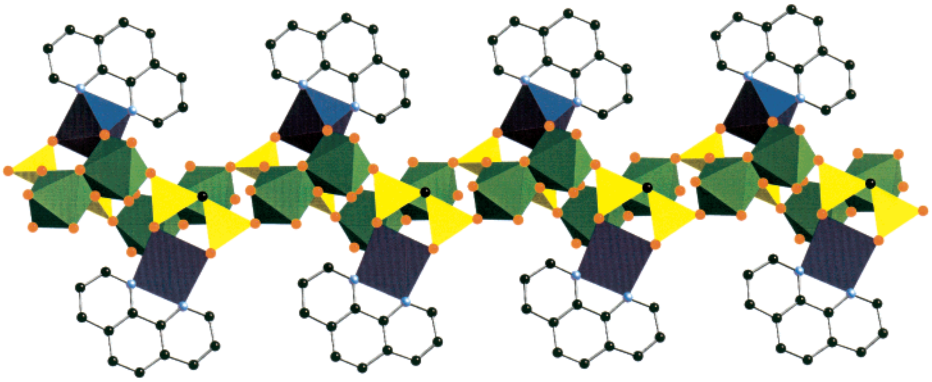

Figure 1. A polyhedral representation of the chain structure of **1**. Color scheme: phosphorus tetrahedra, yellow; copper polyhedra, blue; molybdenum polyhedra, green; oxygen, red spheres.

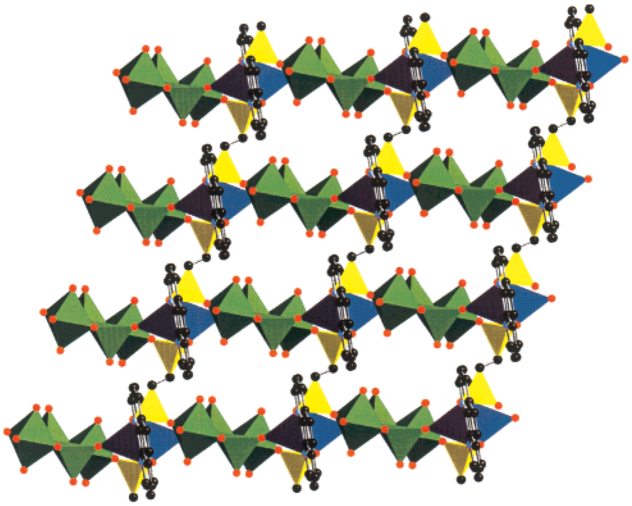

Figure 2. A polyhedral representation of the two-dimensional structure of **2**·$2H_2O$.

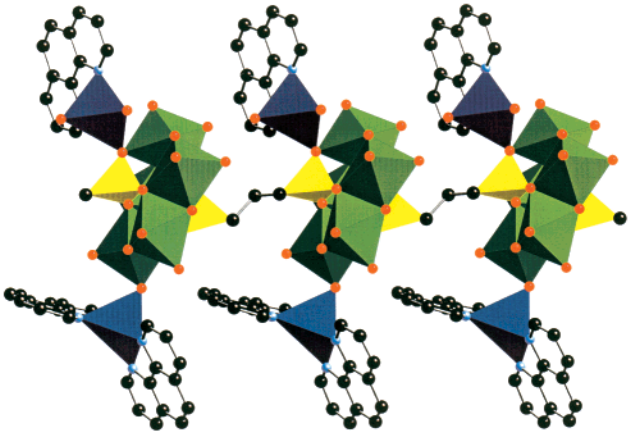

Figure 3. A polyhedral view of the structure of **3**·$2.5H_2O$.

$(H_2O)_2$(o-phen)$\}^{2+}$and $\{$Cu(o-phen)$_2\}^{2+}$ subunits. There are, thus, two distinct Cu(II) environments: a square pyramidal site and an octahedral site. The diphosphonate ligands serve to bridge adjacent clusters, coordinating exclusively to molybdenum sites at one $\{-PO_3\}$ terminus and to Mo and Cu centers at the other. The molybdate cluster is structurally analogous to the well-known $[Mo_5O_{15}(O_3PR)_2]^{4-}$ molecular clusters,[11,12]consisting of a ring of edge-sharing octahedra.

The isolation of **3** suggested that a building-block approach to such chain structures is conceivable. However, attempts to link preformed clusters through diphosphonate ligands of various tether lengths under non-hydrothermal conditions proved futile. Furthermore, adopting pH and stoichiometry conditions favoring such cluster formation under hydrothermal conditions did not yield the analogous $[(Mo_5O_{15})\{O_3P(CH_2)_xPO_3\}]^{4-}$ chains ($x = 1$, 2, or 4) to **3** but rather required the presence of Cu(II) and phenanthroline to yield **1**, **2**, and an unidentified material, respectively. While cluster preorganization and linkage is an attractive strategy for structural design, it appears that such synthetic building blocks persist only under narrowly defined conditions, whereas, in general, dissociation is evident and the system "selects" the appropriate structural unit from the species present in the hydrothermal mix.

The isolation of **1**−**3** illustrates the synergistic influence of diphosphonate tether lengths and the metal−organic component on the structures of hybrid oxide materials. The organic tether serves to expand the distance between molybdate polyhedra or clusters and to direct the relative orientations of the $\{PO_3\}$ termini, consequently influencing the dimensionality of the material. However, the structural influences of the variabilities of polyhedral type and polyhedral connectivities available to the oxometalate substructures are also determinants which may produce unanticipated structural motifs. For example, the common tendency of the V/P/O and Mo/P/O families to form two-dimensional substructures, based on the $MO(PO_4)$ prototype,[13] would suggest that an oxomolybdate material incorporating a diphosphonate of sufficiently extended tether length to buttress such layers would adopt overall three-dimensional connectivity. The steric constraints of the $\{$Cu(o-phen)$_2\}^{2+}$subunit can, of course, passivate the surface of the oxide and result in lower dimensional materials, as previously observed for [Cu(2,2′-bpy)(VO)$(O_3PCH_2CH_2CH_2PO_3)$]·H_2O. The one-dimensional structure of **3** may reflect several influences: the persistence of the $\{Mo_5O_{15}(O_3P-)_2\}^{4-}$ core and the incorporation of significant numbers of passivating subunits, in this case both $\{$Cu$(H_2O)_2$(o-phen)$\}^{2+}$ and $\{$Cu(o-phen)$_2\}^{2+}$.

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Supporting Information Available: X-ray data in CIF format for the structures of **1**−**3**. Figures showing the asymmetric units and thermal ellipsoids for **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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