After evaporation of solvent, a white crystalline solid was isolated (63 mg) in 88% yield. Elemental analysis calcd for $C_{11}H_{16}O_2$: C 73.33, H 8.88; found: C 73.56, H 8.81; m.p. 143 °C (lit.[19] 143 °C). Spectroscopic data are in accordance with previous reports.[19]

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Solid-State Coordination Chemistry: The Self-Assembly of Microporous Organic–Inorganic Hybrid Frameworks Constructed from Tetrapyridylporphyrin and Bimetallic Oxide Chains or Oxide Clusters**

Douglas Hagrman, Pamela J. Hagrman, and Jon Zubieta*

Oxygen is not only the most abundant terrestrial element but it is also highly reactive; consequently, oxides exist for all of the elements with the exceptions of radon and the lighter noble gases.[1] Inorganic oxides constitute a vast family of materials ubiquitous as both naturally occurring and synthetic materials.[2–4] The significant contemporary interest in solid-state oxides reflects a structural and compositional diversity that endows these materials with a range of physical properties that yield applications to heavy construction, sorption, catalysis, biomineralization, microelectronics, and solar energy conversion.[5] However, despite the practical and fundamental importance of inorganic oxides, the designed synthesis of such materials remains an elusive goal.

The synthetic challenge reflects the fact that binary metal oxides, for example, typically possess only one or a few thermodynamically stable modifications, which provides a limited range for design. While such simple oxides possess undeniably useful properties, there is, in general, a correlation between the complexity of the structure of a material and the functionality that it displays. Two general observations provide an insight into the synthesis of structurally complex oxides: a) if the formation of the oxide is carried out at low temperatures, and thus under kinetic control, it is possible to prepare metastable modifications and to influence the reaction process,[6] and b) organic molecules can dramatically influence the inorganic oxide microstructure, thus offering a powerful tool for the design of novel materials.[7]

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[*] Prof. J. Zubieta, D. Hagrman, P. J. Hagrman
Department of Chemistry, Syracuse University
Syracuse, NY 13244 (USA)
Fax: (+001) 315-443-4070
E-mail: jazubiet@syr.edu

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In organic–inorganic hybrid materials the inorganic oxide substructure contributes to the increased complexity and corresponding functionality through incorporation as one component into a multilevel hierarchical material that combines synergistically interacting organic and inorganic components. The interaction within such organic–inorganic hybrid materials derives from the nature of the interface between the organic component and the inorganic oxide, a feature that drives chemists to elaborate the synthetic and structural characteristics of materials with such an interface in an effort to derive structure–function relationships for such hybrid compositions.[8]

Four major classes of compounds in which an organic component exerts a major structural influence on the inorganic oxide substructure are zeolites,[9, 10] mesoporous materials of the MCM-41 class,[11] biomineralized materials,[12] and organically templated transition metal phosphates.[13] More recently, we have described a fifth major class, the organically templated molybdenum oxides.[14] A subclass of this latter family of materials uses rigid multitopic ligands to bridge oxide monomers, clusters, or chains to form complex two-dimensional networks and three-dimensional frameworks. In an effort to design framework materials that combine the porosity of zeolites with the reactivity of transition metal oxides, pyridyl-substituted porphyrins have been introduced as fourfold connectors that are capable of generating significant void space and of providing ordered supramolecular arrays of functional chromophores.[15] Following our general synthetic guidelines, we have isolated the first examples of three-dimensional framework materials constructed from metal oxide and porphyrin subunits. The structure of [Cu(tpypor)$Cu_2Mo_3O_{11}$] (tpypor = tetrapyridylporphyrin (**1**)) consists of a tessellated porphyrin network linked through bimetallic oxide chains into a three-dimensional, covalently connected framework. In assessing the structure-directing role of the metal center ligated with secondary or porphyrin/pyridyl groups, the isolation of $[\{Fe(tpypor)\}_3Fe(Mo_6O_{19})_2] \cdot x\,H_2O$ (**2**), a material constructed from a three-dimensional $[\{Fe(tpypor)\}_3Fe]_n^{4n+}$ framework and isolated $\{Mo_6O_{19}\}^{2-}$ polyoxo anions, was effected.

The structure of the hydrothermally synthesized **1** was determined by a single-crystal X-ray diffraction study[16] and shown to be constructed from $\{Cu(tpypor)Cu_2\}^{4+}$ building blocks and $\{Mo_3O_{11}\}_n^{4n-}$ chains (Figure 1). This structure appears as a tessellated porphyrin network linked through copper–molybdenum oxide chains when viewed along the crystallographic *c* axis. There are three distinct copper(II) environments: one rests in the porphyrin pocket and displays a square planar CuN_4 coordination geometry while the remaining two exhibit square pyramidal CuN_2O_3 and octahedral CuN_2O_4 ligation through coordination to pyridyl nitrogen atoms from two tpypor groups of one planar network and to three or four oxo groups, respectively, of the $\{Mo_3O_{11}\}_n^{4n-}$ chains (Figure 2). Thus, the structure may be described as neutral [Cu(tpypor)] units linked to bimetallic $\{Cu_2Mo_3O_{11}\}$ oxide chains. These oxide chains are constructed from a molybdate ribbon of alternating MoO_6 octahedra and MoO_4 tetrahedra in a corner-sharing arrangement and decorated by MoO_4 tetrahedra, which share a single corner with the octahedral Mo sites, and the square pyramidal and octahedral copper centers, which share three and four vertices, respectively, with the molybdate ribbon. One of these copper sites bridges adjacent octahedral MoO_6 sites and one terminal MoO_4 tetrahedron in corner-sharing modes exclusively while the second engages in corner-sharing interactions with a tetrahedral MoO_4 site and edge-sharing interactions with two adjacent MoO_6 octahedra. This polyhedral arrangement is quite distinct from that observed for "naked" copper–molybdate phases.[17]

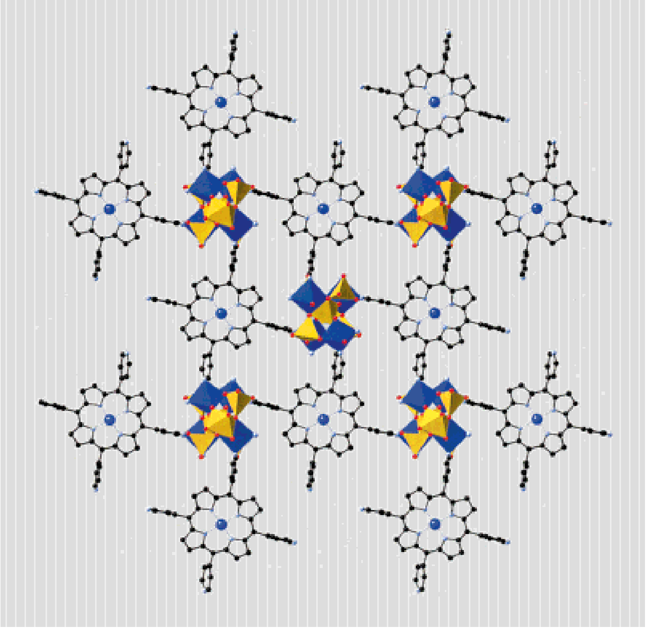

Figure 1. A view of the structure of **1** parallel to the $\{Cu_2Mo_3O_{11}\}$ chains, illustrating the linking of {Cu(tpypor)} building blocks into a tessellated pattern in the *ab* plane and the stacking of porphyrin groups along the *c*-direction. Cu–N(porphyrin) distances [Å]: 1.988(6), 1.989(6), 1.998(6), 2.003(6).

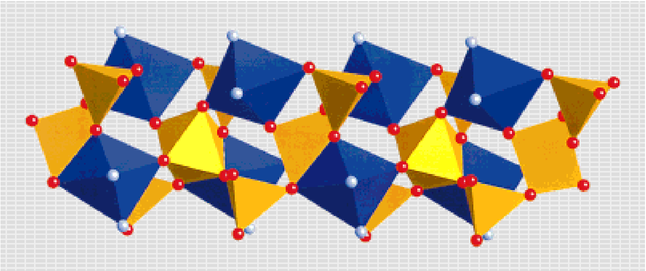

Figure 2. A polyhedral representation of the $\{Cu_2Mo_3O_{11}\}$ chain of **1**. Selected bond distances [Å]: square-pyramidal Cu site: Cu-Npy: 2.019(7), 2.047(7); Cu-O: 1.937(6), 1.980(6), 2.300(7); octahedral Cu site: Cu-Npy: 1.985(6), 1.989(6); Cu-O: 1.973(5), 2.001(5), 2.156(7), 2.408(6); MoO_4-tetrahedra: Mo-O range: 1.704(6)–1.882(5); MoO_6 octahedral site: Mo-O: 1.730(6), 1.734(6), 1.770(6), 2.102(5), 2.220(6), 2.265(6).

The copper molybdate chains of **1** propagate at 90° to the porphyrin planes. Consequently, the porphyrin units stack in a face-parallel fashion, and parallel to the oxide chains with a porphyrin–porphyrin distance of 4.815 Å. Adjacent porphyrin rings in a stack are staggered by approximately 30°.

The structure of **1** reflects not only the rigid geometry of the porphyrin building block, but also the coordination preferences of the Cu^{II} sites that adopt the conventional square planar and "4+1" and "4+2" coordination geometries. In contrast, iron(II) ions would be expected to adopt a six coordinate geometry with concomitant structural consequences. This expectation has been realized in the structure of **2**.

As shown in Figure 3 the structure of **2**[18] is constructed from a three-dimensional cationic framework $[Fe_4(tpypor)_3]_n^{4n+}$ and entrained $\{Mo_6O_{19}\}^{2-}$ cluster anions.

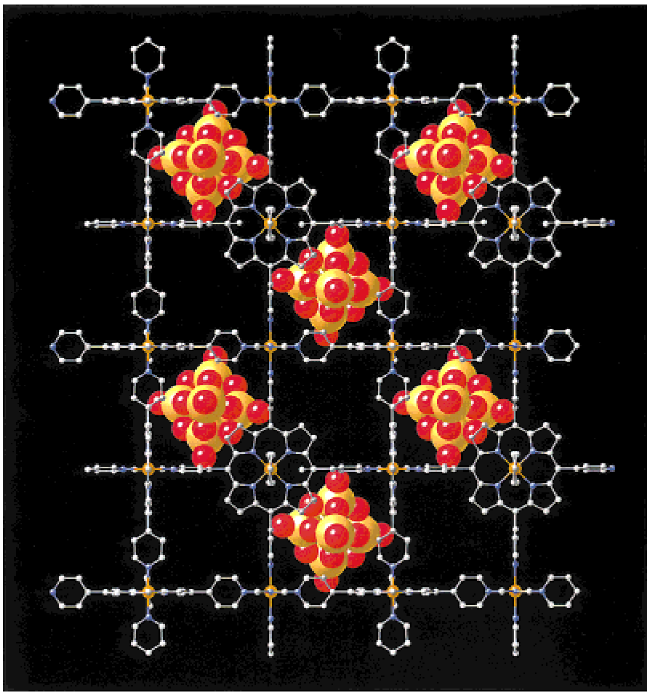

Figure 3. A view of the structure of $[\{Fe(tpypor)\}_3Fe(Mo_6O_{19})_2]\cdot x\,H_2O$ (**2**) parallel to the crystallographic *c* axis.

The cationic matrix consists of cubic building blocks of $[Fe_8(tpypor)_6]^{8+}$ with an edge dimension of 9.833(1) Å. There are two distinct iron centers in the cationic microstructure: one resides in the heme pocket and is additionally axially coordinated to a pyridyl nitrogen atom from two adjacent [Fe(tpypor)] units, while the second iron center is octahedrally coordinated to six pyridyl nitrogen donors (Figure 4). The large cavities generated within these iron–porphyrin cubes are alternately populated by $\{Mo_6O_{19}\}^{2-}$ clusters and diffuse, disordered water molecules. The hexamolybdate ion is well known[19] and adopts a charge-compensating and space-filling role in this material. Each cavity occupied by $\{Mo_6O_{19}\}^{2-}$ is octahedrally surrounded by water-filled cavities.

While the assembly of porphyrin building blocks into two- and three-dimensional structures has witnessed significant activity,[20] the structures of **1** and **2** are unique with respect to the secondary metal–porphyrin microstructures, as well as in regard to the role of the molybdenum oxides in structural elaboration. The structures of **1** and **2** illustrate that molybdenum oxide structures may be readily modified by the porphyrin building blocks and appropriate selection of porphyrin ligated metal centers. The synergistic interaction of the various structural components is revealed in the framework of **1** wherein the Cu^{II} ion exhibits its pronounced tendency to associate directly with the molybdate substruc-

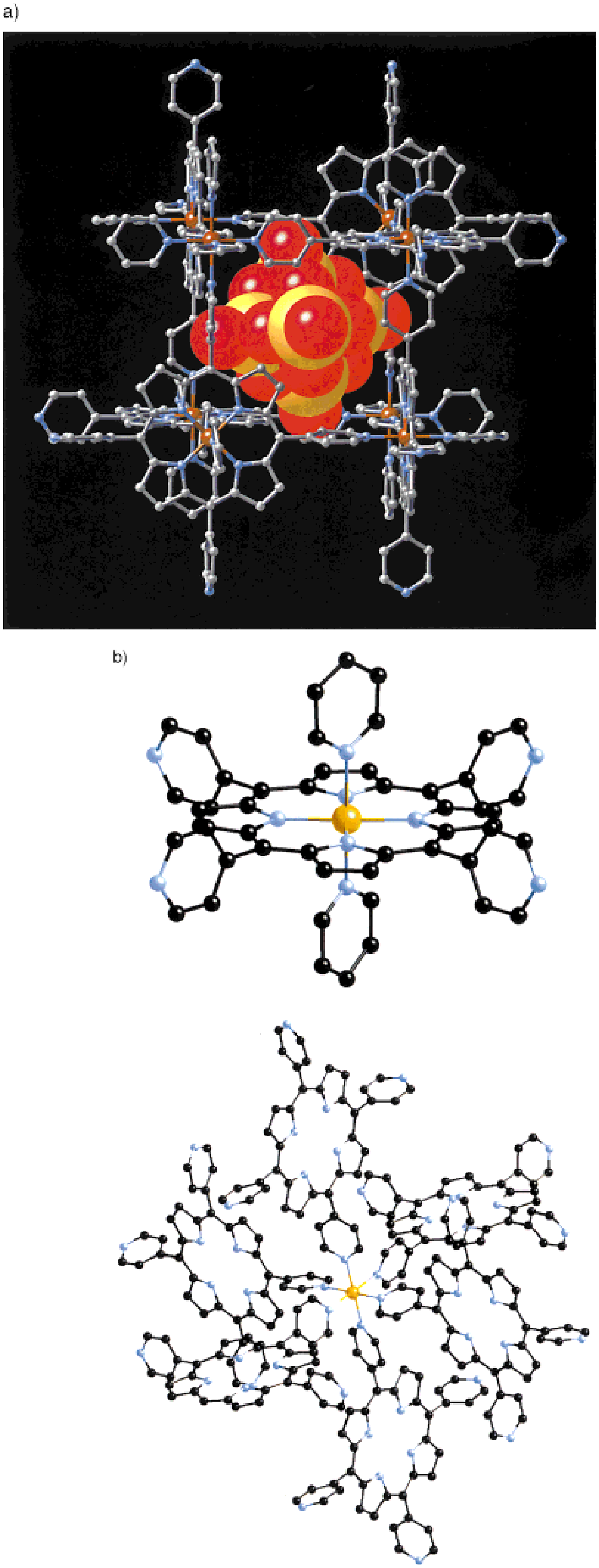

Figure 4. a) A view of the $[Fe_8(tpypor)_6]^{8+}$ building block of the cationic framework of **2** with the entrained $\{Mo_6O_{19}\}^{2-}$ cluster; b) Views of the two Fe sites of **2**. Selected bond lengths [Å]: porphyrin-bound Fe site: Fe-Npor, 1.986(6) × 4; Fe-Npy, 2.050(8) × 2. Pyridyl-bound Fe site: Fe-Npy, 2.165(8) × 6. Mo-O: 1.691(6), 1.869(6), 1.870(6), 1.963(6), 1.979(6), 2.319(1).

ture,in addition to incorporating into the porphyrin pocket. On the other hand, exploitation of the coordination preferences of Fe^{II} ions provides a cationic framework for entrainment of the molybdate oxide substructure; naively this can be considered as a "ship in the bottle" approach to modification of oxide microstructures. These results suggest that oxides and appropriate metal–porphyrin substructures may be fused to produce hybrid bimetallic materials with different metal-containing active sites, framework components providing a variety of pore geometries and dimensionalities, and incipient microporosities. While predictability of product structure remains elusive in view of the paucity of examples, the basic approach is amenable to considerable variation and illustrates not only the ease of modification of oxide microstructure by organic components but also the reciprocal structure-directing influences of anionic oxide constituents on hybrid structures.

Experimental Section

1: Hydrothermal treatment of MoO_3, $Cu(NO_3)_2 \cdot 2.5\,H_2O$, tetrapyridylporphyrin, and H_2O (1:1.03:0.16:182) for 48 h at 200 °C gives dark purple needles of **1** in approximately 50% yield based on porphyrin. Hydrothermal conditions are required to overcome the differential solubilities of the inorganic starting materials and the porphyrin. Aqueous reactions at room temperature and under reflux conditions proved unproductive for isolating hybrid oxide–porphyrin phases, while organic solvents and appropriate metal precursors such as $[Cu^I(CH_3CN)_4]BF_4$ and $MoO_3 \cdot n\,H_2O$ yielded mixtures of [Cu(tpypor)CuBF$_4$] and unidentified molybdates.

The infrared spectrum of **1** exhibits a strong band at $\tilde{\nu} = 794\ cm^{-1}$, which is associated with the tpypor unit, and multiple bands in the $\tilde{\nu} = 890–943\ cm^{-1}$ range, attributed to ν(Mo=O). The electronic spectrum of a suspension of **1** in a gel exhibits a band red-shifted by 10 nm from the Soret absorption of the porphyrin (420 nm) and an extinction coefficient of less than half of that of the native porphyrin. This red shift, reduced extinction coefficient, and a broadening of the Soret half-width indicate some electronic coupling between the porphyrins.[21]

Compound **1** exhibits magnetic properties that are consistent with a simple paramagnet. A somewhat elevated magnetic moment of 2.20 μ_B at room temperature is consistent with temperature-independent paramagnetism. The temperature dependence is unexceptional for a noninteracting d^9 ion.

Thermogravimetric analysis of **1** exhibits successive 6% weight losses in the ranges 230–250 and 470–480 °C, followed by a 12% weight loss between 500–550 °C. These correspond to the loss of one, one, and two pyridyl groups, respectively. A further weight loss of about 12% in the range 575–650 °C is attributed to the loss of the porphyrin. The final thermolysis product is an amorphous gray powder.

2: The hydrothermal reaction of MoO_3, $FeCl_2 \cdot 4\,H_2O$, tetrapyridylporphyrin, and H_2O (1:1.02:0.18:1750) at 200 °C for 68.5 h gave **2** in 35% yield based on porphyrin.

The infrared spectrum of **2** exhibits the characteristic tpypor band at $\tilde{\nu} = 795\ cm^{-1}$ and a single band at $\tilde{\nu} = 925\ cm^{-1}$, which is attributed to ν(Mo=O) of the symmetric $\{Mo_6O_{19}\}^{2-}$ cluster. The electronic spectrum again shows a red shift, reduced extinction coefficient, and broadening of the Soret band associated with electronic coupling of the porphyrins.

Thermogravimetric analyses and density measurements are consistent with 19 water molecules per cavity. Preliminary sorption studies on **2** indicate that the material exhibits a Type I water vapor absorption isotherm[22] and is capable of taking up about 15 wt% water vapor. The material also sorbs alcohols, but excludes hydrocarbons and acetonitrile.

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