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A Two-Dimensional Network Constructed via Hydrogen-Bonded Cross-Linkages of Molybdenum Oxide Chains

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Introduction

The dramatic expansion of supramolecular chemistry into the solid state[1] reflects the intense contemporary interest in the rational design of functional materials.[2] Crystal engineering based on multitopic organic spacer ligands has resulted in architectures based on diamondoid,[3−6] octahedral,[7] honeycomb,[4,8] square grid,[9−11] brick wall,[12] ladder,[13] and railroad motifs.[1e] Polymeric coordination complex cations constructed from Zn(II), Cd(II), Cu(II), Cu(I), and Ag(I) and organodiamine ligands are the prototypical materials of this class.

We have recently demonstrated that this approach to organic−inorganic composite materials may be extended to the synthesis of metal oxides. Organodiamine components in such structures may assume a variety of structural roles: (i) simple counterions, as in [4,4′-bpyH$_2$][Mo$_7$O$_{22}$];[14] (ii) ligands covalently bound to the molybdenum oxide skeleton, as in [MoO$_3$(4,4′-bpy)][15] or [Mo$_3$O$_9$(2,2′-bpy)$_2$];[16] (iii) ligands to a heterometal forming part of a bimetallic molybdenum oxide backbone, as in [Co(2,2′-bpy)Mo$_3$O$_{10}$];[17] and (iv) spacer ligands in a polymeric coordination complex cation providing charge compensation for the negatively charged metal oxide, as in [{Cu(4,4′-bpy)}$_4$Mo$_{15}$O$_{47}$].[18]

In the course of our development of the chemistry of molybdenum oxide−organodiamine solids, we noted that both tether length between the amine nitrogen donors and the relative orientations of the donor groups profoundly influence the structure of the composite material. An obvious variant to the linear rodlike ditopic ligand 4,4′-bipyridine is the bent rod, 4,4′-bipyridylamine, whose synthesis and hydrothermal chemistry with molybdenum oxide are described. The material [Mo$_4$O$_{13}$(Hbpa)$_2$] provides an example of a two-dimensional sheet formed by cross-linking one-dimensional molybdenum oxide chains through hydrogen bonding of the pendant and protonated arm of the 4-pyridyl-4′-pyridinum amine (Hbpa) ligand to the oxo groups of adjacent chains.

Experimental Section

Reagents were purchased from Aldrich and used without further purification, unless specifically noted. The ligand 4,4′-dipyridylamine was prepared by minor modification of a published procedure.[19]

Synthesis of 4,4′-Dipyridylamine (bpa). To 4-aminopyridine (31 g, 0.33 mol) was added PCl$_3$ (29 mL, 0.33 mol). After about 2 min, 60 mL of pyridine (distill before use) was added in one portion. After addition of the pyridine, the mixture began to boil. The reaction flask was fitted with a reflux condenser, and the reaction mixture was heated to 140 °C for 5 h in a preheated oil bath. The volatiles were removed by distillation by increasing the temperature of the oil bath to 180 °C for 1 h. The result was a compact yellow cake, to which was added 15 mL of ethanol, 250 mL of water, and 30 mL of concentrated hydrochloric acid. The mixture was then heated in a hot water bath for about 1 h, at which point most of the product dissolved and the residue disintegrated into a fine yellow powder. The mixture was filtered and washed with a small portion of dilute hydrochloric acid. The yellow precipitate was discarded. To the filtrate was added an excess of 5 M NaOH solution, forming a voluminous white precipitate. The white solid obtained by filtration was dissolved in 3.5 L of boiling water. A small portion of insoluble material was filtered off and discarded. The filtrate was concentrated on a hot plate to approximately 1 L, with any excess pyridine removed by steam distillation during the concentration process. Upon cooling to room temperature and then to 0 °C, white needles of 4,4′-dipyridylamine crystallized from solution. The mother liquor may be further concentrated and cooled to afford more product. The yield obtained was 20.5 g or 72% theoretical yield. Melting point: 273−275 °C.

Synthesis of [Mo$_4$O$_{13}$(Hbpa)$_2$]. A mixture of MoO$_3$(0.20 g, 1.4 mmol) and 4,4′-dipyridylamine (0.31 g, 1.8 mmol) in 10 mL of H$_2$O in the mole ratio 1:1.3:400 was heated at 120 °C for 48 h in a 23 mL Parr acid digestion bomb. After cooling, light yellow crystals of [Mo$_4$O$_{13}$(Hbpa)$_2$] were collected in 60% yield.

X-ray Crystallography. The crystals of [Mo$_4$O$_{13}$(Hbpa)$_2$] were studied on a Siemens SMART system using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Crystal parameters and other experimental details of the data collection are summarized in Table 1, and selected bond lengths and angles are provided in Table 2. A complete description of the crystallographic methods is given in the

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Table 1. Crystal Data and Structure Refinement Parameters for $[Mo_4O_{13}(Hbpa)_2]$

empirical formula	$C_{20}H_{20}Mo_4N_6O_{13}$
fw	936.18
λ, Å	0.710 73
space group	$P\bar{1}$
a, Å	8.1339(4)
b, Å	9.0054(5)
c, Å	9.6200(5)
α, deg	92.218(1)
β, deg	102.299(1)
γ, deg	107.021(1)
V, Å^3	654.47(6)
Z	1
ρ_{calc}, g cm^{-3}	2.375
μ, cm^{-1}	19.53
R1 (all data)[a]	0.0269
wR2[b]	0.0713

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0322p)^2 + 1.63p]$, $p = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Mo_4O_{13}(Hbpa)_2]$[a]

Mo(1)−O(3)	1.709(2)	Mo(1)−O(4)	1.715(2)
Mo(1)−O(6)	1.9017(2)	Mo(1)−O(7)	2.016(2)
Mo(1)−O(2)	2.236(2)	Mo(1)−N(3)	2.426(2)
Mo(2)−O(5)	1.716(2)	Mo(2)−O(1)	1.725(2)
Mo(2)−O(7)	1.862(2)	Mo(2)−O(2)#1	1.862(2)
Mo(2)−O(2)	2.402(2)	H(1)−O(2)	2.250(9)
H(1)−O(5)	2.195(8)		

O(3)−Mo(1)−O(4)	103.80(10)	O(3)−Mo(1)−O(6)	101.99(7)
O(4)−Mo(1)−O(6)	99.38(7)	O(3)−Mo(1)−O(7)	94.53(9)
O(4)−Mo(1)−O(7)	95.19(9)	O(6)−Mo(1)−O(7)	154.60(6)
O(3)−Mo(1)−O(2)	161.91(9)	O(4)−Mo(1)−O(2)	90.92(9)
O(6)−Mo(1)−O(2)	85.61(5)	O(7)−Mo(1)−O(2)	73.41(8)
O(3)−Mo(1)−N(3)	81.06(9)	O(4)−Mo(1)−N(3)	171.70(9)
O(6)−Mo(1)−N(3)	85.99(6)	O(7)−Mo(1)−N(3)	77.59(8)
O(2)−Mo(1)−N(3)	83.15(8)	O(5)−Mo(2)−O(1)	105.75(10)
O(5)−Mo(2)−O(7)	110.47(10)	O(1)−Mo(2)−O(7)	99.89(10)
O(5)−Mo(2)−O(2)#1	112.13(9)	O(1)−Mo(2)−O(2)#1	102.99(10)
O(7)−Mo(2)−O(2)#1	123.05(9)	O(5)−Mo(2)−O(2)	86.40(8)
O(1)−Mo(2)−O(2)	167.40(9)	O(7)−Mo(2)−O(2)	72.14(8)
O(2)#1−Mo(2)−O(2)	74.69(8)	Mo(1)−O(6)−Mo(1)#2	180.0
Mo(2)−O(7)−Mo(1)	117.78(10)	Mo(2)#1−O(2)−Mo(1)	144.91(11)
Mo(2)#1−O(2)−Mo(2)	105.31(8)	Mo(1)−O(2)Mo(2)	91.38(7)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 1$, $-y + 1$, $-z$; #2, $-x$, $-y + 1$, $-z$.

Supporting Information. The structure was solved by direct methods.[20] Neutral atom scattering factors were taken from Cromer and Waber,[21] and anomalous dispersion corrections were taken from Creagh and McAuley.[22] All calculations were performed using SHELXTL. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at idealized positions. No anomalies were encountered in the refinement.

Intercalation Studies. Samples of $[Mo_4O_{13}(Hbpa)_2]$ were stirred in the appropriate organoamine at room temperature for 24 h. After the crystals were collected and washed with alcohol and ether, the infrared spectra were taken. These exhibited ν(Mo═O) bands in the 900−950 cm^{-1} region, as observed for the parent compound, and medium-intensity bands in the 3100−3200, 1150−1200, and 700−800 cm^{-1} regions which are not present in the parent compound and which are assigned to the intercalated amine. Anal. Calcd for $[Mo_4O_{13}(Hbpa)_2(C_2H_5NH_2)]$: C, 26.9; N, 9.99; H, 2.75. Found: 26.6; N, 9.32; H, 2.51. Calcd for $[Mo_4O_{13}(Hbpa)_2(Me_2NM)_{0.5}]$: C, 26.3; N, 9.49; H, 2.45. Found: C, 25.7; N, 9.22; H, 2.29.

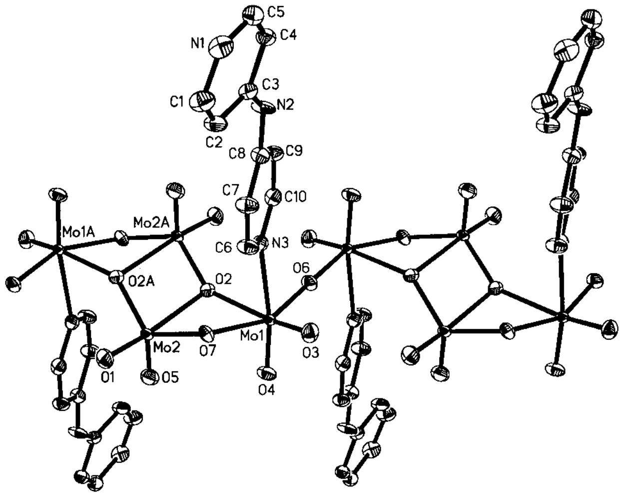

Figure 1. View of the one-dimensional chain of $[Mo_4O_{13}(Hbpa)_2]$, showing the atom-labeling scheme and 50% thermal ellipsoids. Also note the chain puckering.

Results and Discussion

Hydrothermal synthesis has been exploited recently as a routine method for the preparation of inorganic materials,[23] most notably in the syntheses of materials of the oxomolybdenum−phosphate[24] and oxovanadium−phosphate and −organophosphonate systems.[25] Hydrothermal reactions, typically carried out in the temperature range 110−260 °C under autogenous pressure, exploit the self-assembly of the product from soluble precursors. The reduced viscosity of the solvent under these conditions results in enhanced rates of solvent extraction of solids and crystal growth from solution. Since differential solubility problems are minimized, a variety of simple starting materials may be introduced, as well as a number of organic and/or inorganic structure-directing (templating) agents from which those of appropriate shape(s) and size(s) may be selected for efficient crystal packing during the crystallization process.[26,27] Thus, the reaction of a mixture of MoO_3 and 4,4′-dipyridylamine in water in the mole ratio 1:1.3:400 heated to 120 °C for 48 h yielded light yellow crystals of $[Mo_4O_{13}(Hbpa)_2]$ (**1**). The infrared spectrum of **1** exhibited an intense band at 910 cm^{-1} attributed to ν(Mo═O) and medium-intensity features in the 700−750 cm^{-1} range assigned to ν(Mo−O−Mo).

As shown in Figure 1, the structure of $[Mo_4O_{13}(Hbpa)_2]$ consists of molybdenum oxide chains linked through covalently bonded and hydrogen-bonded $Hbpa^+$ groups into two-dimensional sheets. The one-dimensional chain is constructed from edge- and corner-sharing $\{MoO_5\}$ square pyramids and $\{MoO_5N\}$ octahedra. The fundamental building block of the chain is the $\{Mo_4O_{13}(Hbpa)_2\}$ tetranuclear unit, which exhibits a central binuclear core of edge-sharing square pyramids, each in turn edge-sharing to a peripheral $\{MoO_5N\}$ octahedron. The square pyramidal sites adopt a *cis*-dioxo orientation of the terminal oxo groups; furthermore, the terminal oxo groups of the binuclear unit exhibit an unusual anti-orthogonal, anti-coplanar configuration of the $\{MoO_2(\mu\text{-}O_2)MoO_2\}$ core.[28] The oxo groups bridging the square pyramidal sites are also implicated

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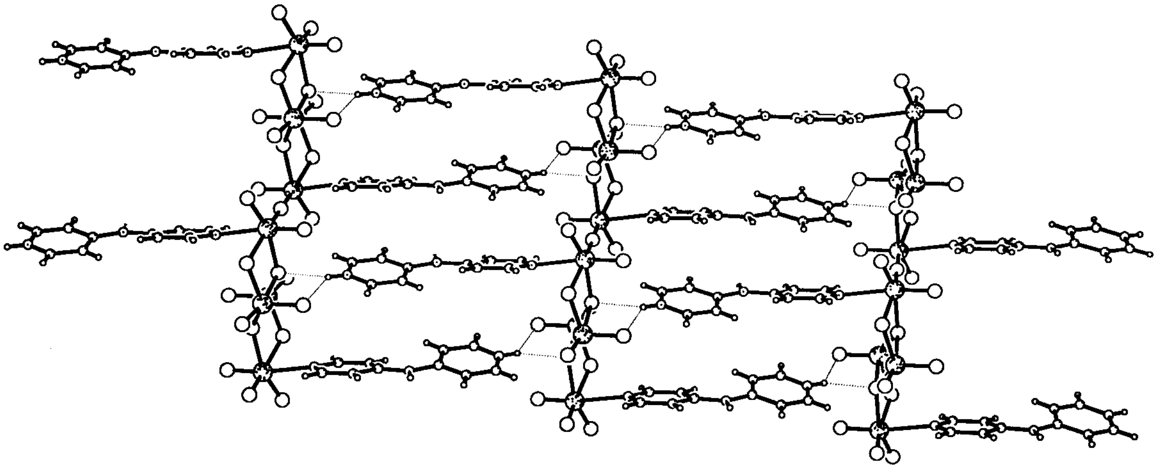

Figure 2. View of the hydrogen bonding between adjacent chains to form a two-dimensional sheet.

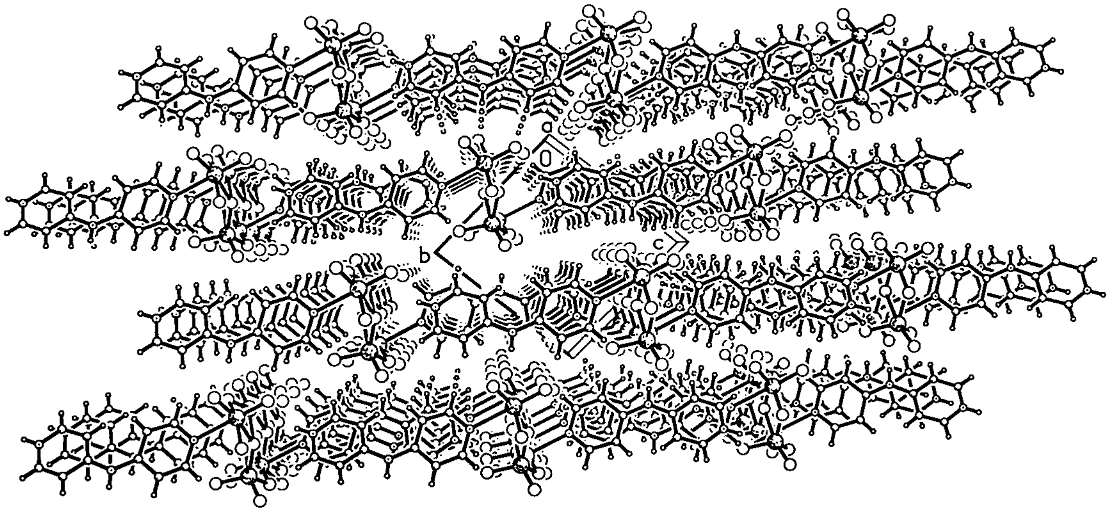

Figure 3. View down the *a* axis of the stacking of sheets.

in bridging to the octahedral site, hence adopting a μ^3-bridging mode. The octahedral sites also exhibit terminal *cis*-dioxo coordination with the oxo groups in the syn-orthogonal and syn-coplanar configurations with respect to the $\{Mo(1)O_2(\mu\text{-}O_2)\text{-}Mo(2)O_2\}$ moiety. The nitrogen donor of the $Hbpa^+$ ligand is situated trans to a terminal oxo group, and the Mo−N distance of 2.426(2) Å reflects the strong trans influence of the oxo group.

The tetranuclear building blocks find extension into one dimension through corner-sharing interactions between the peripheral octahedral sites producing a linear {Mo−O−Mo} moiety. The terminal oxo groups of the fused octahedral sites are oriented in an anti configuration; consequently, the $Hbpa^+$ groups of adjacent octahedral sites project from opposites sides of the molybdenum oxide chain. The steric requirements of the edge- and corner-sharing pattern of molybdenum polyhedra result in a puckered chain, shown in Figure 1. While one-dimensional chains are a common feature of molybdenum oxide solid state chemistry, the detailed polyhedral connectivity displayed by $[Mo_4O_{13}(Hbpa)_2]$ is unique. In contrast to the structure of the title compound, the "tetramolybdate" $[H_3N(CH_2)_6\text{-}NH_3][Mo_4O_{13}]$[29] is constructed from octanuclear units of edge-sharing octahedra linked through corner-sharing into a one-dimensional chain. This observation suggests that the $Hbpa^+$ ligand serves to passivate the molybdenum oxide surface so as to limit the condensation of metal polyhedra and prevent more efficient packing of polyhedral building blocks.

While one arm of the $Hbpa^+$ group coordinates to a molybdenum site, the second is protonated and pendant. As shown in Figure 2, the protonated pyridyl nitrogens form bifurcated hydrogen bonds to the terminal and bridging oxo groups of adjacent chains (NH···O range 2.195−2.250 Å), so as to generate a two-dimensional sheet. The pyridyl groups from adjacent chains interdigitate and provide weak $\pi-\pi$ stacking interactions[30] within the sheet (ca. 3.25 Å average interplanar separations). The stacking of sheets, shown in Figure 3, results in weak hydrogen bonding between the hydrogen attached to the ligand bridging amine site N2 and terminal oxo groups of the adjacent sheet. The structure of $[Mo_4O_{13}(Hbpa)_2]$ manifests two of the noncovalent forces, hydrogen-bonding and $\pi-\pi$ stacking interactions, which are common in the self-assembly of supramolecular species.[31]

It is noteworthy that the $Hbpa^+$ component adopts a multiple role: as ligand covalently linked to the molybdenum oxide chain, as charge-compensating cation, and as the locus of the dimensionality defining hydrogen bonding. Two-dimensional structures generated from one-dimensional chains are a common

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motif in the chemistry of polymeric coordination complexes constructed from rodlike ditopic organoamine ligands.[32] However, in contrast to the structure of the oxide [Mo_4O_{13}(Hbpa)$_2$], these latter materials typically consist of $\{M(4,4'\text{-bpy})(H_2O)_x\}^{n+}$ linear chains cross-linked through hydrogen bonding of the aquo ligands to noncoordinated 4,4′-bpy groups, to produce a square grid pattern.

Intercalation studies of [Mo_4O_{13}(Hbpa)$_2$] indicate that primary and secondary amines such as $C_2H_5NH_2$ and $(CH_3)_2NH$ are readily introduced by warming at room temperature in nonaqueous solvents such as propylene carbonate to give materials of approximate composition [Mo_4O_{13}(Hbpa)$_2$($C_2H_5NH_2$)] and [Mo_4O_{13}(Hbpa)$_2$(Me_2NH)$_{0.5}$], respectively. However, tertiary amines do not intercalate, suggesting that hydrogen bonding between the intercalate and the oxo groups of the chain may dictate the process.

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Supporting Information Available: Tables of atomic coordinates, complete bond lengths and bond angles, anistropic temperature factors, and hydrogen atom coordinates for [Mo_4O_{13}(Hbpa)$_2$] (5 pages). Ordering information is given on any current masthead page.

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