

One- and two-dimensional organic–inorganic composite solids constructed from molybdenum oxide clusters and chains linked through $\{M(2,2'\text{-bpy})\}^{2+}$ fragments ($M = \text{Co, Ni, Cu}$)

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Hydrothermal reactions of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and MoO_3 with $\text{MCl}_2 \cdot x\text{H}_2\text{O}$ ($M = \text{Co, Ni, Cu}$) and 2,2'-bipyridine yield one- and two-dimensional solids, characterized by molybdenum oxide monomers, clusters and chains linked by $\{M(2,2'\text{-bpy})\}^{2+}$ groups and represented by the formulae $[\text{M}(\text{bpy})_x(\text{H}_2\text{O})_y\text{Mo}_n\text{O}_{3n+1}]$ ($n = 2, M = \text{Cu}, x = 1, y = 0; n = 3, M = \text{Co}, x = 1, y = 0; n = 4, M = \text{Ni}, x = 2, y = 0$).

Metal oxide-based solids have provoked significant contemporary interest by virtue of their applications to areas as diverse as catalysis, sorption, molecular electronics, energy storage, optical materials and ceramics.^{1,2} While the rational synthesis of new solids possessing unique structures and properties remains a challenge,³ the structure-directing properties of organic components have been successfully exploited in the synthesis of metastable composite materials which retain the structural characteristics of the starting materials.^{4,5} These organic constituents are most commonly present in the roles of tethers between metal sites, a mode adopted by 4,4'-bipyridine and related ligand types,⁶ of charge-compensating cations such as organoammonium units,⁷ or of ligands covalently linked to the inorganic backbone of the solid.⁸ We recently demonstrated an additional type of composite material based on amine-ligated transition- or post-transition-metal cation complexes intercalated between mixed-valence vanadium oxide layers.⁹ This observation suggested that appropriate transition-metal coordination compounds could also be incorporated directly into the covalent backbone of the solid either as peripheral metal/organic components or as complex bridging ligands. This expectation has been realized in the preparation and characterization of the one-dimensional solids $[\text{Ni}(2,2'\text{-bpy})_2\text{Mo}_4\text{O}_{13}]$ **1** and $[\text{Cu}(2,2'\text{-bpy})\text{Mo}_2\text{O}_7]$ **2** and the two-dimensional phase $[\text{Co}(2,2'\text{-bpy})\text{Mo}_3\text{O}_{10}]$ **3**.

Compounds **1–3** were prepared from mixtures of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, MoO_3 , $\text{MCl}_2 \cdot x\text{H}_2\text{O}$, and 2,2'-bpy, heated to 160 °C for 72–120 h.[†] The IR spectra of **1–3** exhibit strong bands in the range 910–970 cm^{-1} attributed to $\nu(\text{Mo}=\text{O})$, and a series of bands characteristic of 2,2'-bpy in the range 1100–1600 cm^{-1} .

The structure of $[\text{Ni}(2,2'\text{-bpy})_2\text{Mo}_4\text{O}_{13}]$ **1** (Fig. 1) is constructed from the common β -molybdate clusters $[\text{Mo}_8\text{O}_{26}]^{4-}$,



Fig. 1 A polyhedral representation of the one-dimensional structure of **1**. The lighter polyhedra represent the molybdenum sites and the darker the nickel octahedra. The carbon atoms of the bipyridyl ligands are shown as light spheres. Selected bond lengths (Å): Ni–N, 2.053(7), 2.058(7), 2.060(6), 2.072(7); Ni–O, 2.056(6), 2.090(5).

linked through $\{\text{Ni}(\text{bpy})_2\text{O}_2\}^{2+}$ octahedra into a one-dimensional ribbon. The molybdenum core consists of edge-sharing $\{\text{MoO}_6\}$ octahedra in the compact β -molybdate geometry.¹⁰ Two adjacent molybdenum sites on either side of the cluster engage in corner-sharing interactions through bridging oxo-groups to a $\{\text{NiN}_4\text{O}_2\}$ octahedron, such that each $\{\text{Mo}_8\text{O}_{26}\}^{4-}$ cluster is linked through four $\{\text{NiN}_4\text{O}_2\}$ octahedra to the two neighboring clusters of the ribbon. The nickel site is defined by four nitrogen donors from two 2,2'-bpy ligands and *cis*-oxo groups from two adjacent molybdenum clusters.

Examination of the structure of **1** would suggest that further condensation of molybdenum oligomers into one-dimensional molybdenum oxide motifs should be feasible. As illustrated in Fig. 2, the structure of $[\text{Cu}(2,2'\text{-bpy})\text{Mo}_2\text{O}_7]$ **2** consists of a buckled one-dimensional molybdenum oxide chain linked to peripheral $\{\text{CuN}_2\text{O}_4\}$ octahedra. The $\{\text{Mo}_2\text{O}_7\}$ chain is constructed from edge-sharing $\{\text{MoO}_6\}$ octahedra and $\{\text{MoO}_5\}$ square pyramids. Each molybdenum octahedron shares common edges with a neighboring molybdenum octahedron, a

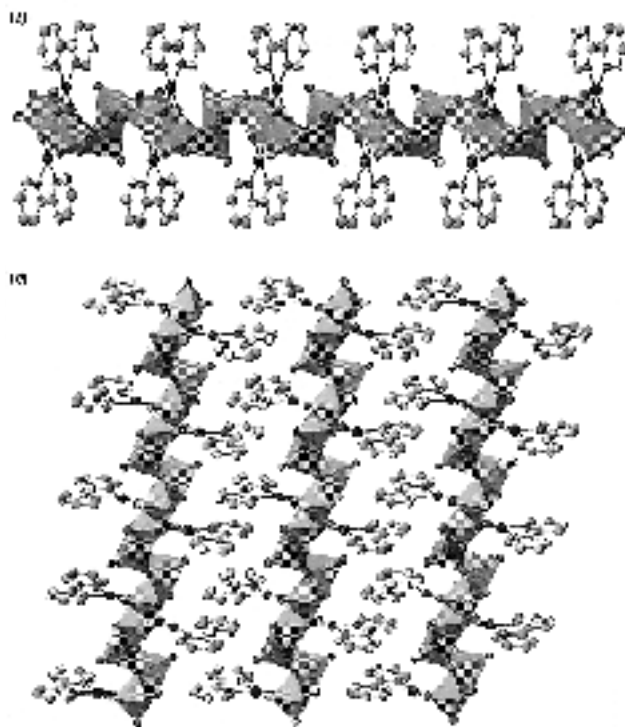


Fig. 2 (a) A view of the one-dimensional structure of **2**. The molybdenum sites are represented as polyhedra, while the Cu centers are shown as dark spheres. (b) The packing of adjacent one-dimensional strands, showing the stacking of bipyridyl rings from adjacent chains. Selected bond lengths (Å): Cu(1)–N, 2.011(14), 2.003(14); Cu(1)–O, 1.989(11), 1.995(10), 2.355(11), 2.405(10); Cu(2)–N, 1.974(14), 1.976(14); Cu(2)–O, 1.995(11), 1.997(11), 2.355(11), 2.360(11). The longer Cu–axial oxygen bonds have been omitted for clarity.

molybdenum square pyramid, and two copper octahedra, and a common corner with one square-pyramidal unit. One square-pyramidal site engages in edge-sharing with an adjacent square pyramid and a molybdenum octahedron and displays corner-sharing with a second molybdenum octahedron and two $\{\text{CuN}_2\text{O}_4\}$ octahedra, while the second $\{\text{MoO}_5\}$ site exhibits edge-sharing to a square-pyramidal and an octahedral molybdenum site and corner-sharing to a $\{\text{MoO}_6\}$ site and a $\{\text{CuN}_2\text{O}_4\}$ octahedron. Consequently, each $\{\text{CuN}_2\text{O}_4\}$ unit links to four molybdenum polyhedra of the chain, sharing four vertices in two edge and two corner interactions with the molybdenum sites. The folding of the molybdenum chain reflects the incorporation of the $\{\text{CuN}_2\text{O}_4\}$ units through four-point, two-edge attachments and illustrates the role of the M^{2+} site in defining chain geometry.

Since one-dimensional molybdenum oxide chains are a recurring theme in oxide structural chemistry,^{16,17} the incorporation of appropriate metal–ligand subunits should allow bridging into higher dimensional solids. The structure of $[\text{Co}(2,2'\text{-bpy})\text{Mo}_3\text{O}_{10}]$ **3** (Fig. 3) illustrates this point. The structure consists of one-dimensional molybdenum oxide chains, constructed of molybdenum tetrahedra, octahedra and square pyramids, linked through $\{\text{CoN}_2\text{O}_4\}$ octahedra into a two-dimensional covalent network. The oxide chain itself results from the edge-sharing of $\{\text{MoO}_6\}$ octahedra and $\{\text{MoO}_5\}$ square pyramids. The $\{\text{MoO}_4\}$ tetrahedra link to the chain through a single corner-sharing interaction, but bridge two $\{\text{CoN}_2\text{O}_4\}$ octahedra through two additional corner-sharing linkages. Each Co site is defined by the nitrogen donors of the bpy ligand and four oxygen donors from three $\{\text{MoO}_4\}$ groups

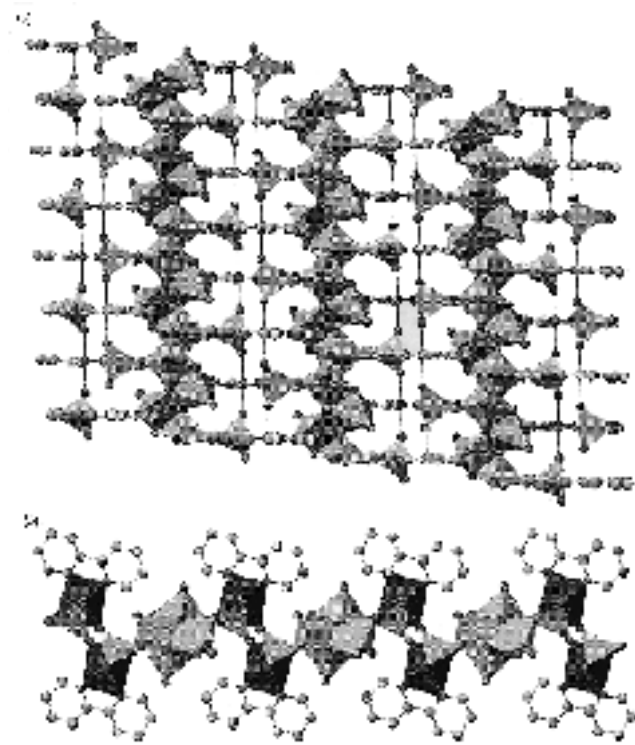


Fig. 3 (a) A view of the two-dimensional structure of **3** parallel to the crystallographic c axis. The molybdenum sites are represented as polyhedra, while the cobalt sites are illustrated as larger darkened spheres. (b) A view down the a axis showing the linking of molybdenum polyhedral chains through $\{\text{MoO}_4\}_2[\text{Co}(\text{bipy})]_2$ units in parallel chains. Selected bond lengths (Å): Co–N, 2.082(9), 2.105(9); Co–O, 2.092(8), 2.094(8) \times 2, 2.119(7).

and one $\{\text{MoO}_6\}$ octahedron. The overall structure may be described as folded chains of edge-sharing molybdenum polyhedra linked through double chains of alternating $\{\text{CoN}_2\text{O}_4\}$ octahedra and $\{\text{MoO}_4\}$ tetrahedra into a two-dimensional network.

Molybdenum oxides have received considerable attention for their catalytic properties in organic oxidations^{13,14} and for their intercalation properties.^{15,16} Recent studies^{11,12} have focused on structural modification and design of metal oxides through the introduction of organic components as templates, charge-compensating cations, tethers, or covalently linked network constituents. Another approach to composite metal oxide/organic solids is that illustrated in the preparation of **1–3**, which employs metal–organic ligand fragments as covalent linkers to metal oxide components of various nuclearities or dimensionalities. A curious feature of these initial investigations is the range of structural types which evolve from the introduction of $\{\text{M}'(\text{bpy})_n\}^{2+}$ units as the divalent d-block element is varied. A degree of primitive synthetic design appears inherent in the systematic variation of the divalent metal, the diamine ligand, and the hydrothermal conditions employed.

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Footnotes and References

† Reactions were carried out in Teflon-lined Parr acid digestion bombs at 30% fill volume. *Reaction conditions summary*: **1**, mole ratio for $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} : \text{MoO}_3 : \text{NiCl}_2 : 2,2'\text{-bpy} : \text{H}_2\text{O}$ of 1.0 : 1.1 : 6.0 : 2.0 : 1990; 160 °C, 72 h; **2**, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} : \text{MoO}_3 : \text{CuCl}_2 : 2,2'\text{-bpy} : \text{H}_2\text{O}$ of 1.0 : 1.0 : 4.1 : 2.1 : 2068; 160 °C, 72 h; **3**, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} : \text{MoO}_3 : \text{CoCl}_2 : 2,2'\text{-bpy} : \text{H}_2\text{O}$ of 1.0 : 1.0 : 1.7 : 1.4 : 881; 160 °C, 117 h.

‡ *Crystal data*: $\text{C}_{20}\text{H}_{16}\text{Mo}_4\text{N}_4\text{NiO}_{13}$ **1**: monoclinic, space group $P2_1/n$, $a = 10.0516(3)$, $b = 16.2988(5)$, $c = 15.8084(5)$ Å, $\beta = 100.074(1)^\circ$, $U = 2550.0(1)$ Å³, $R_1 = 0.0705$ for 6000 reflections. $\text{C}_{10}\text{H}_8\text{CuMo}_2\text{N}_2\text{O}_7$ **2**: triclinic, space group $P\bar{1}$, $a = 7.1835(3)$, $b = 11.5682(5)$, $c = 16.9615(7)$ Å, $\alpha = 89.568(1)^\circ$, $\beta = 79.995(1)^\circ$, $\gamma = 81.739(1)^\circ$, $U = 1373.5(1)$ Å³, $Z = 4$, $R_1 = 0.065$ for 3821 reflections. $\text{C}_{10}\text{H}_8\text{CoMo}_3\text{N}_2\text{O}_{10}$ **3**: triclinic, space group $P\bar{1}$, $a = 6.9889(6)$, $b = 10.5877(9)$, $c = 11.0077(9)$ Å, $\alpha = 88.674(2)^\circ$, $\beta = 89.930(2)^\circ$, $\gamma = 79.985(1)^\circ$, $U = 801.9(1)$ Å³, $Z = 2$, $R_1 = 0.064$ for 3567 reflections. CCDC 182/534.

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