

Crystal engineering of inorganic/organic composite solids: the structure-directing role of aromatic ammonium cations in the synthesis of the 'step'-layered molybdenum oxide phase [4,4'-H₂bpy][Mo₇O₂₂] \cdot H₂O

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The hydrothermal reaction of MoO₃, Mo metal, NiCl₂ and 4,4'-bipyridine yields a step-layered molybdenum oxide [4,4'-H₂bpy][Mo₇O₂₂] \cdot H₂O, a material structurally related to layered MoO₃.

Among the inorganic materials enjoying widespread contemporary interest, the metal oxide-based solid phases occupy a prominent position by virtue of their applications to catalysis, sorption, molecular electronics, energy storage, optical materials and ceramics.^{1,2} The evolution of metal oxide chemistry is critically dependent on the synthesis of new solids possessing unique structures and properties.³ While the synthesis of solid-state materials remains a challenge,^{4,5} the techniques of hydrothermal synthesis, in combination with the structure-directing properties of organic components, may be exploited in the isolation of metastable inorganic/organic composites which retain the structural elements of the synthetic precursors.^{6,7} The cooperative assembly of metal oxide/organic phases has been demonstrated by the recent reports of novel one-dimensional molybdenum oxide polymers, incorporating organoammonium cations.^{8,9} More significantly, we have demonstrated that incorporation of organoammonium or amine-ligated transition- or post-transition-metal cations situated between mixed-valence vanadium oxide layers yields materials structurally related to V₂O₅, with the degree of reduction and condensation within the layers reflected in the charge per volume ratio of the interlamellar cation. In addition to functioning as structure-directing cations or as components of complex cations, organoamines may serve as multifunctional ligands, forming an integral part of the covalent skeleton of the solid. While crystal 'engineering' based on transition-metal coordination to appropriate ligands has evolved dramatically since the seminal work of Robson and Hoskins,^{10,11} applications to metal oxides have remained largely unexplored. We have shown recently that 4,4'-bipyridine may be incorporated into metal oxide phases as a ligand serving to buttress the inorganic layers, as illustrated by [MoO₃(4,4'-bpy)_{0.5}].¹² It was anticipated that under more acidic reaction conditions, protonation of the aromatic amine would provide an aromatic ammonium cation which would serve as a structure-directing template by virtue of the interplay of hydrophobic/hydrophilic interactions¹³ and of multipoint hydrogen bonding between the cation and the metal oxide scaffolding of the composite.

The title compound [4,4'-H₂bpy][Mo₇O₂₂] \cdot H₂O (**1** \cdot H₂O) was prepared as colourless rhombs in 10–15% yield in the hydrothermal reaction of MoO₃, Mo (250 mesh), 4,4'-bipyridine, NiCl₂ and H₂O in the mole ratio 5 : 1 : 2 : 2 : 300 at 200 °C for 93 h in a Parr acid-digestion bomb.

Under the acidic conditions of the reaction, the pyridyl nitrogen atoms are protonated, precluding coordination to the oxide skeleton and resulting in incorporation of the organic component as the bipyridinium dication.

As shown in Fig. 1, the structure of **1** \cdot H₂O⁺ consists of the molybdenum oxide layers, separated by an interlamellar region populated by [4,4'-H₂bpy]²⁺ cations and H₂O molecules of

crystallization. The inorganic subunit of **1** \cdot H₂O is both structurally and compositionally related to the layered oxide MoO₃. In a formal sense, **1** \cdot H₂O may be considered to derive from MoO₃ through intercalation of [4,4'-H₂bpy]²⁺ cations and water, requiring the addition of an oxide anion to the inorganic framework to achieve charge compensation. Since charge/volume considerations result in one bipyridinium cation for seven molybdenum oxide sites, compound **1** \cdot H₂O may be reformulated as [4,4'-H₂bpy][(MoO₃)₇O] \cdot H₂O to reflect its relationship to the MoO₃ parent.

However, while the [Mo₇O₂₂]_n²ⁿ⁻ layers are constructed from edge- and corner-sharing {MoO₆} octahedra as observed for MoO₃,¹⁴ the consequences of adding one O²⁻ group every seven molybdenum sites are manifested in a layer structure significantly different from that adopted by MoO₃. The MoO₃ layer is constructed from linear ribbons, two polyhedra thick, of edge-sharing {MoO₆} octahedra; adjacent ribbons are linked through corner-sharing to produce the layer structure. Consequently, each Mo site in MoO₃ displays three triply bridging, two doubly bridging, and one terminal oxo group.

In contrast to the planar layers adopted by MoO₃, the oxide layers of **1** \cdot H₂O are distinctly stepped. Examinations of the detailed structure of the layers of **1** \cdot H₂O reveals a motif again based on ribbons of edge-sharing {MoO₆} octahedra. However, as shown in Fig. 2, the ribbon executes a 90° turn and shifts one polyhedral length along the *b*-direction at the 'step' juncture at every seventh Mo site. Adjacent ribbons are again linked through corner-sharing interactions, but in such a fashion as to produce three distinct {MoO₆} sites. The molybdenum centres Mo(2) and Mo(3) exhibit bonding patterns essentially identical to that observed for MoO₃: each projects a single terminal oxo

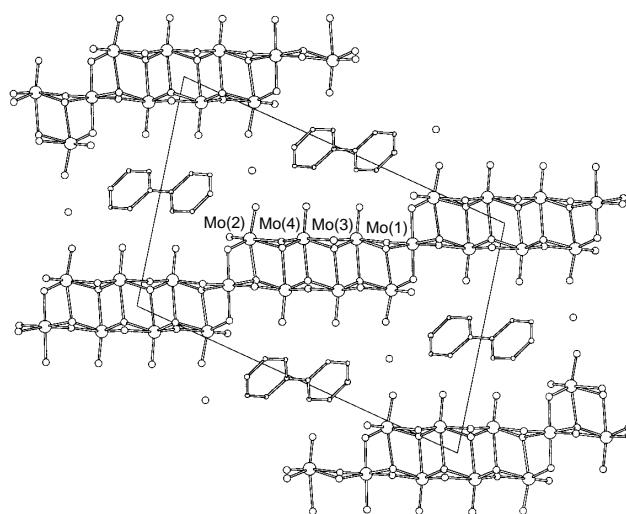


Fig. 1 A view of the structure of **1** \cdot H₂O, showing the [Mo₇O₂₂]_n²ⁿ⁻ inorganic layers and the H₂O molecules and [C₁₀H₈N₂]²⁺ cations occupying the interlamellar regions

group to either surface of the metal oxide layers and participates in three triply bonding oxo interactions within the ribbon and two doubly bonding oxo linkages to adjacent ribbons. On the other hand, the Mo(4) site is constrained by the folding of the ribbon to provide a second terminal oxo unit, which projects into the 'step' domain of the metal oxide network and adopts the conventional *cis* configuration with respect to the terminal oxo group directed toward the interlamellar region. The most unusual coordination site is occupied by Mo(1) which exhibits only doubly and triply bridging oxo groups and provides the locus of the dislocation of the layer structure of $1 \cdot \text{H}_2\text{O}$ with respect to the parent MoO_3 structure.

There is an extensive hydrogen-bonding network formed among the $-\text{NH}^+$ groups of the bipyridinium cations, the waters of crystallization, and the *cis* terminal oxo groups of Mo(4). This extensive hydrogen-bonding motif causes water and the organic component to be released only at elevated temperatures. Thermogravimetric analysis of $1 \cdot \text{H}_2\text{O}$ at a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 revealed no mass loss until 170°C when release of water commences. The organic component is not removed until ca. $250\text{--}300^\circ\text{C}$.

There has been considerable interest in MoO_3 for its catalytic properties in the oxidation of methanol to formaldehyde¹⁵ and for its intercalation properties,¹⁶ for example, intercalation of hydrogen from oxide bronzes of the H_xMoO_3 family with applications to electrochromic displays and proton mobility in solids.¹⁷ Oxide $1 \cdot \text{H}_2\text{O}$ represents a new class of organically based molybdenum oxides which are different from those

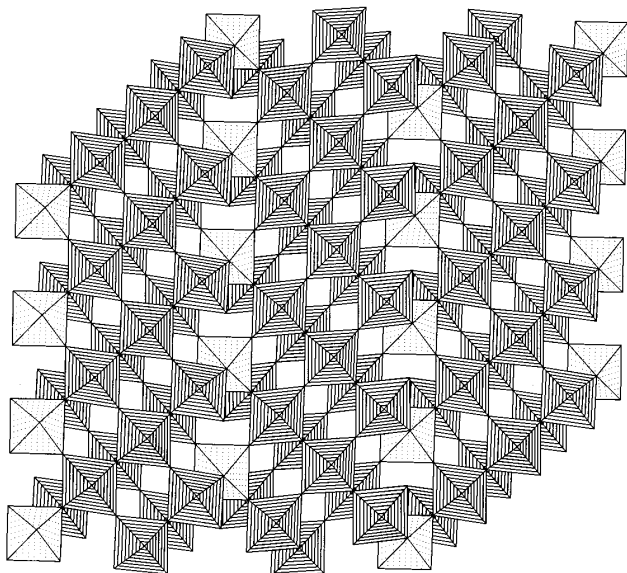


Fig. 2 A polyhedral representation of the $[\text{Mo}_7\text{O}_{22}]_n^{2n-}$ layer. The stippled polyhedra represent the Mo(1) sites which provide the location of the dislocations in the $1 \cdot \text{H}_2\text{O}$ structure with respect to the parent MoO_3 structure.

obtained from intercalation reactions.¹⁸ The structural modifications of composite metal oxide/organic solids may be realized by introducing organic components as ligands, tethers or structure-directing cations, roles which reflect hydrophobic–hydrophilic interactions and/or multipoint directional hydrogen bonding. Thermal removal of the organic templates from these materials may lead to new metal oxides, with different physical properties and selectivities with respect to interactions with organic substrates. The characterization of the thermal decomposition products of $1 \cdot \text{H}_2\text{O}$ is in progress, and their structures and physical properties will be presented in future publications.

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Footnote

† Crystal data for $1 \cdot \text{H}_2\text{O}$, $\text{C}_{10}\text{H}_{12}\text{Mo}_7\text{N}_2\text{O}_{23}$: monoclinic, space group $P2_1/n$, $a = 12.219(2)$, $b = 5.532(1)$, $c = 18.322(4)$ Å, $\beta = 103.28(3)^\circ$, $U = 1205.4(7)$ Å³, $Z = 2$; $R = 0.032$ for 2107 reflections with $I_0 \geq 3.0\sigma(I_0)$ (Mo-K α radiation, $\mu = 36.35 \text{ cm}^{-1}$). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/347.

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