A two-dimensional network constructed from hexamolybdate, octamolybdate and [Cu$_3$(4,7-phen)$_3$]$^{3+}$ clusters: [{Cu$_3$(4,7-phen)$_3$}$_2${Mo$_{14}$O$_{45}$}]

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The hydrothermal reaction of Cu(SO$_4$)·H$_2$O, MoO$_3$, 4,7-phenanthroline and water yields [{Cu$_3$(4,7-phen)$_3$}$_2${Mo$_{14}$O$_{45}$}], a material exhibiting a two-dimensional network constructed from (Mo$_6$O$_{19}$)$^{2-}$ and (Mo$_8$O$_{26}$)$^{4-}$ clusters linked through planar cyclic {Cu$_3$(4,7-phen)$_3$$^{3+}$} clusters.

Inorganic oxides are ubiquitous in the geosphere and the biosphere[1,2] and are represented not only by the complex aluminosilicates which make up vast proportions of igneous rocks,[3] by ores and gems but also by complex oxides fashioned by biomineralization, such as bones, shells, teeth and spicules.[4,5] The intense contemporary interest in solid state oxides reflects their properties, which endow these materials with applications ranging from heavy construction to microcircuitry.[5] Consequently, there has evolved a significant effort in the manipulation of inorganic oxide microstructures.

One synthetic approach is to mimic Nature's remarkable mixtures of inorganic oxides coexisting with organic molecules. In such materials, the inorganic oxide contributes to the increased complexity and hence functionality through incorporation as one component in a multilevel structured material where there is synergistic interaction between organic and inorganic components.[6] There are now four major classes of materials in which organic components exert a significant structural role in controlling the inorganic oxide microstructure: zeolites,[7,8] mesoporous oxides of the MCM-41 class,[9] bimineralized materials,[10] and microporous octahedral–tetrahedral or square-pyramidal–tetrahedral framework transition metal phosphates (TMPO) with entrained organic cations.[11,12] We have recently identified a fifth class of organic–inorganic oxide hybrid materials: ditopic organonitrogen-templated molybdenum oxides.[13] A common structural motif for this class of materials consists of a molybdate cluster entrained within a scaffolding provided by a coordination cation polymer; for example, [{Cu(4,4′-bpy)$_4$}Mo$_8$O$_{26}$] and [{Ni(H$_2$O)$_2$(4,4′-bpy)$_2$}$_2$Mo$_8$O$_{26}$] exhibit the δ- and ε- forms of the octamolybate cluster, respectively. As part of our continuing studies of this class of materials, we have sought to exploit rigid linkers other than the linear rod, such as 4,7-phenanthroline which has resulted in the isolation of an unusual two-dimensional array of clusters[14,15] in the material [{Cu(4,7-phen)$_3$}$_2$-{Mo$_{14}$O$_{45}$}]·0.5H$_2$O (**1**).

The hydrothermal reaction of Cu(SO$_4$)·H$_2$O, MoO$_3$, 4,7-phenanthroline and water in the mole ratio 1:1.8:1.7:1654 at 200 °C for 99.5 h yielded **1** in 90% yield as brown rhombs. The IR spectrum exhibited a complex pattern of bands in the range 700–950 cm^{-1}, ascribed to ν(Mo=O) and ν(Mo–O–Mo).

As shown in Fig. 1(*a*) and (*c*), the structure of **1**‡ is constructed from the linking of three independent molecular clusters: {Cu$_3$(4,7-phen)$_3$}$^{3+}$, β-(Mo$_8$O$_{26}$)$^{4-}$ and (Mo$_6$O$_{19}$)$^{2-}$. While the hexa- and octa-molybdate clusters are well known aggregates,[16] the trinuclear copper(I) cluster cation provides a novel twenty-one membered cyclic structure. The extended structure is generated through the bonding of terminal and bridging oxo-groups of the clusters to the Cu^I sites of the rings. As shown in Fig. 1(*a*), one motif consists of linear chains of β-(Mo$_8$O$_{26}$)$^{4-}$ clusters linked through {Cu$_3$(4,7-phen)$_3$}$^{3+}$ rings

into a one-dimensional ribbon. Adjacent parallel ribbons are linked through {Mo$_6$O$_{19}$}$^{2-}$ clusters into a two-dimensional sheet structure, as shown in Fig. 1(*a*). Each hexamolybdate

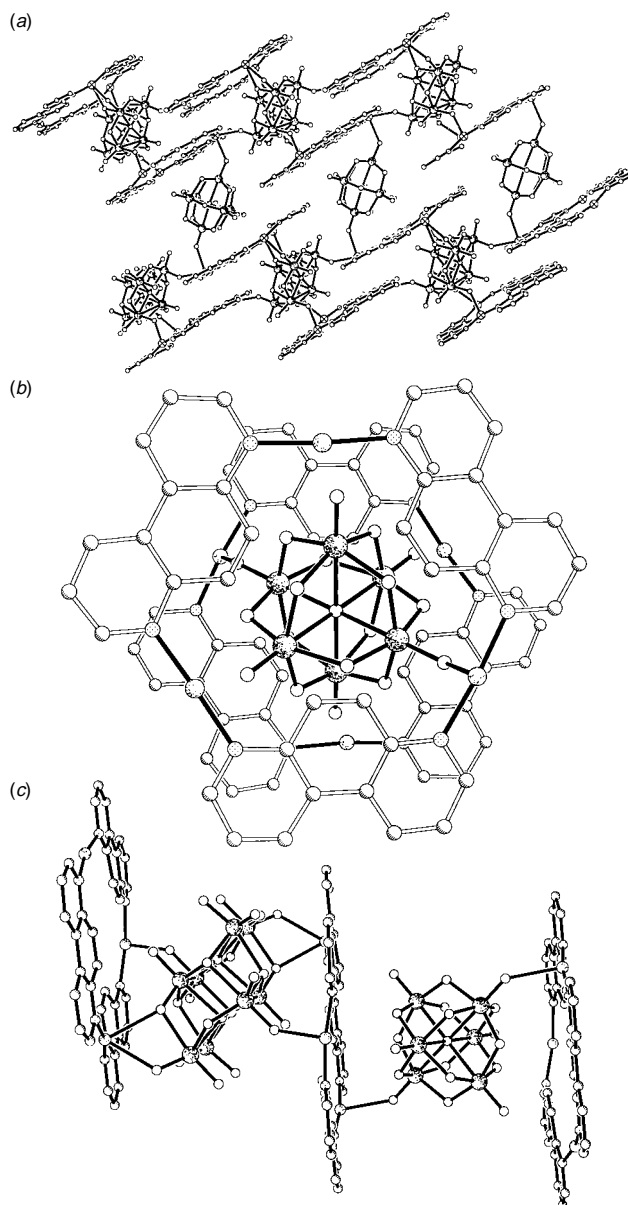**Fig. 1** (*a*) A view of the sheet structure of [{Cu$_3$(4,7-phen)$_3$}$_2$-{Mo$_{14}$O$_{45}$}]·0.5H$_2$O **1** along the (112) plane, illustrating the linking of [{Cu$_3$(4,7-phen)$_3$}$_2${Mo$_8$O$_{26}$}]$_n^{n+}$ chains by (Mo$_6$O$_{19}$)$^{2-}$ clusters. (*b*) A view of the sandwiching of the (Mo$_6$O$_{19}$)$^{2-}$ cluster between two nearly coplanar {Cu$_3$(4,7-phen)$_3$}$^{3+}$ clusters. (*c*) A view of the crosslinking chain of alternating hexanuclear and octanuclear molybdate clusters, contrasting the alignment of the (Mo$_6$O$_{19}$)$^{2-}$ cluster with the centroids of the {Cu$_3$(4,7-phen)$_3$}$^{3+}$ rings and the displacement of the (Mo$_8$O$_{26}$)$^{4-}$ cluster from the centroid causing a parallel shearing of the subsequent Cu$_3$ ring.
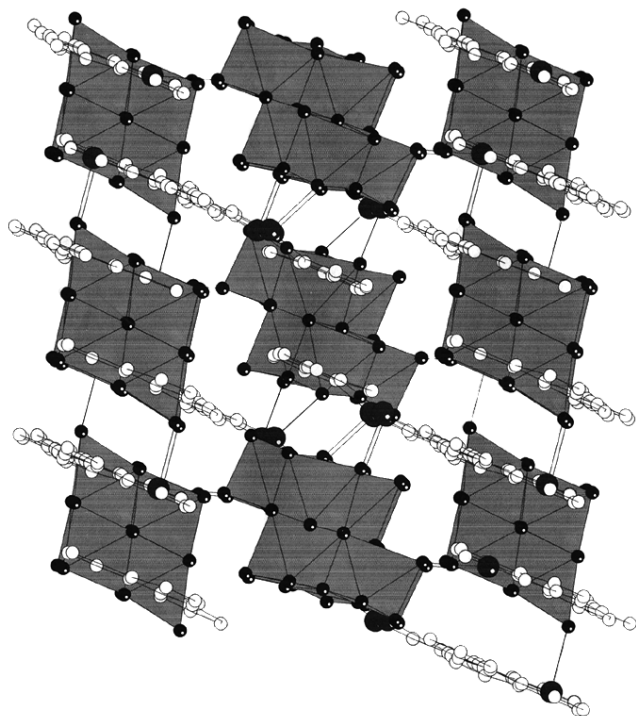
Fig. 2 A polyhedral representation of the cluster stacking parallel to the planes of the $\{Cu_3(4,7\text{-phen})_3\}^{3+}$ rings

cluster is sandwiched between two planar $\{Cu_3(4,7\text{-phen})_3\}^{3+}$ rings as shown in Fig. 1(*b*). The hexanuclear clusters are aligned with opposite Mo_3 triangular faces of the Mo_6 octahedron parallel to the Cu_3 rings. In contrast, the centroid of the $\beta\text{-}(Mo_8O_{26})^{4-}$ cluster does not align with the centroids of the sandwiching Cu_3 rings, which are displaced *ca.* 4.5 Å by parallel shearing with respect to each other. This allows the approach of two additional Cu_3 rings whose interactions with the oxo-groups of the octanuclear cluster propagate the chain. In this fashion, each octamolybdate cluster bonds to four Cu_3 rings, while each hexamolybdate cluster links only two such rings. Each Cu_3 ring bonds to one hexamolybdate and two octamolybdate clusters.

A curious feature of the structure is the presence of both $(Mo_6O_{19})^{2-}$ and $\beta\text{-}(Mo_8O_{26})^{4-}$ clusters as building blocks for the two-dimensional sheet, as shown in Fig. 2. However, this observation reflects the synthetic approach of exploiting hydrothermal conditions which requires a shift from the thermodynamic to the kinetic domain, such that equilibrium phases are replaced by structurally more complex metastable phases.[17] The structure-directing role of the copper coordination complex cluster is manifest in interactions whose geometric correspondence produces the architecture of the network. While it remains premature to classify such syntheses in terms of 'designed' routes, it should be noted that the very complexity of the hybrid material produces a limit on the degree of predictability. Moreover, design may not require total predictability, but rather a reciprocity of structure–function relationships for a class of materials which evolve as sufficient numbers of examples are characterised. Indeed, the chemistry of

the Cu–organodiamine–molybdate system appears to be extraordinarily diverse, encompassing a variety of molybdate clusters, chains and sheets as building blocks. In the specific case of 4,7-phenanthroline as ligand, compound **1** was observed in a fairly narrow pH range (*ca.* 6–8), outside of which other as yet unidentified phases were observed.

Upon thermal treatment, **1** exhibits a 0.5 mass% loss at *ca.* 120 °C owing to the loss of the water of crystallization and a further 30 mass% loss between 310 and 350 °C, corresponding to the loss of the organic ligand. When carried out in oxygen, the product of thermolysis is a pale green material of approximate composition $Cu_6Mo_{14}O_{45}$, whose powder diffraction pattern is distinct from that of known copper molybdates. We are investigating the use of hybrid materials such as **1** in the preparation of novel heterometallic molybdate phases.

Notes and References

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