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The hydrothermal syntheses and characterization of one- and two-dimensional structures constructed from metal–organic derivatives of polyoxometalates: $[\{Cu(bpy)_2\}\{Cu(bpy)(H_2O)\}(Mo_5O_{15})\{O_3P(CH_2)_4PO_3\}]\cdot H_2O$ and $[\{Cu_2(tpypyz)(H_2O)_2\}(Mo_5O_{15})(O_3PCH_2CH_2PO_3)]\cdot 5.5H_2O$ [bpy = 2,2′-bipyridine, tpypyz = tetra(2-pyridyl)pyrazine]

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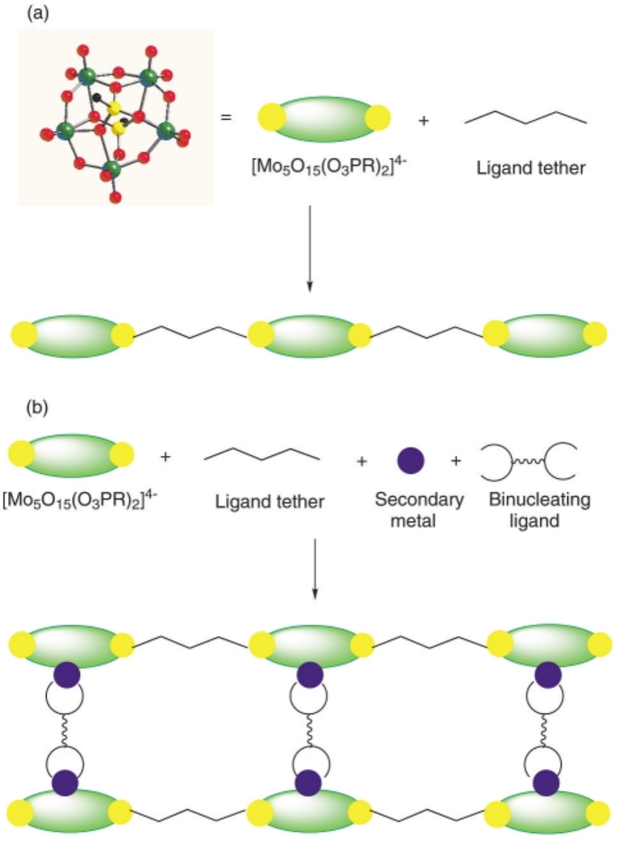
The hydrothermal reaction of $CuSO_4\cdot 5H_2O$, $Na_2MoO_4\cdot 2H_2O$ and 2,2′-bipyridine with the bridging diphosphonate ligand $H_2O_3P(CH_2)_4PO_3H_2$ yields the one-dimensional chain $[\{Cu(bpy)_2\}\{Cu(bpy)(H_2O)_2\}(Mo_5O_{15})\{O_3P(CH_2)_4PO_3\}]\cdot H_2O$; the introduction of a second bridging component in the reaction of $Cu(MeCO_2)_2\cdot H_2O$, MoO_3, $H_2O_3PCH_2CH_2PO_3H_2$ and tetra(2-pyridyl)pyrazine yields the network solid $[\{Cu_2(tpypyz)(H_2O)_2\}(Mo_5O_{15})(O_3PCH_2CH_2PO_3)]\cdot 5.5H_2O$.

The widespread contemporary interest in inorganic oxides reflects the ubiquitous nature of this family of materials which exhibit a diverse compositional range and considerable structural versatility,[1] as well as possessing useful electronic, magnetic, optical and mechanical properties for the design of functional materials.[2] Several strategies for the systematic construction of specific architectures from molecular building blocks have been described in recent years.[3–7] However, the inherent complexity of these primitive examples of hierarchically ordered materials has often rendered predictability of structure an elusive goal. By exploiting well-defined clusters with a fixed number of directional bonding sites as building blocks, the ultimate connectivity and architecture of the material may be predetermined.[8–11] In this respect, the 'venerable' polyoxomolybdates[12] of the type $[Mo_5O_{15}(O_3PR)_2]^{4-}$ provide conceptually attractive building blocks for one-dimensional organic/inorganic oxides through the simple expedient of tethering the organophosphonate components with appropriate organic linkers, as shown in Scheme 1(a). However, attempts to link preformed clusters through diphosphonate ligands of varying spatial extensions under conventional conditions, using a variety of organoammonium and metal cations, proved futile. The key to the successful syntheses of the target chains of linked polyoxoanions proved to be the introduction under hydrothermal conditions of secondary metal–ligand components as both charge-compensating and intimate structural subunits. In this fashion, the one-dimensional hybrid material $[\{Cu(bpy)_2\}\{Cu(bpy)(H_2O)\}(Mo_5O_{15})\{O_3P(CH_2)_4PO_3\}]\cdot H_2O$ ($\mathbf{1}\cdot H_2O$) was isolated.

Compound **1** was prepared as blue blocks in 25% yield based on molybdenum in the hydrothermal reaction of $CuSO_4\cdot 5H_2O$, $Na_2MoO_4\cdot 2H_2O$, 2,2′-bipyridine (bpy), $H_2O_3P(CH_2)_4PO_3H_2$ and water in the mole ratio 1.0 : 1.7 : 1.9 : 2.5 : 3760 at 180 °C for 39 h. The IR spectrum of **1** exhibited a strong band at 916 cm^{-1} attributed to $\nu(Mo{=}O)$ and a group of three medium to strong intensity features between 1030 and 1125 cm^{-1} associated with $\nu(P–O)$ of the diphosphonate ligand.

As shown in Fig. 1,† the structure of **1** consists of a one-dimensional chain constructed from $\{Mo_5O_{21}\}$ cyclic clusters, linked through diphosphonate ligands and decorated by $\{Cu(bpy)_2\}^{2+}$ and $\{Cu(bpy)(H_2O)_2\}^{2+}$ square pyramidal subunits. The diphosphonate ligands serve to bridge to adjacent clusters, coordinating exclusively to Mo sites at one $\{O_3P–\}$ terminus and to Mo and Cu centers at the other.

The disposition and number of phosphonate groups associated with the cyclic molybdate core of the cluster building block of **1** limits structural expansion to one dimension. However, the presence of the secondary metal–ligand subunits decorating the surfaces of the molybdate clusters suggested a strategy for extension into two dimensions by tethering the Cu(II) sites through an appropriate binucleating ligand. Thus,



Scheme 1 The construction of a one-dimensional structure, exploiting cluster building blocks linked through organic tethers; (b) a two-dimensional network fashioned from a chain of tethered clusters, decorated by secondary metal sites which are in turn connected through a binucleating ligand.

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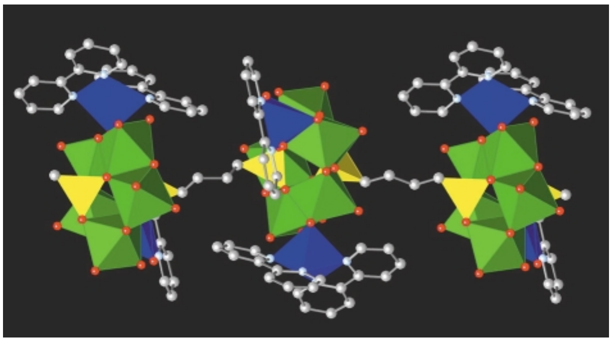

Fig. 1 A polyhedral representation of the structure of $[\{Cu(bpy)_2\}\{Cu(bpy)(H_2O)\}(Mo_5O_{15})\{O_3P(CH_2)_4PO_3\}]\cdot H_2O$ (**1**·H_2O). Molybdenum, green polyhedra; copper, blue polyhedra; oxygen, red spheres; carbon, silver spheres; nitrogen, light blue spheres.

the three component system illustrated in Scheme 1(b) contains the structural information for the self assembly of a hybrid network.

This expectation was realized with the isolation of $[\{Cu_2(tpypyz)(H_2O)_2\}(Mo_5O_{15})(O_3PCH_2CH_2PO_3)]\cdot 5.5H_2O$ (**2**·$5.5H_2O$). Compound **2** was prepared as dark yellow crystals in 25% yield based on molybdenum in the hydrothermal reaction of $Cu(MeCO_2)_2\cdot H_2O$, MoO_3, tetra(2-pyridyl)pyrazine, $H_2O_3PCH_2CH_2PO_3H_2$ water and H_2SO_4 in the mole ratio 2.2 : 5.6 : 1.0 : 2.5 : 2600 : 10 at 150 °C for 48 h.

As shown in Fig. 2,† the structure of **2** consists of one-dimensional $\{(Mo_5O_{15})(O_3PCH_2CH_2PO_3)\}_n{}^{4n-}$ chains linked through $\{Cu_2(tpypyz)(H_2O)_2\}^{4+}$ subunits into a two-dimensional network. While the molybdophosphonate chain of **2** is constructed from identical $\{(Mo_5O_{15})(O_3P\text{–})_2\}$ substructures as those described for **1** and the parent clusters, the dispositions of the secondary metal–ligand subunits about the clusters are quite different in **1** and **2**. The two distinct square pyramidal Cu(II) sites of **1** are associated with a single polyoxomolybdate cluster. In contrast, each molybdate cluster of **2** associates with three Cu(II) sites, one octahedral and two square pyramidal. The square pyramidal $\{CuN_3O_2\}$ centers bridge Mo sites on two adjacent rings in a chain, while the octahedral $\{CuN_3O_3\}$ sites shares a single corner with one cluster. The remaining coordination sites are occupied by the three nitrogen donors of one terminus of the tpypyz ligand and two aqua ligands. The coordinated water molecules project into a cavity in the network, whose perimeter is defined by terminal oxo-groups from the Mo sites of adjacent chains. The water of crystallization occupies interlamellar sites disposed above and below these cavities.

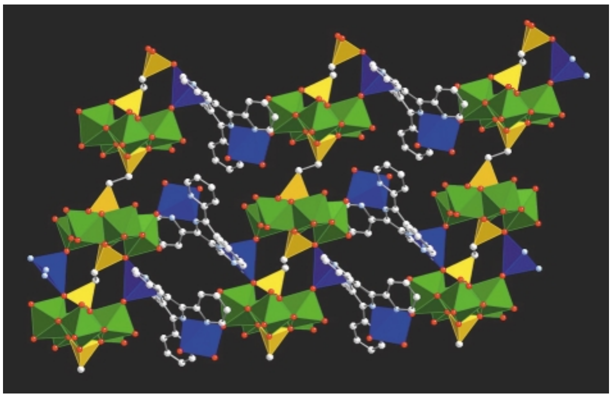

Fig. 2 A polyhedral representation of the network structure of $[\{Cu_2(tpypyz)(H_2O)_2\}(Mo_5O_{15})(O_3PCH_2CH_2PO_3)]\cdot 5.5H_2O$ (**2**·$5.5H_2O$). Color scheme as above.

These observations demonstrate not only that modification of oxide microstructure by organic components is readily accomplished, but also that extended hybrid oxide structures may be constructed by design. The synthetic approach draws on the fundamental principles of coordination chemistry. Thus, the information required for the self-assembly of the extended hybrid structures is present at the molecular level in the component building blocks. However, it must be recognized that the design principles inherent in this strategy provide only a broad blueprint, relying as often as not on serendipitous discovery of novel architectures and requiring a judicious selection of component substructures for further elaboration.

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Notes and references

† *Crystal data*: $C_{34}H_{31}Cu_2Mo_5N_6O_{23}P_2$ (**1**·H_2O), M_w = 1560.37, triclinic, space group $P\bar{1}$, a = 11.3132(6), b = 12.8735(7), c = 18.297(1) Å, α = 71.690(1), β = 82.910(1), γ = 65.580(1)°, V = 2303.5(2) Å^3, Z = 2, D_c = 2.250 g cm^{-3}, T = 90 K; structure solution and refinement based on 10748 reflections converged at R_1 = 0.0545, wR_2 = 0.1060. The carbon atoms of the diphosphonate bridge exhibit disorder over two sites and consequently have been treated isotropically in the refinement. All other non-hydrogen atoms have been refined anisotropically.

$C_{26}H_{35}Cu_2Mo_5N_6O_{28.5}P_2$ (**2**·$5.5H_2O$), M_w = 1556.32, triclinic, space group $P\bar{1}$, a = 12.0806(5), b = 14.6803(6), c = 15.5760(c) Å, α = 107.613(1), β = 101.480(1), γ = 113.935(1)°, V = 2236.26(2) Å^3, Z = 2, D_c = 2.311 g cm^{-3}, T = 90 K; structure solution and refinement converged at R_1 = 0.0409 and wR_2 = 0.0991. While the water molecules of crystallization exhibit some disorder, the total water content is confirmed by thermal gravimetric analysis. A weight loss of *ca.* 6.5% between 120–150 °C corresponds to the loss of 5.5 water molecules (6.4%, theoretical). A further weight loss of *ca.* 3.0% at 180–220 °C is consistent with the loss of the two aqua ligands.

CCDC reference numbers 165559 and 165560. See http://www.rsc.org/suppdata/cc/b1/b104860k/ for crystallographic data in CIF or other electronic format.

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