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Phosphomolybdate clusters as molecular building blocks in the design of one-, two- and three-dimensional organic–inorganic hybrid materials

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Abstract

An attractive approach to the design of inorganic solids exploits the tethering of inorganic clusters through organic spacers to produce hybrid materials with composite properties. We have recently described a modified strategy in which polyoxometalate clusters are linked through organic subunits to give an anionic hybrid substructure which may be further modified through the introduction of secondary metal–ligand complex (SMLC) cations, serving as a third component building block. In this application, the molybdophosphonate cluster $\{Mo_5O_{15}(O_3PR)_2\}^{4-}$ serves as a secondary building unit (SBU) with alkyl $(CH_2)_n$ or aromatic $-(C_6H_4)_n-$ tethers providing one-dimensional structural expansion. A binucleating ligand such as tetrapyridylpyrazine (tpyprz) is used to bridge secondary metal sites into a binuclear $\{Cu_2(tpyprz)\}^{4+}$ SBU which may link phosphomolybdate clusters into two- or three-dimensional structures. The influence of a variety of structural determinants is discussed, including the tether length of the diphosphonate ligand, the coordination preferences of the secondary metal, expansion of the ligand component of the SMLC, and substitution of As for P in the oxide SBU.

Keywords: Inorganic oxides

1. Introduction

The significant contemporary interest in the rational design of inorganic oxide materials reflects their impressive range of compositions [1], structures [2], physical properties [3] and applications [4,5]. Rather than relying on the self-assembly of individual $\{MO_x\}$ polyhedra or fundamental building units, an alternative synthetic strategy exploits discrete transition metal oxide clusters as oligomeric secondary building units (SBU) [6] with more or less predictable connectivity with appropriate tethering groups [7,8]. These tethering groups may be organic molecules, such as dipodal organonitrogen ligands [7,9], dicarboxylates [10] or diphosphonates [11,12], which have been demonstrated to profoundly influence the structures of inorganic oxides in the resultant hybrid material. Such organic–inorganic hybrid materials can combine appropriate characteristics of each component to produce novel structural types, as well as new properties arising from the interplay of the two components [13,14].

However, since the combination of the oxide cluster with organic tethering units provides an anionic substructure, a change-compensating component is required, in our application a secondary metal cation (SMC) with a chelating organoamine ligand, which occupies a number of coordination sites on the SMC so as to dictate the availability and geometry of attachment sites to the oxide clusters. In effect, the coordination complex cation provides charge-compensation, space-filling, passivating and structure-directing roles [15].

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Under the hydrothermal conditions of synthesis [16], self-assembly of the components occurs through competing hydrophilic/hydrophobic interactions to provide hierarchical structures whose properties may be tunable by appropriate manipulation of reaction conditions or components [17].

2. The molybdophosphonate–copper ligand system

We have recently demonstrated this general strategy in the development of a class of materials constructed from the linking of molybdophosphonate clusters of the $[Mo_5O_{15}(O_3PR)_2]^{4-}$ type [18] by tethering the O_3P– groups through organic linkers [19–26]. The general design concept for the construction of a one-dimensional material $[\{Cu(terpy)(H_2O)\}_2Mo_5O_{15}(O_3PCH_2CH_2PO_3)] \cdot 7H_2O$ ($\mathbf{1} \cdot 7H_2O$) is illustrated in Fig. 1. A noteworthy feature of the structure is the adhesion of the $\{Cu(terpy)(H_2O)\}^{2+}$ subunit to the surface of the molybdate cluster, suggesting that the dimensionality of the material may be expanded through the simple expedient of introducing a binucleating organonitrogen ligand to tether phosphomolybdate chains through $\{Cu_2(L{\sim}L)\}^{4+}$ units. The successful implementation of this strategy is shown in Fig. 2 for the structure of $[\{Cu_2(tpyprz)(H_2O)_2\}Mo_5O_{15}(O_3PCH_2CH_2PO_3)] \cdot 5.5H_2O$ ($\mathbf{2} \cdot 5.5H_2O$), where tpyprz is tetra-2-pyridinylpyrazine.

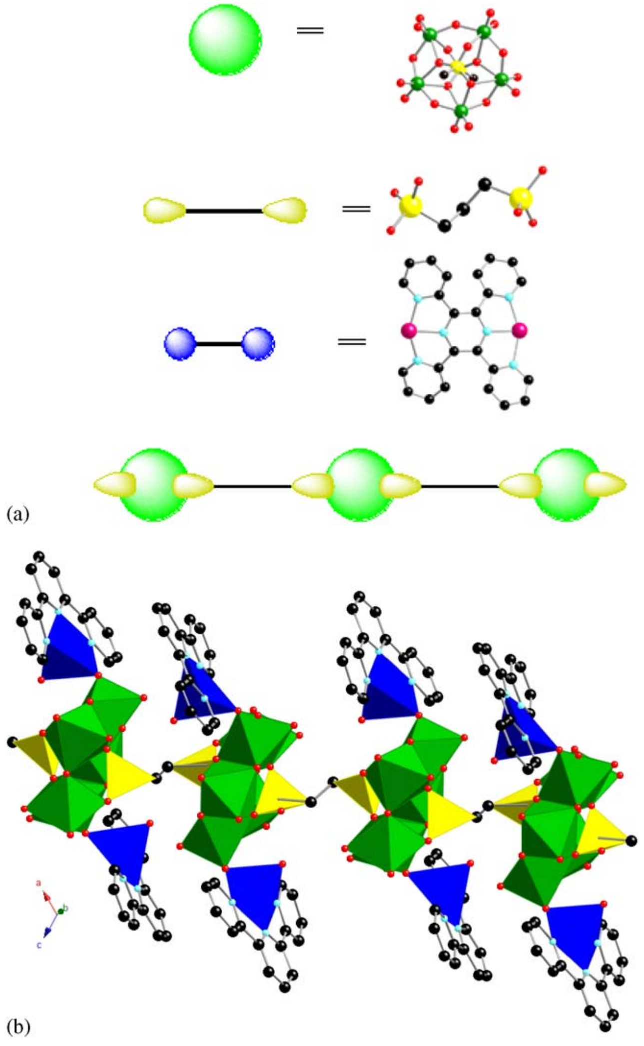

Fig. 1. (a) A polyhedral representation of the phosphomolybdate SBU $\{Mo_5O_{15}(O_3PR)_2\}^{4-}$ and the construction of a one-dimensional chain. (b) The structure of $[\{Cu(terpy)(H_2O)\}_2Mo_5O_{15}(O_3PCH_2CH_2PO_3)]$.

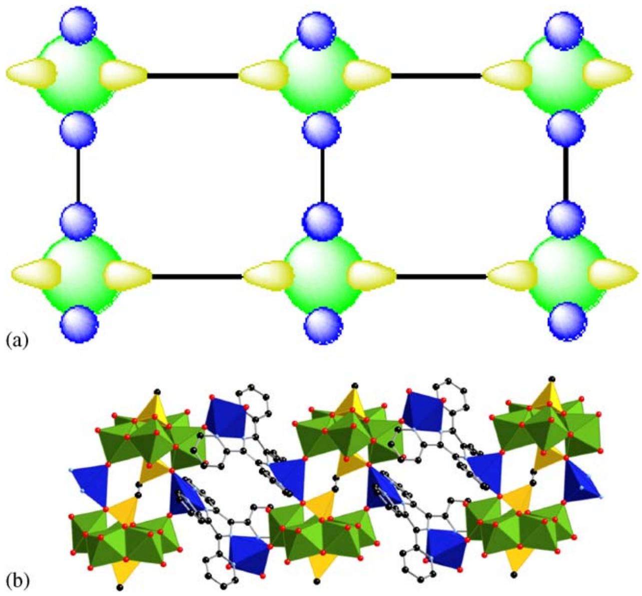

Fig. 2. (a) Schematic representation of the construction of a two-dimensional network, based on the molybdophosphonate SBU and binuclear Cu(II) subunits. (b) A polyhedral representation of the structure of $[\{Cu_2(tpyprz)(H_2O)_2\}Mo_5O_{15}(O_3PCH_2CH_2PO_3)]$.

However, the dimensionality of the product depends both on the number of points of attachment on the surface of the molybdate cluster and on their relative juxtapositions, as shown in Fig. 3 for the three-dimensional structure of $[\{Cu_2(tpyprz)(H_2O)_2\}Mo_5O_{15}\{O_3P(CH_2)_3PO_3\}] \cdot 2.25H_2O$ ($\mathbf{3} \cdot 2.25H_2O$).

While these studies in primitive design illustrate that one-, two- and three-dimensional structures may be accessed with some degree of predictability, they also alert us to the manipulation of other potential structural determinants, which include the identity of the diphosphonate ligand, the secondary metal, the design of the binucleating ligand and the size of the molybdate cluster.

3. The diphosphonate ligand

A relatively straightforward modification is variation of the diphosphonate tether length or functionality. The

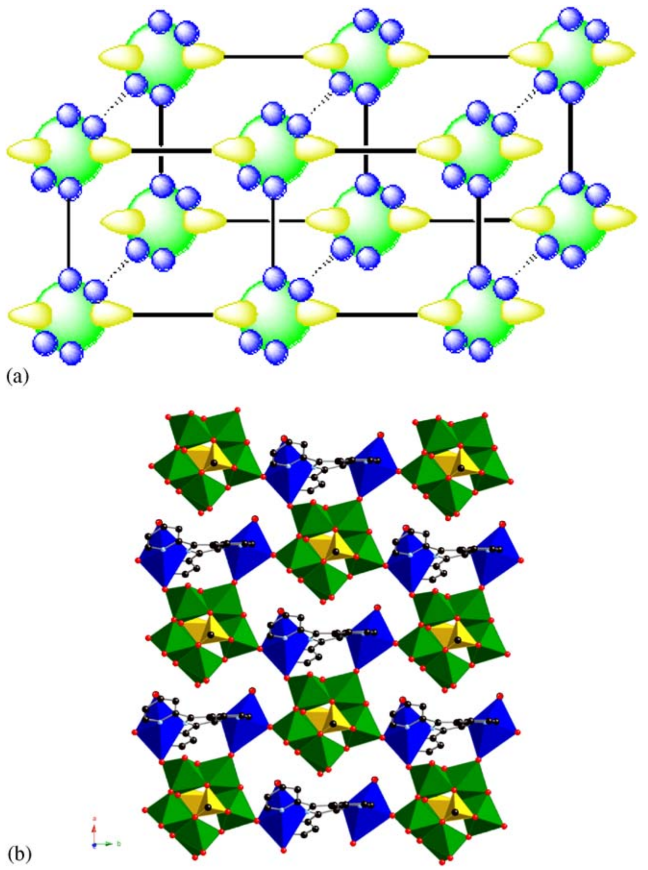

Fig. 3. (a) Schematic representations of linkage modes of the secondary metal–ligand subunit $\{Cu_2(tpyprz)\}^{4+}$ to the phosphomolybdate SBU resulting in two- and three-dimensional structures. (b) The three-dimensional structure of $[\{Cu_2(tpyprz)(H_2O)_2\}Mo_5O_{15}\{O_3P(CH_2)_3PO_3\}]$.

structural influence of the tether length and geometry is most dramatically illustrated by reducing the chain length of the $\{O_3P(CH_2)_nPO_3\}^{4-}$ unit to 1. The donor groups of methylenediphosphonate are positioned to favor the formation of a six-membered {*M*–O–P–C–P–O–} chelate ring rather than to provide expansion in one dimension through cluster bridging. The structural consequences are illustrated quite nicely in the one-dimensional phase $[\{Cu_2(tpyprz)(H_2O)\}Mo_3O_8(HO_3PCH_2PO_3)_2]\cdot 8H_2O$ (**4**·$8H_2O$), shown in Fig. 4. It is noteworthy that the adoption of the chelating mode by the diphosphonate ligand precludes formation of the $\{Mo_5O_{15}(O_3PR)_2\}^{4-}$ cluster, resulting in the isolation of a new cluster subunit, $\{Mo_3O_8(HO_3PCH_2PO_3)_2\}^{4-}$. This is a persistent subunit which also appears in the one-dimensional $[\{Cu_2(tpyprz)(H_2O)\}_2(Mo_3O_8)_2(O_3PCH_2PO_3)_3]$ (**5**) and the three-dimensional $[\{Cu_2(tpyprz)(H_2O)_2\}(Mo_3O_8)_2(O_3PCH_2PO_3)_2]$ (**6**), which is shown in Fig. 5. The molybdophosphonate building blocks of **4**, **5**, and **6** are the isolated $\{Mo_3O_8(HO_3PCH_2PO_3)_2\}^{4-}$ SBU, two fused SBUs in $\{(Mo_3O_8)_2(O_3PCH_2PO_3)_3\}^{8-}$ and a chain of SBUs in $\{(Mo_3O_8)_2(O_3PCH_2PO_3)_2\}_n{}^{4n-}$, respectively.

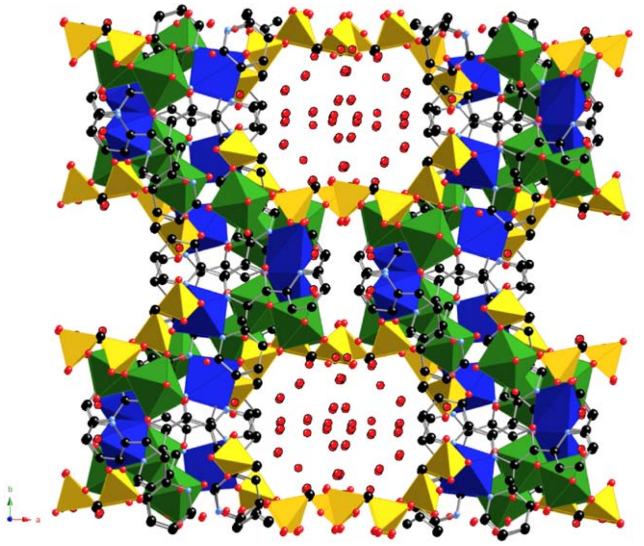

Fig. 4. A polyhedral representation of the one-dimensional structure of $[\{Cu_2(tpyprz)(H_2O)\}Mo_3O_8(HO_3PCH_2PO_3)_2]$.

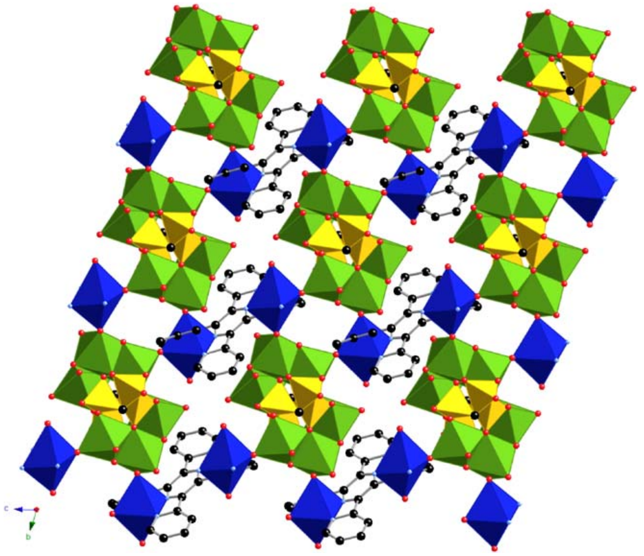

Fig. 5. A view of the three-dimensional structure of $[\{Cu_2(tpyprz)(H_2O)_2\}(Mo_3O_8)_2(O_3PCH_2PO_3)_2]$.

Replacing the alkyl tether of the diphosphonate with aromatic groups also results in unusual structural consequences, as illustrated by $[\{Cu(tpyprz)(H_2O)\}_2M_5O_{15}\{O_3P(C_6H_4)_2PO_3\}]$ (**7**) (*M* = Mo, W), shown in Fig. 6. Curiously, the tpyprz ligand binds a single Cu(II), leaving a set of pendant pyridyl groups. The $\{Cu(tpyprz)(H_2O)\}^{2+}$ subunits do not project from the molybdophosphonate chain at angles of 60–90° but rather orient nearly parallel to the chain axis.

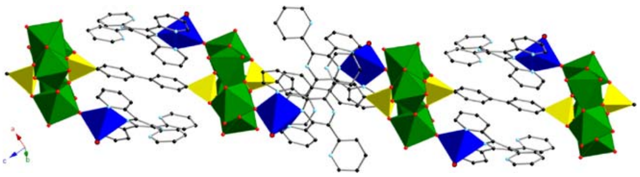

Fig. 6. A polyhedral representation of the one-dimensional structure of $[\{Cu(tpyprz)(H_2O)\}_2Mo_5O_{15}\{O_3P(C_6H_4)_2PO_3\}]$.

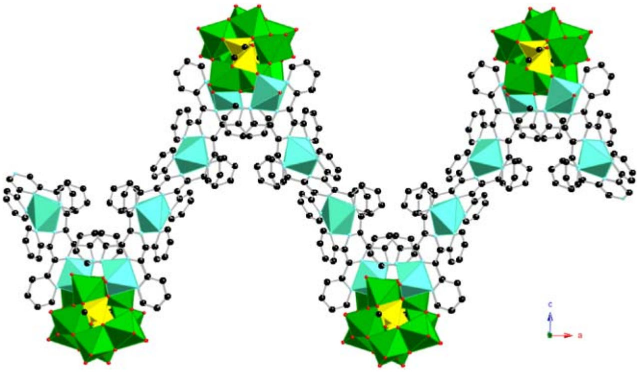

Fig. 7. The two-dimensional structure of $[\{Ni_4(tpyprz)_3\}\{Mo_5O_{15}(O_3PCH_2CH_2PO_3)\}_2]$.

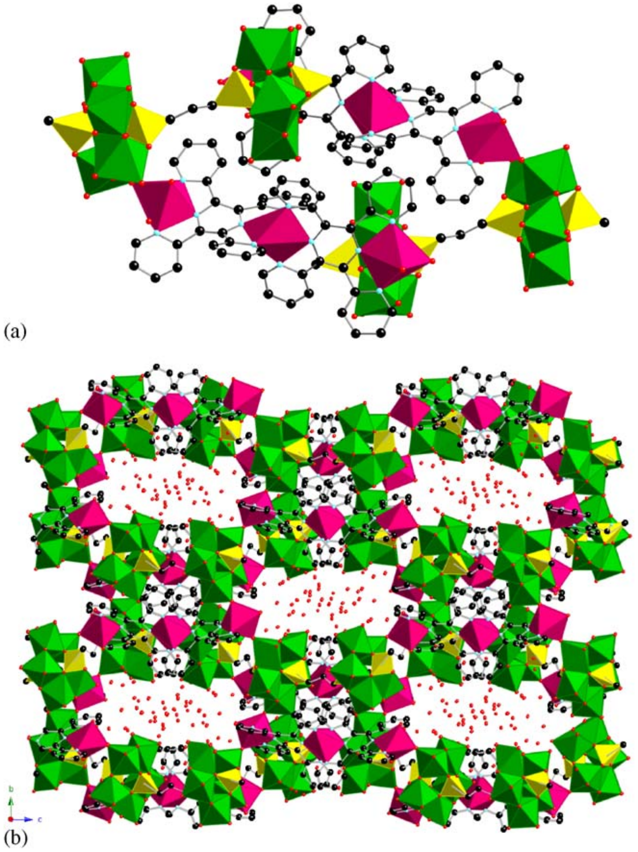

Fig. 8. (a) A view of the catenation to provide $\{Co_3(tpyprz)_2(H_2O)_3\}^{6+}$ building blocks. (b) A polyhedral representation of the structure of $[\{Co_3(tpyprz)_2(H_2O)_3\}[Mo_5O_{15}\{O_3P(CH_2)_3PO_3\}]_2]$, showing the large cavities occupied by the H_2O solvate molecules.

4. The secondary metal component

The identity of the secondary metal must also serve as a structural determinant since the coordination preferences of different transition metal centers are quite distinct. The examples described above contain Cu(II) as the secondary metal, a cation distinguished by Jahn–Teller distortions from regular octahedral geometry and characteristically displaying square planar, "4 + 1" or "4 + 2" axially distorted coordination. While these distorted geometries afford considerable flexibility of attachment to the surface of the oxide clusters, they preclude regular $\{CuN_6\}$ coordination modes through attachment to two tpyprz ligands and catenation into $\{Cu_2(tpyprz)\}_n^{4n+}$ chains. In contrast, Ni(II) exhibits more regular six coordination which allows the $\{NiN_6\}$ binding pattern to compete effectively with the $\{NiN_3O_3\}$ coordination mode adopted in linking to the cluster surface. This characteristic is representative of the structure of $[\{Ni_4(tpyprz)_3\}\{Mo_5O_{15}(O_3PCH_2CH_2PO_3)\}_2]\cdot 23H_2O$ (**8** $\cdot\, 23H_2O$) whose structure is shown in Fig. 7, where catenation provides the oligomeric $\{Ni_4(tpyprz)_3\}^{8+}$ building block.

Catenation is not restricted to the Ni(II)-containing structures, but rather is also observed for the Co(II) analogues, of which $[\{Co_3(tpyprz)_2(H_2O)_3\}[Mo_5O_{15}\{O_3P(CH_2)_3PO_3\}]_2]\cdot 23H_2O$ (**9** $\cdot\, 23H_2O$), shown in Fig. 8, is typical. The cobalt series exhibits other unique characteristics: the first is consistent incorporation of aqua ligands at the Co(II) sites and the second is assembly of new cluster SBUs. This latter observation is illustrated by the structure of $[\{Co_2(tpyprz)(H_2O)_2\}Mo_6O_{18}\{O_3P(CH_2)_5PO_3\}]\cdot 5H_2O$ (**10** $\cdot\, 5H_2O$) shown in Fig. 9, which is distinguished by the presence of a hexanuclear phosphomolybdate SBU, $\{Mo_6O_{18}[O_3P(CH_2)_5PO_3]\}^{4-}$.

The identity of the ligand of the secondary metal coordination complex subunit may also be varied, often with unpredictable results. Thus, replacement of tpyprz by 2,2′:4′,4″:2″,2‴-quarterpyridyl-6′,6″-di-2-pyridine (bisterpy) provides $[\{Cu_2(bisterpy)(H_2O)_2\}Mo_4O_{12}(O_3PCH_2CH_2PO_3)]$ (**11**), a two-dimensional material exhibiting yet another cluster SBU, $\{Mo_4O_{12}(O_3PR)_2\}^{4-}$, as shown in Fig. 10.

5. The molybdate building block

For structures based on the $\{Mo_5O_{15}(O_3PR)_2\}^{4-}$ SBU, the number of points of attachment accessible to the secondary metal components appears to be limited

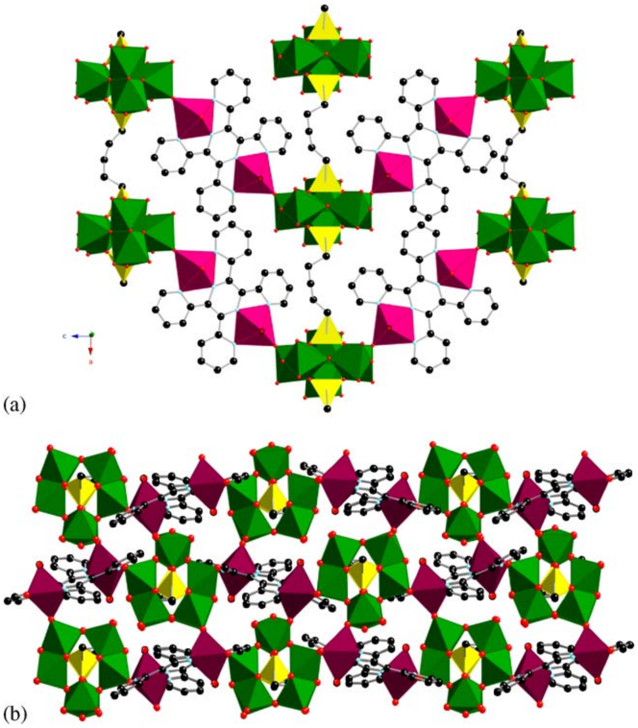

Fig. 9. Two views of the structure of [{Co_2(tpyprz)$(H_2O)_2$}Mo_6O_{18}{$O_3P(CH_2)_5PO_3$}]. In the top view, the expanded cluster [Mo_6O_{18}{$O_3P(CH_2)_5PO_3$}]$^{4-}$ is apparent.

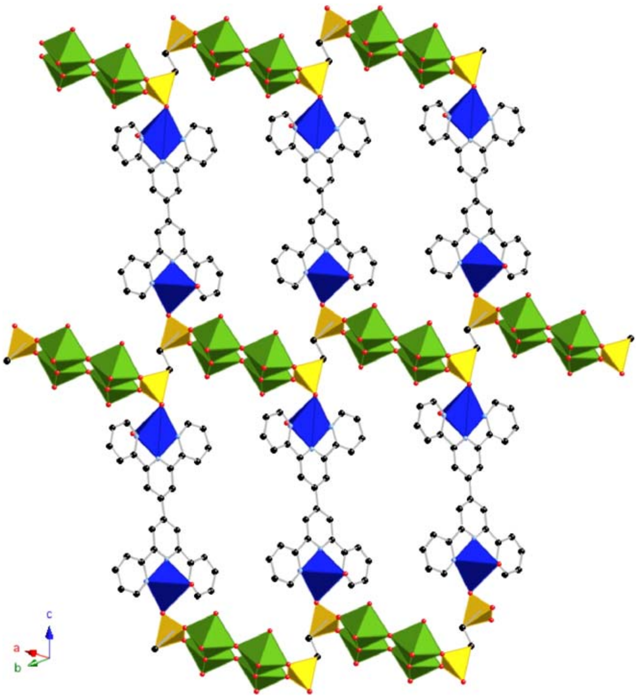

Fig. 10. A polyhedral representation of the structure of [{Cu_2(bisterpy)$(H_2O)_2$}$Mo_4O_{12}(O_3PCH_2CH_2PO_3)$].

to no more than four. In order to expand the number of binding loci on the cluster surface and possibly influence structural dimensionality, the obvious expedient is to increase the size of the cluster. This is readily accomplished by replacing the O_3P– unit with its arsonate analogue O_3As–. In fact, it is well documented that the molybdoarsonate clusters are hexanuclear rings of the type $\{Mo_6O_{18}(O_3AsR)_2\}^{4-}$ [27], as a consequence of the larger covalent radius of arsenic in comparison to that of phosphorus. Thus, the two-dimensional structure of [{Cu(tpyprz)}$Mo_6O_{18}(O_3AsC_6H_5)_2$] · $2H_2O$ (**12** · $2H_2O$), shown in Fig. 11, exhibits six Cu–O–Mo linkages per hexanuclear cluster.

We anticipated that substitution of the phenylarsonate by a bridging diarsonate ligand would provide expansion in the third dimension to give a framework structure. In fact, the introduction of a diarsonate provided the unusual two-dimensional phase [{Cu_2(tpyprz)(H_2O)}$Mo_6O_{18}(H_2O)${$O_3AsCH_2CH(OH)CH_2AsO_3$}] (**13**), shown in Fig. 12. The structure is distinguished

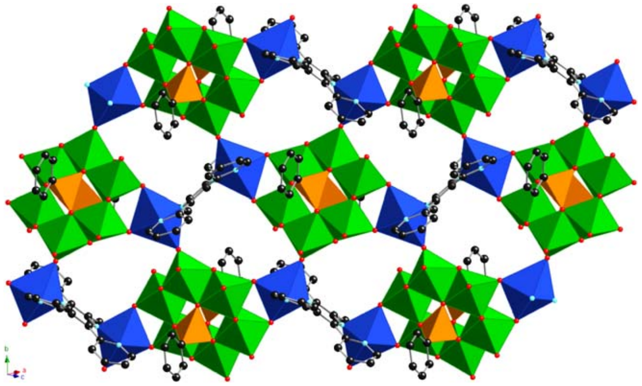

Fig. 11. The two-dimensional structure of [{Cu_2(tpyprz)}$Mo_6O_{18}(O_3AsC_6H_5)_2$].

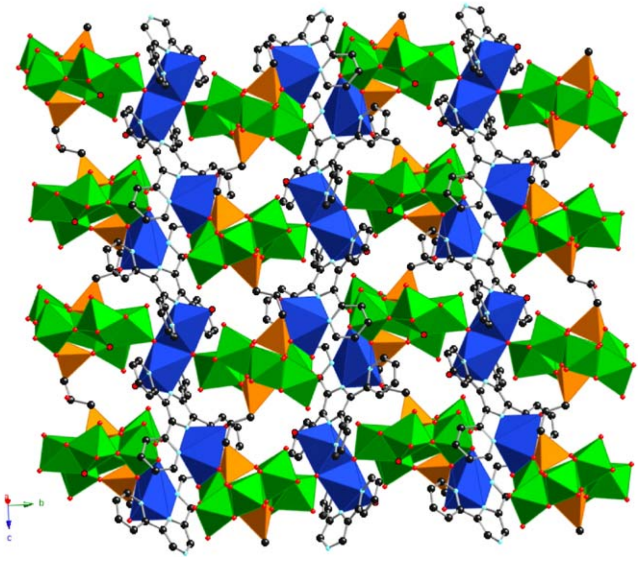

Fig. 12. A polyhedral representation of the two-dimensional structure of [{Cu_2(tpyprz)(H_2O)}$Mo_6O_{18}(H_2O)(O_3AsCH_2CH(OH)CH_2AsO_3)$].

by the presence of a tetranuclear Cu(II) subunit $\{Cu_4(tpyprz)_2(H_2O)_2\}^{8+}$ which results from the edge-sharing of two copper square pyramids of two adjacent binuclear $\{Cu_2(tpyprz)(H_2O)\}^{2+}$ units through oxo-groups of neighboring molybdoarsonate clusters. Furthermore, an unusual $\{Mo_6O_{18}(H_2O)(O_3AsR)_2\}^{4-}$ cluster SBU, which contains a pair of face sharing $\{MoO_6\}$ octahedra, is embedded in the structure.

6. Conclusions

The investigations of the family of materials constructed from molybdophosphonate anions and secondary metal coordination complex cations reveal that the $\{Mo_5O_{15}(O_3PR)_2\}^{4-}$ building block is a recurrent theme of the structural chemistry. While the Cu(II), Ni(II) and Co(II) families of materials share this structural motif, the details of the connectivities between the building blocks are generally quite distinct. The structural systematics reveal the importance of the SMC as a structural determinant, a not unanticipated observation in view of the different coordination preferences of the divalent metal cations.

While the chemistry reveals a degree of predictability which offers some primitive design principles, the interplay of a variety of structural determinants is reflected in the observation of novel cluster SBUs. For example, manipulation of the tether length of the diphosphonate ligand results in materials based on the trinuclear $\{Mo_3O_8(O_3PR)_2\}^{2-}$ cluster, while expansion of the ligand length in the secondary metal coordination complex cation has provided the $\{Mo_4O_{12}(O_3PR)_2\}^{4-}$ substructure. Similarly, substitution of arsenic for phosphorus in the anionic SBU provides the expanded cluster $\{Mo_6O_{18}(O_3AsR)_2\}^{4-}$ as a recurrent structural theme.

Consequently, while the molecular building block approach to new oxide materials is demonstrably feasible, total predictability of structure remains elusive due to the complexity of the hydrothermal parameter space and the diversity of linkage modes available to the constituent building blocks. Despite such limitations, predictable structural propagation in one to three dimensions has been achieved in this case and has been most elegantly described recently for the porous titanophosphates [6], suggesting that as the structural database and the systematic investigation of the synthetic domain for such materials continues to evolve, the correlation of reactivity, properties and structure will fully emerge.

Acknowledgments

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