Inorganic Chemistry Communications 14 (2011) 107–110

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Construction of bimetallic oxide materials from molybdate building blocks and copper–ligand tethers with flexible spaces: Structures of the two-dimensional $[\{Cu_2(L4)(H_2O)_2\}Mo_8O_{26}(H_2O)_2]$ and of the three-dimensional $[\{Cu_2(L4)\}_2(Mo_8O_{26})(MoO_4)_2]$ (L4 = N^1, N^1, N^4, N^4-tetrakis(pyridin-2-ylmethyl)butane-1,4-diamine)

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ARTICLE INFO

Article history:
Received 13 September 2010
Accepted 30 September 2010
Available online 30 October 2010

Keywords:
Copper molybdate coordination polymers
Octamolybdate cluster building blocks
Organonitrogen dipodal ligands
Hydrothermal synthesis

ABSTRACT

The hydrothermal reactions of cupric acetate, MoO_3 and the dipodal linker ligand N^1, N^1, N^4, N^4-tetrakis(pyridin-2-ylmethyl)butane-1,4-diamine (L4) provided a high temperature phase $[\{Cu_2(L4)(H_2O)_2\}Mo_8O_{26}(H_2O)_2]\cdot 2H_2O$ (**1**$\cdot 2H_2O$) and a low temperature phase $[\{Cu_2(L4)\}_2\{Mo_8O_{26}\}\{MoO_4\}_2]\cdot 2H_2O$ (**2**$\cdot 2H_2O$). Compound **1** is two-dimensional, constructed from $\{Mo_8O_{26}(H_2O)_2\}^{4-}$ clusters linked through $\{Cu_2(L4)(H_2O)_2\}^{4+}$ rods. In contrast, compound **2** is three-dimensional with two distinct molybdate building blocks, γ-$\{Mo_8O_{26}\}^{4-}$ clusters and $\{MoO_4\}^{2-}$ tetrahedra, linked through two distinct $\{Cu_2(L4)\}^{4+}$ subunits, one connecting four $\{MoO_4\}^{2+}$ tetrahedra and the second a $\{MoO_4\}^{2+}$ tetrahedron and one octamolybdate cluster.

The significant contemporary interest in inorganic oxides reflects their vast compositional range and considerable structural diversity, characteristics related to a range of useful physical properties and applications [1–11]. The rational design of new oxide phases drives the development of synthetic strategies. One approach that has witnessed considerable attention in recent years exploits organic components or secondary metal complexes to modify the structure and properties of the oxide [12–19].

In this respect, an attractive bottom-up strategy for the design of complex organic–inorganic hybrid oxide materials is the building block approach that links molecular oxide clusters through organic tethers of secondary metal–ligand complexes [20–27]. An example is the use of chemically robust and structurally diverse polyoxometalate clusters [28–34] as nodes from which organic or metal complex tethers radiate to provide spatial expansion. Complex structures have been derived from polyoxomolybdate clusters [34], Anderson [35,36], Keggin [37–41], Silverton [42] and Wells–Dawson and double Dawson type polyanions [43–45]. In the specific case of polyoxomolybdate clusters, chains, networks and frameworks have been prepared through bridging of the clusters by secondary metal complexes [46–51]. Of this class of materials, composites constructed from embedded octamolybdate clusters, $\{Mo_8O_{26}\}^{4-}$, in one of eight possible isomeric forms α through Θ, are quite common [52–62].

The second component of the material is some linker to provide connectivity between the oxide cluster nodes. Suitable oxophilic metals bridged through rigid binucleating ligands have proved most effective in this respect. For example, the $\{Cu_2(tpyprz)\}^{4+}$ rod-like moiety (tpyprz = tetrapyridyl pyrazine) has proved most effective as a component of materials of the $[Cu_2(tpyprz)(H_2O)_x(Mo_8O_{26})]$ class. We have recently begun to investigate the structural chemistry of such composite materials using flexible, rather than rigid, binucleating ligands. In this paper, we describe the structures of two novel copper-molybdates, isolated from the hydrothermal reactions of cupric acetate, molybdenum oxide and the linker ligand N^1,N^1,N^4,N^4-tetrakis(pyridin-2-ylmethyl)butane-1,4-diamine (L4): the two dimensional $[\{Cu_2(L4)(H_2O)_2\}Mo_8O_{26}(H_2O)_2]\cdot 2H_2O$ (**1**$\cdot 2H_2O$) and the three-dimensional $[\{Cu_2(L4)\}_2(Mo_8O_{26})(MoO_4)_2]\cdot 2H_2O$ (**2**$\cdot 2H_2O$).

The hydrothermal reactions of cupric acetate, molybdenum(VI) oxide and L4 at 100 °C and 85 °C provided blue crystals of **1**$\cdot 2H_2O$ and **2**$\cdot 2H_2O$, respectively [63]. As shown in Fig. 1, the structure of **1** is two-dimensional, constructed from the novel octamolybdate clusters $\{Mo_8O_{26}(H_2O)_2\}^{4-}$ linked through $\{Cu_2(L4)(H_2O)_2\}^{4+}$ tethers [64]. The anionic component is the centrosymmetric $\{Mo_8O_{26}(H_2O)_2\}^{4-}$ cluster, which consists of eight corner- and edge-sharing octahedra. Four octahedra exhibit two terminal oxo-groups, and two

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doi:10.1016/j.inoche.2010.09.043

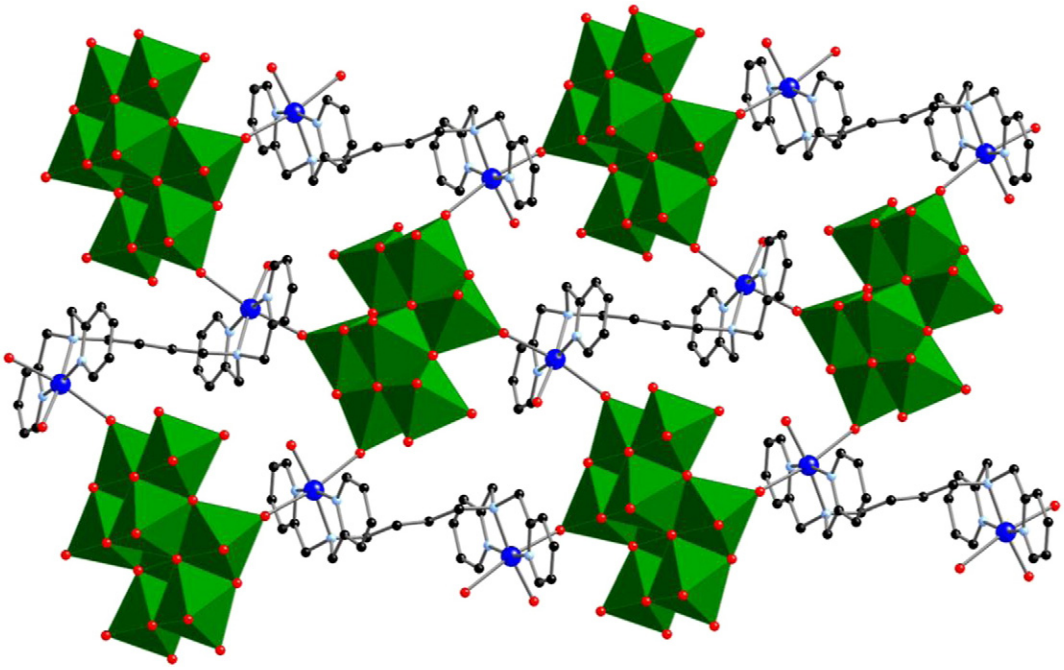

Fig. 1. Mixed polyhedral and ball and stick representation of the structure of **1**.

molybdates exhibit a single terminal oxo-group, while the remaining two molybdenum sites have two terminal oxo-groups and a terminal aqua ligand. The aqua oxygen donor is clearly identified by the Mo–O distance of 2.209(3)Å, compared to an average Mo–O$_t$ distance of 1.715(3)Å. This is the first report of the $\{Mo_8O_{26}(H_2O)_2\}^{4-}$ cluster, although the previously reported $\{Mo_8O_{26}(OH)_2\}^{6-}$ and $\{Mo_8O_{26}(HCO_2)_2\}^{6}$ $^{-}$anions are structurally analogous [65–67]. The $\{Cu_2(L4)(H_2O)_2\}^{4+}$ rods each link four clusters in the *bc* plane, through two copper to terminal oxo-group bonds at each terminus of the bridging unit. The Cu(II) sites exhibit axially distorted '4 + 2' coordination. The equatorial plane is defined by the three nitrogen donors of the L4 and an aqua ligand, while the axial positions are occupied by oxo-groups from two adjacent clusters at elongated bond lengths of 2.371(3) Å and 2.478(3) Å.

In contrast to the two-dimensional structure of **1**, compound **2** adopts the three-dimensional structure, shown in Fig. 2. In this case, there are two distinct molybdate building blocks: the γ-$\{Mo_8O_{26}\}^{4-}$ cluster and $\{MoO_4\}^{2-}$ tetrahedral units. The γ-$\{Mo_8O_{26}\}^{4-}$ cluster consists of edge- and corner-sharing octahedra and square pyramids, in contrast to the exclusively octahedral components of $\{Mo_8O_{26}(H_2O)_2\}^{4-}$. The cluster has been previously identified as a building block in $[\{Cu(pyrimidine)\}_4Mo_8O_{26}]$ [47] and $[\{Cu(en)\}_2Mo_8O_{26}]$ [68].

There are also two distinct copper–ligand components linking the molybdate nodes. The first $\{Cu_2(L4)\}^{4+}$ tether connects four $\{MoO_4\}^{2-}$ tetrahedra, two at each terminus. This linkage produces $[Cu_2(L4)(MoO_4)_2]_n$ chains that propagate parallel to the *a* axis. The bonding pattern generates eight membered heterocyclic rings, {Mo–O–Cu–O–}$_2$.

The second binuclear tether bonds to an $\{Mo_8O_{26}\}^{4-}$cluster and an $\{MoO_4\}^{2-}$tetrahedron at each terminus. While the first $\{Cu_2(L4)\}^{4+}$ unit sits in the *bc* plane, this second unit projects above and below the plane along the *a*-direction. Consequently, the structure may be described as $[\{Cu_2(L4)\}_2(Mo_8O_{26})(MoO_4)_2]_n$ layers linked through the butylene tethers of this latter $\{Cu_2(L4)\}^{4+}$ unit.

It is also noteworthy that the $[\{Cu_2(L4)\}_2(MoO_4)_2]_n^{4n+}$ substructure is itself three-dimensional, suggesting that the structure can be viewed as a $[\{Cu_2(L4)\}_2(MoO_4)_2]_n^{4n+}$ framework with embedded $\{Mo_8O_{26}\}^{4-}$ charge compensating anions.

The copper sites exhibit '4 + 1' axially distorted geometries. One site displays a basal plane defined by the three nitrogen donors of the ligand and an oxo-group from an $\{MoO_4\}^{2-}$ unit, with an oxo-group from a second $\{MoO_4\}^{2-}$ tetrahedron in the apical position. In contrast the second Cu(II) site bonds to an oxo-group from a $\{Mo_8O_{26}\}^{4-}$ cluster at the elongated apical site.

In conclusion, hydrothermal synthesis has provided two novel examples of copper–ligand-molybdate materials. The two-dimensional $[\{Cu_2(L4)(H_2O)_2\}Mo_8O_{26}(H_2O)_2]$ (**1**) is constructed from a novel octamolybdate cluster $\{Mo_8O_{26}(H_2O)_2\}^{4-}$, while the three-dimensional phase $[\{Cu_2(L4)\}_2(Mo_8O_{26})(MoO_4)_2]$ (**2**) is an unusual example of an oxide constructed from two distinct molybdate building blocks. The unanticipated structural chemistry reinforces the argument that the binucleating ligand is a significant structural determinant in hybrid materials of this type. It is also apparent that small changes in hydrothermal reaction conditions can result in dramatic structural consequences.

Acknowledgment

This work was supported by a grant from the National Science Foundation (CHE0907787).

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2010.09.043.

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