

Two novel 3D bimetallic oxide framework with 16-membered wheel clusters based on $\{\text{Mo}_5\text{O}_{16}\}$ ribbon-like chains

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ABSTRACT

Two hybrid compounds based on $\{\text{Mo}_5\text{O}_{16}\}$ ribbon-like chains, $[\text{M}(3\text{-pt})_2(\text{Mo}_5\text{O}_{16})] \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Mn}$) (1 and 2) {3-pt = 5-(3-pyridyl)-tetrazole}, have been hydrothermally synthesized and characterized by single crystal X-ray diffraction. Three-dimensional Mo/O/M^{II}/tetrazole frameworks of the title compounds are constructed from 1D infinite ribbon-like $[\text{Mo}_5\text{O}_{16}]^{2-}$ chains covalently linked through $[\text{M}(3\text{-ptz})]^{2+}$ fragments via O–M and N–Mo coordinate bonds. It is noteworthy that the isostructural compounds contain an unprecedented 3D bimetallic oxide network with 16-membered wheel clusters in which two parallel interdigitated stacks of 3-pt ligands are trapped. Remarkably, the title complexes represent the first two examples of the solid materials containing $\{\text{Mo}_5\text{O}_{16}\}$ ribbon-like chains.

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Polyoxometalates (POMs) have attracted extensive interests owing to their enormous variety of intriguing structural topologies, their fascinating properties as well as great potential applications in many fields, such as catalysis, medicine, sorption, electron conductivity, magnetism and photochemistry [1–4]. As an important family of polyoxometalates (POMs), the polyoxomolybdate system is attracting much more attention [3,5]. Many examples of various inorganic–organic hybrid molybdenum oxides with discrete clusters, one-dimensional (1D) chain, two-dimensional (2D) layer and three-dimensional (3D) open-framework structures have recently been hydrothermally synthesized. However, by comparison with a great number of the molybdenum oxides cluster which are structurally modified by incorporating transition metal complexes, the solid materials containing decorated 1D $[\text{Mo}_x\text{O}_y]^{n-}$ chain still are a fairly small subset of POM-based composites [6–10]. The 1D $[\text{Mo}_x\text{O}_y]^{n-}$ polyanions in these reported solids are limited to $\{\text{Mo}_2\text{O}_7\}$ [6], $\{\text{Mo}_3\text{O}_{10}\}$ [7], $\{\text{Mo}_4\text{O}_{13}\}$ [7], $\{\text{Mo}_8\text{O}_{27}\}$ [8], $\{\text{Mo}_9\text{O}_{30}\}$ [9], $\{\text{Mo}_{10}\text{O}_{33}\}$ [10] and $\{\text{Mo}_{15}\text{O}_{47}\}$ [10] chains, and hybrid solid-state materials based on $\{\text{Mo}_5\text{O}_{16}\}$ chain are unexplored hitherto.

The development of new ligand systems is very important for the complexity of the structure of molybdenum-oxide-based organic–inorganic hybrid compound. The 5-substituted tetrazole, which exhibits variation in the possible binding mode of its nitrogen donor atoms, has been introduced into the polyoxomolybdate system to constitute 2D or

3D fascinating structures with intriguing properties, such as magnetic and optical properties [6,7a,11].

As a continuation of these investigation two interesting three-dimensional Mo/O/M^{II}/tetrazole compounds, $[\text{M}(3\text{-pt})_2(\text{Mo}_5\text{O}_{16})] \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Mn}$) {3-pt = 5-(3-pyridyl)-tetrazole}, were obtained [12]. The 3D frameworks are built from 1D infinite ribbon-like $[\text{Mo}_5\text{O}_{16}]^{2-}$ chains and $[\text{M}(3\text{-pt})]^{2+}$ fragments via the O–M and N–Mo coordinate bonds. They contain novel 3D bimetallic oxides frameworks with 16-membered wheels clusters in which two parallel interdigitated stacks of 3-pt ligands are trapped. The title compounds are the first two examples of the solid materials containing $\{\text{Mo}_5\text{O}_{16}\}$ chain.

Single crystal X-ray crystallography analysis [13] reveals that the compounds 1 and 2 are isomorphous. Complex 1 is composed of one Co^{II} cation, one $\text{Mo}_5\text{O}_{16}^{2-}$ anion and two 3-pt ligands, as shown in Fig. 1. Each Co^{II} center is coordinated by four oxo groups from two adjacent chains and two nitrogen donor atoms of two 3-pt ligands giving an octahedral adduct. The four oxo groups constitute the equatorial plane, and the two nitrogen atoms of 3-pt molecules occupy the apical positions with longer distances. The Mo1 and Mo2 atoms are both six-coordinated by five oxo groups and one nitrogen atom from a 3-pt ligand. The central Mo3 atom is located on a crystallographic twofold rotation axis and has a distorted tetrahedral geometry completed by two μ_2 -oxygen atoms and two terminal oxo-group atoms. All Mo atoms are connected to each other through μ_2 -oxygen atoms to form a Mo_5O_{16} unit which are further linked together to form infinite 1D ribbon-like chains along the *c* direction through sharing one common vertex (Fig. 2). As a result, the 1D pentamolybdate chain is formed by corner-sharing one $[\text{MoO}_4]$ tetrahedron and four $[\text{MoO}_5]$ square pyramids. The $\{\text{Mo}_5\text{O}_{16}\}$ units in the title compounds feature more interesting 1D ribbon-like chains, which are very different from the

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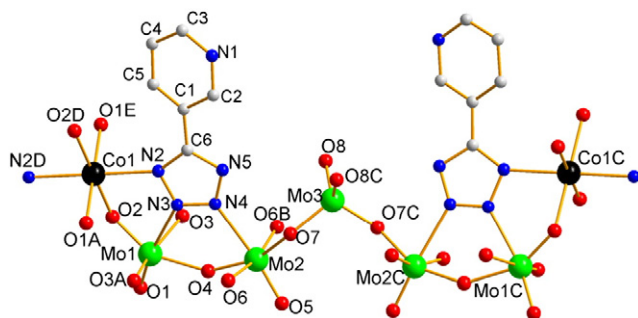


Fig. 1. View of the basic building block unit of the crystal structure of compound 1 showing the atom labeling scheme (hydrogen atoms are omitted for clarity).

2D layer structure as reported in compounds such as $[M_2(\text{pzc})_2(\text{H}_2\text{O})_x][\text{Mo}_5\text{O}_{16}]$ ($M = \text{Co}, \text{Ni}$) [14], $(\text{C}_{12}\text{H}_{14}\text{N}_2)[\text{Mo}_5\text{O}_{16}]$ [15] and $(\text{C}_4\text{H}_{12}\text{N}_2)[\text{Mo}_5\text{O}_{16}]$ [16].

The adjacent $\{\text{Mo}_5\text{O}_{16}\}$ ribbon-like chains are covalently linked through heterometal-organic units $[\text{M}(3\text{-pt})]^{2+}$ fragments via the O–M and N–Mo coordinate bonds to generate novel 3D Mo/O/Co^{II}/tetrazole frameworks (Figs. 3 and 4). It is noteworthy that the inorganic $\text{Co}^{2+}\text{-Mo}_5\text{O}_{16}^{2-}$ framework exhibits open 3D bimetallic oxide network with 16-membered wheel clusters with sufficient diameter to accommodate two parallel interdigitated stacks of 3-pt organic ligands. While the secondary metals in the reported compound $[\text{Mn}(2\text{-pt})_2(\text{Mo}_2\text{O}_7)]$ [6] are directly coordinated to the adjacent $\{\text{Mo}_2\text{O}_7\}$ chains to generate 3D heterometallic 10-membered wheel clusters in which only one stack of ligands are trapped.

The 3-pt ligand in the title compound acts as a tridentate ligand to link three adjacent metal atoms (Co1, Mo1, Mo2) with one of its tetrazolyl nitrogen atom uncoordinated, leading to formation and stabilization of the bimetallic oxide tunnels in $[\text{Co}(3\text{-pt})_2(\text{Mo}_5\text{O}_{16})]\cdot\text{H}_2\text{O}$. In addition, the pyridyl substituents of 3-pt ligand in $[\text{Co}(3\text{-pt})_2(\text{Mo}_5\text{O}_{16})]\cdot\text{H}_2\text{O}$ and 2-pt ligand in $[\text{Mn}(2\text{-pt})_2(\text{Mo}_2\text{O}_7)]$ [6] are uncoordinated, respectively, but different positions of the pyridyl substituents in the above-mentioned compounds result in the formation of different chains (Mo_5O_{16} and Mo_2O_7). It indicates that organic templating agents could dramatically influence the microstructures of molybdenum oxide frameworks. Compound 2, $[\text{Mn}(3\text{-pt})_2(\text{Mo}_5\text{O}_{16})]\cdot\text{H}_2\text{O}$, is structurally analogous to compound 1, $[\text{Co}(3\text{-pt})_2(\text{Mo}_5\text{O}_{16})]\cdot\text{H}_2\text{O}$ except for the secondary metals.

Thermogravimetric experiments of compounds 1 and 2 were performed to explore their thermal stabilities. As shown in Figs. S1 and S2, the TG curves of 1 and 2 are similar, and they both exhibit a three-step weight loss, probably due to their structural similarity. The first weight losses of 1.82% (calcd. 1.63%) in 30–225 °C for 1 and 2.05%

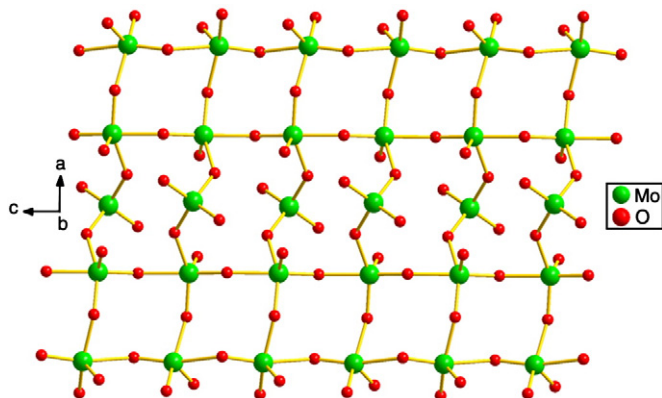


Fig. 2. The 1D $\{\text{Mo}_5\text{O}_{16}\}^{2-}$ ribbon-like chain along the c direction in 1.

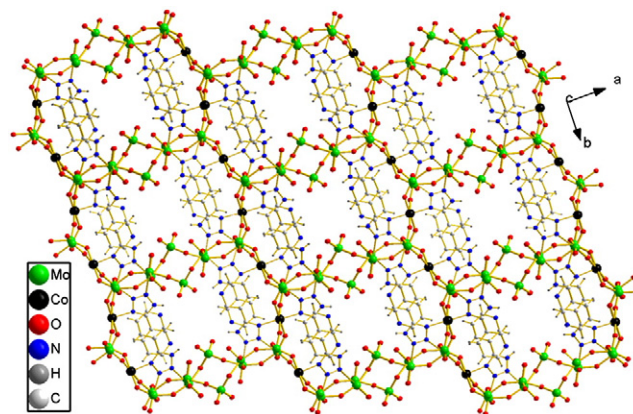


Fig. 3. View of 3D network down the c-axis for 1.

(calcd. 1.64%) in 30–220 °C for 2 are attributed to the release of crystalline water, while the following two weight losses of about 26.06% (calcd. 26.59%) in 370–800 °C for 1 and 26.11% (calcd. 26.73%) in 375–750 °C for 2 are attributed to the decomposition of 3-pt ligands. The TGA measurement indicates that the 3D M–O–M frameworks of the two compounds exhibit good thermal stability. The purity of complexes 1 and 2 is confirmed by powder X-ray diffraction (PXRD). As shown in Figs. S3 and S4, the XRD patterns of as-synthesized complexes 1 and 2 match well with their corresponding simulated patterns from single crystal data.

Cyclic voltammetry of compound 1-bulk-modified carbon paste electrode [17] in 1 M H_2SO_4 aqueous solution shows three reversible redox peaks in the potential range from –100 to +700 mV shown in Fig. 5. The peak potentials $E_{1/2} = (E_{pc} + E_{pa})/2$ are 37, 241 and 400 mV (scan rates: 50 mV/s), and the values of peak-to-peak separation between the corresponding anodic and cathodic peaks (ΔE_p) are 36 (I–I'), 32 (II–II') and 35 mV (III–III'), respectively, which are ascribed to three consecutive two-electron processes of Mo [18]. The peak potentials change gradually following the scan rate from 50 to 500 mV/s: the cathodic peak potentials shift to the negative direction and the corresponding anodic peak potentials to the positive direction. The peak-to-peak separation between the corresponding cathodic and anodic peaks increases with the scan rate increasing, but the mean peak potentials do not change on the whole. It indicates that compound 1 may be used as a potential electrocatalyst in solutions owing to its good electrochemical activity.

In conclusion, two molybdenum-oxide-based inorganic-organic hybrid compounds, $[\{\text{M}(3\text{-pt})_2((\text{Mo}_5\text{O}_{16})\cdot\text{H}_2\text{O})\}(\text{M} = \text{Co}, \text{Mn})$ have

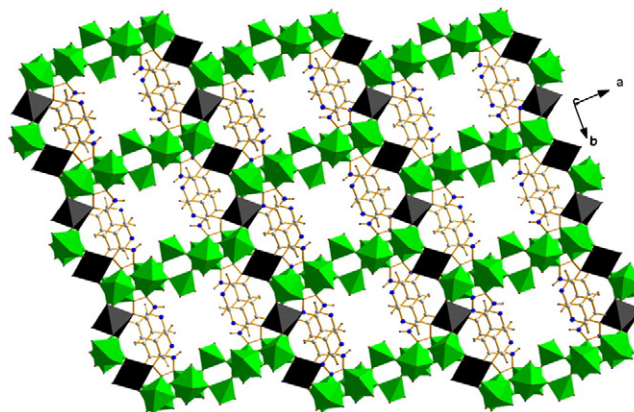


Fig. 4. Polyhedron view of a corrugated 16-membered heterometal wheels for 1 (green and black polyhedrons represent Mo, Co atoms, respectively).

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