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From Molecular Double-Ladders to an Unprecedented Polycatenation: A Parallel Catenated 3D Network Containing Bicapped Keggin Polyoxometalate Clusters

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A new three-dimensional coordination polymer, $\{Cu_3(4,4'\text{-}bpy)_3(H_2O)[PMo_{12}O_{40}(VO)_2]\cdot 5H_2O\}_n$ (**1**) (4,4′-bpy = 4,4′-bipyridine), which represents the first example of 3D polycatenation generated by unprecedented parallel catenation of the 1D double ladders, has been hydrothermally synthesized.

Introduction

Self-assembly of entangled network structures based upon the principle of crystal engineering has attracted much attention not only because of their promising potential applications in catalysis, ion exchange, photochemistry, and electromagnetism, but also because of their intriguing architectures and topologies.[1] Up to now, a number of entangled networks have been reported, however, the “true” engineering is still a great challenge because of the existence of numerous weak interactions in crystal packing. Recently, thanks to the work of Robson, Batten, Ciani and others,[1a,2] many entangled networks have been engineered under a strategy of “network approach”. Success in producing such structures depends on understanding and controlling the topological and geometric relationships between molecular modules, along with the coordination characteristics of the metal ions. Of the many reported entangled network structures, those constructed from molecular ladder motifs are very attractive, while relatively rare.[1a] The main reason is probably attributed to the difficulty of obtaining T-shaped building blocks, which are essentially used to build up the ladder structures. So far two kinds of entanglement modes have been found in polycatenated ladders, namely, inclined catenation and parallel catenation (Scheme 1). Usually, inclined catenation of 1D ladders can generate 1D→2D and 1D→3D arrays,[3] while parallel catenation can produce 1D→1D, 1D→2D,[4] and 1D→3D arrays. To the best of our knowledge, no 3D polycatenation produced by parallel catenation of 1D ladders (1D→3D parallel) has been reported.

Scheme 1. Schematic representation of two kinds of entanglement modes of 1D molecular ladders: (top) inclined catenation, (bottom) parallel catenation.

Polyoxometalate (POM) clusters, known to have large sizes and interesting properties for medicine and nonlinear optics, are an outstanding class of linkers for the construction of interpenetrating networks.[1f] They have capabilities similar to those of organic ligands in linking metal centers, as evidenced in the recently reported literature.[5] Hence, directly utilizing POM clusters as linkers promises to be an appealing route to design new entangled network structures. Unfortunately, this strategy remains unexplored owing to the difficulties in choosing suitable POM clusters as a linker whose skeleton can be fully maintained during preparation. Our previous work has proved that bicapped Keggin POM clusters can function as rigid bidentate bridging ligands.[6] Thus, our synthetic strategy is to introduce two kinds of bidentate bridging ligands, i.e. Keggin clusters and 4,4′-bpy, as linkers into the metal centers with potential T-type coordination sites in order to construct new molecular ladders.

Herein, we report a new compound, $\{Cu_3(4,4'\text{-}bpy)_3(H_2O)[PMo_{12}O_{40}(VO)_2]\cdot 5H_2O\}_n$ (**1**) (4,4′-bpy = 4,4′-bipyr-

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idine), which is based on a new motif 1D double ladder. The polycatenation of 1D double ladders in **1** gives a 3D polycatenation (1D→3D parallel). In comparison with other catenated ladders, **1** has several unique features: (i) a bicapped Keggin cluster $\{PMo_{12}O_{40}(VO)_2\}$ is utilized as a linker, (ii) the new motif, 1D double ladder, is introduced into an entangled system for the first time, and (iii) the 3D architecture is generated by unusual 1D→3D parallel catenation.

Results and Discussion

The successful isolation of compound **1** relies on the exploitation of hydrothermal techniques and the choice of organic reductant species. So far hydrothermal synthesis has become a powerful method for the preparation of organic-inorganic hybrid materials because of its advantages over other methods (e.g., diffusion and sol-gel techniques), such as the effective use of inorganic and organic reagents with low solubility. Although in most cases the reaction mechanisms under hydrothermal conditions remain elusive and the control and prediction of crystal structures are very difficult, the architecture of the final product depends directly on the interplay of starting materials, pH value, reaction temperature, and pressure. Our interest is to construct new molecular ladders by using 4,4′-bpy and presynthesized Keggin clusters as linkers. Experiments demonstrated that triethylamine was crucial for obtaining compound **1**. Under hydrothermal conditions, triethylamine with moderate ability to reduce can activate the Keggin cluster by reducing Mo^{VI} to Mo^{V} without metal-exchange or decomposition. On the other hand, Cu^{II} ions can also be reduced by it to Cu^{I} ions with potential T-type coordination sites.[6c]

Single crystal X-ray diffraction reveals that **1** is a polycatenated 3D molecular double ladder. As shown in Figure 1, the 1D double ladder is composed of three crystallographically unique Cu^{I} atoms as nodes linked by bicapped Keggin clusters $\{PMo_{12}O_{40}(VO)_2\}$ and 4,4′-bpy molecules. Each Cu^{I} atom displays T-shaped trigonal geometry. Atoms Cu1 and Cu2 are coordinated by two nitrogen atoms from two 4,4′-bpy ligands and one oxygen atom from one {VO} group belonging to a $[PMo^{VI}_8Mo^{V}_4O_{40}(V^{IV}O)_2]^{3-}$ polyanion, while the Cu3 atom is coordinated by two nitrogen atoms from two 4,4′-bpy ligands and one oxygen atom from a water molecule. All the Cu2 atoms are joined together by 4,4′-bpy to form a middle rail of the double ladder. The alternate Cu1 and Cu3 atoms are also linked together by 4,4′-bpy to form the edge rails. The polyanion $[PMo^{VI}_8Mo^{V}_4O_{40}(V^{IV}O)_2]^{3-}$ functions as a rung of the double ladder, linking the two adjacent atoms Cu1 and Cu2 together. The structure of the polyanion $[PMo^{VI}_8Mo^{V}_4O_{40}(V^{IV}O)_2]^{3-}$, similar to that of $[PMo^{V}_6Mo^{VI}_6O_{40}(V^{IV}O)_2]^{5-}$,[7] can best be described as a bicapped Keggin structure that is essentially built on an α-Keggin core $\{PMo_{12}O_{40}\}$ capped by two {VO} units. The central atom P in the polyanion is located at the inversion center, which results in a disordered PO_4 tetrahedron, that is, the central atom P is surrounded by a cube of eight oxygen atoms, and each oxygen site is half-occupied. The valence sum calculations,[8] ESR and XPS spectra show that all the vanadium atoms are in the +4 oxidation state, while the four molybdenum atoms are in the +5 oxidation state, which confirms the molecular formula of **1**.

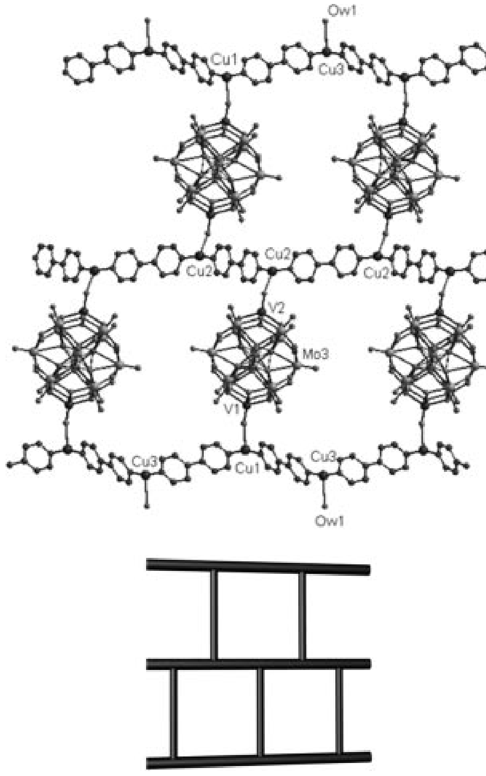

Figure 1. (top) View of part of the infinite 1D double ladder; (bottom) the schematic representation of the 1D double ladder.

In **1**, each rectangle (size ca. 17 × 14 Å) of the double ladder is penetrated by two other parallel double ladders that are staggered with each other (Figure 2). Although all the ladders run in the same direction (*b* axis), the staggered interpenetration by the parallel ladders increases the dimensionality of the whole polymeric system and thus leads to the 1D→3D expansion (Figure 3). To the best of our knowledge, among the few examples of polycatenated 3D molecular ladders (1D→3D), this is the first example of 3D structures generated by parallel catenation. Interpenetration in nature is a space-filling effect to produce a dense framework, but, surprisingly, the multiple catenation of the 1D double ladder does not occupy all the voids formed by one independent ladder. As shown in Figure S1 (Supporting Information), there are 1D channels running along the *c* axis direction that are filled by the guest water molecules. Hydrogen-bonding interactions between the ladders and clathrate water molecules generate a 3D complex supramolecular architecture (Figure S2).

Compared with recently reported Keggin-based compounds with 4,4′-bpy ligands, whose structures are very interesting but noninterpenetrated,[5] compound **1** is a polycatenated 3D molecular double ladder. The formation of such catenation may be ascribed to the bigger sizes of the rectangle grids.

Figure 2. Schematic illustration of entanglement modes of the double ladder in compound **1**.

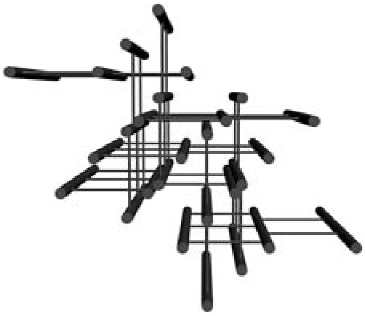

Figure 3. Schematic view of the 3D structure of compound **1** generated by parallel catenation of 1D double ladders.

The IR spectrum exhibits the characteristic peaks of the α-Keggin structure at 1060, 945, 860, and 775 cm^{-1} in **1**, which are attributed to ν(P–O$_a$), ν(M–O$_t$), ν(M–O$_b$–M), and ν(M–O$_c$–M) (M = V or Mo). The peaks at 1640, 1515, and 1462 cm^{-1} are characteristic of the 4,4′-bpy molecules. In the UV spectrum of **1**, there is a strong absorption peak at 206 nm and a weaker absorption band at 236 nm, which are consistent with the characteristic absorption bands of the Keggin skeleton. The EPR spectrum of **1** exhibits the V^{IV} signal at 293 K with $g = 1.9704$ (Figure S3). The XPS spectra give a peak at 516.2 eV for **1**, which is attributed to V^{IV}, and two overlapped peaks at 232.4 and 231.0 eV attributed to Mo^{VI} and Mo^{V}, respectively (Figure S4). All of these results further confirm the structure analysis.

Thermogravimetric analysis in N$_2$ indicates three steps of weight loss. The first two stages of weight loss of 3.98% occur in the temperature range 45–320 °C and correspond to the release of the guest water molecules. The third weight loss of 17.51% occurs from 360 to 570 °C, because of the release of the 4,4′-bpy ligands (Figure S5).

In order to study the redox property of **1**, a **1**-bulk-modified carbon paste electrode (**1**-CPE) was fabricated as the working electrode because of its insolubility in water and most organic solvents. The cyclic voltammetric behavior of **1**-CPE was measured in an aqueous solution of NaCl and HCl (0.2 M, pH = 2.3). In the potential range from +600 to –350 mV, there are three pairs of reversible redox peaks, and the average peak potentials, $E_{1/2}$ = (Ecp + Eap)/2, are +370, +50, and –150 mV (Figure S6). Each pair of redox peaks can be ascribed to a two-electron process involving molybdenum.[9]

In conclusion, using the Keggin cluster and 4,4′-bpy ligand as linkers, we have successfully isolated the first example of polycatenated 3D molecular double ladders generated from parallel catenation. This method may lead to a new family of interpenetrated networks that can be obtained by using suitable POM clusters as linkers.

Experimental Section

Materials: All reagents and solvents for syntheses were purchased commercially and used as received.

Physical Methods: Elemental analyses (C, H, and N) were performed with a PerkinElmer 2400 CHN Elemental Analyzer. P, Mo, V, and Cu were determined with a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra were obtained with an Alpha Centaurt FT/IR spectrometer with KBr pellets in the 400–4000 cm^{-1} region. XPS analyses were performed with a VG ESCALAB MK II spectrometer with a Mg-K_α (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during analysis. The ESR spectrum was recorded with a Japanese JES-FE3AX spectrometer at room temperature. UV/Vis spectra were recorded with a 756 CRT UV/Vis spectrophotometer made in Shanghai, China. The TG analyses were performed with a Perkin–Elmer TGA7 instrument in flowing N$_2$ at a heating rate of 10 °C min^{-1}. Cyclic voltammograms were obtained with a CHI 660 electrochemical workstation at room temperature. Platinum gauze was used as the counter electrode and an Ag/AgCl was used as the reference electrode. A chemically bulk-modified carbon paste electrode (CPE) was used as the working electrode.

Synthesis of {Cu$_3$(4,4′-bpy)$_3$(H$_2$O)[PMo$_{12}$O$_{40}$(VO)$_2$]·5H$_2$O}$_n$ (1): The starting materials Cu(NO$_3$)$_2$·4H$_2$O (0.1298 g, 0.5 mmol), H$_3$[PMo$_{12}$O$_{40}$]·xH$_2$O (0.4658 g, 0.25 mmol), NH$_4$VO$_3$ (0.0585 g, 0.5 mmol), 4,4′-bpy (0.0961 g, 0.5 mmol), triethylamine (0.14 mL), and H$_2$O (9 mL) were mixed together. The resulting suspension was stirred for 1 h, sealed in a Teflon-lined reactor, and heated at 160 °C for 72 h. Then the autoclave was cooled at 5 °C h^{-1} to room temperature. Black prism crystals of compound **1** were filtered, washed with water, and dried at room temperature. Yield: 0.395 g (58% based on molybdenum). $C_{30}H_{36}Cu_3Mo_{12}N_6O_{48}PV_2$ (2723.46): calcd. C 13.23, H 1.33, Cu 7.00, Mo 42.27, N 3.08, P 1.14, V 3.74; found C 13.31, H 1.22, Cu 7.09, Mo 42.13, N 3.01, P 1.03, V 3.81. IR (KBr): 1640 (w), 1515 (m), 1462 (w), 1060 (w), 945 (m), 860 (w), 775 (m) cm^{-1}.

Preparation of 1-CPE: Graphite powder (90 mg) and **1** (15 mg) were mixed and ground together by an agate mortar and pestle to achieve an even, dry mixture. Nujol (0.12 mL) was added to the mixture and stirred with a glass rod. The homogenized mixture was then packed into a 1.2 mm inner diameter glass tube, and the surface was wiped with paper. Electrical contact was established with a copper rod through the back of the electrode.

X-ray Crystallography: Crystal data for the compound were collected with a Rigaku R-AXIS RAPID IP diffractometer, with Mo-K_α monochromated radiation (λ = 0.71073 Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL crystallographic software package.[10] The positions of the hydrogen atoms on carbon atoms were calculated theoretically. Crystal data: $C_{30}H_{36}Cu_3Mo_{12}N_6O_{48}PV_2$, orthorhombic, *Pnma*, $M_r = 2723.46\,\mathrm{g\,mol^{-1}}$, $a = 27.962(6)$, $b = 21.174(4)$, $c = 11.802(2)$ Å, $V = 6988(2)$ Å^3, $T = 293$ K, $Z = 4$, $D_c = 2.577\,\mathrm{g\,cm^{-3}}$, $F(000) = 5128$, θ range 3.07–25.00°. A total of 47481 reflections were collected and 6009 were independent ($R_{\mathrm{int}} = 0.0940$). The final refinement including hydrogen atoms converged to $R = 0.0753$, $wR = 0.1705$.

CCDC-271165 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): The detailed bond valence sum calculations and the figures illustrating the 3D structures, ESR, XPS, TG spectra, and electrochemical behavior of compound **1** are provided.

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