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Unprecedented Eight-Connected Self-catenated Network Based on Heterometallic $\{Cu_4V_4O_{12}\}$ Clusters as Nodes

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An interesting eight-connected self-catenated metal–organic framework, based on bimetallic $\{Cu_4V_4O_{12}\}$ clusters as nodes, defines a new self-catenated topology for eight-connected networks and represents the first self-catenated framework using heterometallic clusters as nodes.

An entangled system, as defined by Ciani et al., is an extended array more complex than its constituents that is comprised of individual motifs forming, via interlocking or interweaving, a periodic architecture infinite in at least one dimension.[1] The interest in entangled systems is rapidly increasing not only for their potential applications as functional solid materials[2] but also for their intriguing architectures and topologies.[3] Recently, thanks to the work of Robson, Batten, Ciani, and others, many entangled networks have been engineered under a strategy of "network approach".[1,4] Of the many reported types of entanglements in polymeric architectures, the phenomenon of self-catenation (self-entanglment or polyknotting) has attracted much attention in recent times. These species are single nets having the peculiarity that the smallest topological rings are catenated by other rings belonging to the same network.[1] Until now, only a few self-catenated nets have been observed in metal−organic frameworks, implying a challenging issue in coordination chemistry.[5]

Of concurrent interest has been the construction of highly connected coordination frameworks (namely, connectivities larger than six).[6] This has been a formidable task to chemists because of the limited coordination sites of metal centers and the steric hindrance of most commonly used organic ligands. At present, two strategies have been used to overcome these two problems. One is to take advantage of high coordination numbers and flexible coordination modes of lanthanide metals. A few noteworthy examples have been reported by Champness and Schröder and co-workers using this method.[6a,b,7] The other strategy, which is far less developed than the first, is the use of polynuclear metal clusters as building blocks, with their large surface areas (sometimes even nanoscale), so that they can more readily accommodate the steric demands of organic linkers. To date, a handful of highly connected networks are all based on monometallic clusters.[4a,8] The further extension of this strategy to heterometallic clusters is hindered by a lack of suitable cluster building blocks.

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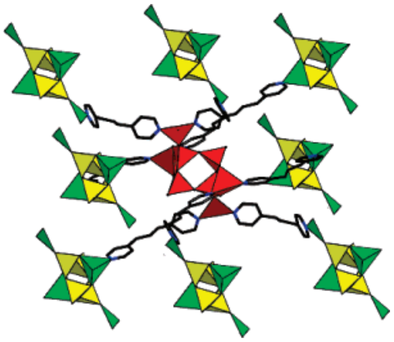

Figure 1. Perspective view of the eight-connecting bimetallic [$Cu_4V_4O_{12}$] cluster. The central octanuclear cluster is highlighted in red.

It has been confirmed that metal−oxo anion groups can form effective M−O−Cr or M−O−Mo bonds, where M is a typical late transition metal.[9] Polyoxovanadates are a unique class of negatively charged M−O clusters that have attracted an increasing interest in recent years owing to their structural diversity and potential applications in catalysts, biochemistry, medicine, and electrode materials and have also proven to be outstanding multidentate ligands.[10] Therefore, they should be ideal candidates in the assembly of heterometallic clusters. Herein, we report on an unprecedented eight-connected network, [$Cu_4(bpp)_4V_4O_{12}$]•$3H_2O$ [**1**; bpp = 1,3-bis(4-pyridyl)propane], in which neutral heterometallic {$Cu_4V_4O_{12}$} clusters act as eight-connected nodes. To the best of our knowledge, this framework not only defines a new topology for eight-connected coordination networks but also represents the first example of the self-catenated framework using heterometallic clusters as nodes.

Compound **1** was prepared by the hydrothermal reaction of $NaVO_3$•$2H_2O$, $Cu(CH_3COO)_2$•H_2O, bpp, and H_2O at 130 °C for 84 h.[11] Single-crystal X-ray analysis reveals that the structure of **1** contains neutral bimetallic {$Cu_4V_4O_{12}$} clusters as nodes, which consist of a central {V_4O_{12}}$^{4-}$ cluster decorated with four Cu^I units (Figures 1 and S1 in the Supporting Information).[12] The polyanion {V_4O_{12}}$^{4-}$ ring is constructed from four corner-sharing VO_4 tetrahedra with a distinctly chairlike configuration. Each of two crystallographically independent vanadium atoms is coordinated by four oxygen atoms in tetrahedral geometries. The V−O distances range from 1.613(3) to 1.801(3) Å, with O−V−O angles in the range of 108.04(17)−152.4(2)°. The bond valence sum calculations[13] give the values of 5.338 and 5.200 for V(1) and V(2), respectively, suggesting that all vanadium sites are in the 5+ oxidation state. The {V_4O_{12}}$^{4-}$ cluster corresponds to a tetradentate ligand bonding to four copper atoms via six terminal oxygen atoms, thus resulting in a bimetallic octanuclear cluster (Figure 1). Tetrahedral and plane-trigonal coordination geometries of Cu^I ions are established in the cluster, as shown in Figure 1. The Cu(1) ion is coordinated by two nitrogen atoms from two bpp ligands and two terminal oxygen atoms from one {V_4O_{12}}$^{4-}$ anion, forming a tetrahedral geometry. The Cu(2) ion is ligated by two nitrogen atoms from two bpp ligands and one terminal oxygen atom from one {V_4O_{12}}$^{4-}$ anion to complete a plane-trigonal geometry. The average Cu−O distance [2.332(5) Å] and Cu−N distance [1.937(6) Å] in the tetrahedron are longer than the corresponding values [2.059(4) and 1.912(5) Å] in the trigon. The reduction of Cu^{II} into Cu^I may be attributed to the excessive N-containing ligand during the hydrothermal synthesis.[14] All of the bpp ligands adopt a trans−trans conformation with torsion angles along the propane chain of 164°, 172.73°, and 178.73° respectively, while the mean planes of the py rings form angles of 3.1°, 86.5°, and 100.7°. The bpp ligand can assume different conformations and consequently different N−N distances ranging from 3.9 to 10.1 Å,[15] and the present N−N distance is 9.715−9.944 Å. As such, each bimetallic {$Cu_4V_4O_{12}$} cluster is surrounded by eight bridging bpp ligands; this thus defines an eight-connected node. Each bimetallic {$Cu_4V_4O_{12}$} cluster is further linked to eight nearest neighbors, with distances of 13.783(2)−22.876(2) Å, through eight bpp ligands, thus resulting in a unique three-dimensional uninodal eight-connected framework.

The total Schläfli symbol of this net is 4^{24}•6^4, and the long vertex symbol with rings is [4•4•4•4•4•4•4•4•4•4•4•4•4•4•4•4•4•4•4•4•4•4•4•4•8_{30}•8_{180}•*•*]. Notably, the structure of **1** is completely different from that of the familiar body-centered-cubic lattice (bcu, sometimes called the CsCl net) in spite of having the same Schläfli symbol with it.[3f,16] The long vertex symbol with rings of the bcu net is [4•4•4•4•4•4•4•4•4•4•4•4•4•4_3•4_3•4_3•4_3•4_3•4_3•4_3•4_3•4_3•4_3•4_3•4_3•*•*•*•*]. So, the unicity of this net is that it has eight rings. As shown in Figure 2, the parallel (4,4) nets (yellow) of both bcu (Figure 2a) and **1** are cross-linked by zigzag chains (green); however, the detailed connection modes are different. In bcu, the green zigzag chain in the interlayer region bridges across the diagonal of a single window in the (4,4) net. In **1**, however, it bridges across the diagonal of eight windows (Figure 2d).

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(11) Synthesis of {$Cu_4[C_{13}N_2H_{14}]_4[V_4O_{12}]$•$3H_2O$}$_n$ (**1**): A mixture of $NaVO_3$•$2H_2O$ (0.48 g, 3.03 mmol), $Cu(CH_3COO)_2$ (0.30 g, 1.50 mmol), bpp (0.30 g, 1.51 mmol), and H_2O (10 mL) in a molar ratio of 2:1:1:556 was sealed in a Teflon-lined stainless steel autoclave and heated at 130 °C for 84 h. Red crystals of compound **1** were collected in 30% yield based on copper). Anal. Calcd for $C_{52}H_{62}Cu_4N_8O_{15}V_4$: C, 41.72; H, 4.14; N, 7.49. Found: C, 42.0; H, 4.27; N, 7.33.

(12) Crystal and intensity data were collected on a Rigaku R-AXIS RAPID IP diffractometer at 293 K using graphite-monochromated Mo Kα radiation (λ = 0.710 73). Data processing was accomplished with the RAXWISH processing program. Crystallographic data of compound **1** are as follows: $C_{52}H_{62}Cu_4\ N_8O_{15}V_4$, MW = 1497.06, monoclinic $P2/c$, a = 12.560(6) Å, b = 9.927(5) Å, c = 26.238(7) Å, β = 115.121(12)°, V = 2962(2) Å^3, D_{calcd} = 1.679 g cm^{-1}. Final R1 = 0.0479, wR2 = 0.0963 (for $I > 2\sigma$), GOF = 0.927, and Z = 2. CCDC number: 627904.

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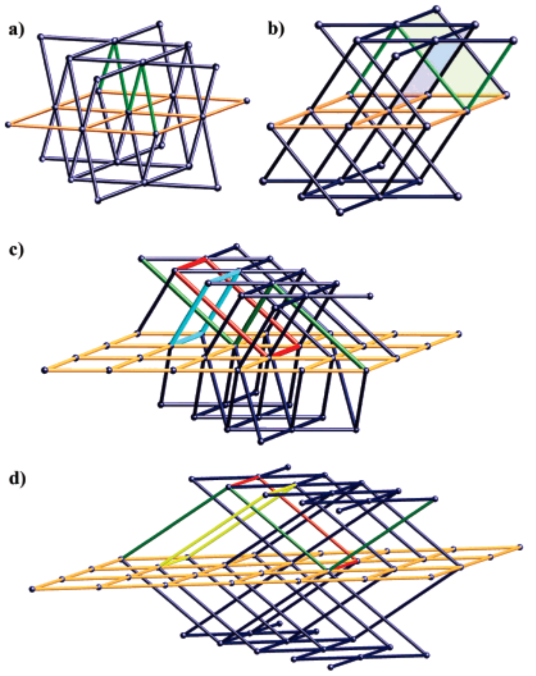

Figure 2. Four eight-connected nets illustrating the different links between the 4^4 nets: (a) bcu net; (b) self-catenated $4^{24}\cdot5\cdot6^3$ topological net; (c) self-catenated $4^{20}\cdot6^8$ net; (d) topology of **1**.

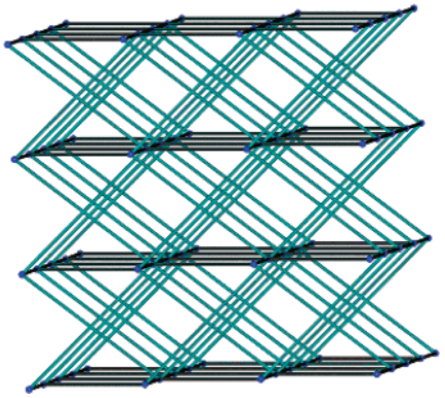

Figure 3. Eight-connected self-catenated network of **1**.

Such an unusual linkage mode is also distinct from previously known nonentangled non-bcu eight-connected nets.[6b] As a result of this unique bridging of parallel layers, the catenated four-membered shortest rings are observed at the intersection of the crossing of two-dimensional layers. Therefore, the resulting array is a single eight-connected self-catenated network (Figure 3).

Up to now, only two eight-connected self-catenated structures have been reported. One example is $[Zn_5(\mu_3\text{-}OH)_2(bdc)_4(phen)_2]$ (phen = 1,10-phenanthroline) in which the zigzag chains bridge across the diagonal of two neighboring windows (Figure 2b). Another example is $[Cd_3(bdc)_3(L)_2(H_2O)_2]$ [L = 1,4-bis(1,2,4-triazol-1-yl)butane and bdc = 1,4-benzenedicarboxylate] in which the zigzag chains bridge across the diagonal of six windows (Figure 2c). The topologies $4^{24}\cdot5\cdot6^3$ and $4^{20}\cdot6^8$ [5a,c] of the two examples are significantly different from that of the coordination polymer described here. Moreover, it is worth noting that in the above two cases eight-connected nodes are assumed by monometallic clusters while in **1** bimetallic clusters act as eight-connected nodes for the first time.

It should be mentioned that there are crossing edges[17] (the cyan-colored edges) in the eight-connected self-catenated network. Another way to avoid the crossing and describe the structure with less simplification is to keep the copper atom and V_4O_{12} as different nodes. The final net is now a three-nodal three- and four-connected (Cu1,Cu2 3-conn and V_4O_{12} cluster 4-conn) self-catenated net (see Figure S2 in the Supporting Information). The long topological vertex symbol is [8·8·8] for the Cu node and $[8_2\cdot8_2\cdot12_4\cdot12_4\cdot12_6\cdot12_6]$ for the V_4O_{12} node, thus giving a short vertex symbol $\{8^2\cdot12^4\}\{8^3\}_4$.

The IR spectrum of **1** (Figure S3 in the Supporting Information) exhibits a strong band at 907 cm^{-1} attributed to $\nu(V{=}O)$; the 810, 739, and 659 cm^{-1} bands are assigned to $\nu(V{-}O{-}V)$ and $\nu(Cu{-}O{-}V)$. The O−H stretching bands of the water of crystallization are observed at 3429 cm^{-1}. The characteristic ones for the bpp ligand are at 2933, 1612, 1498, and 1425 cm^{-1}.

The thermal stability of **1** has been determined by thermogravimetric analysis (TGA). The plot exhibits three steps of weight loss (Figure S4 in the Supporting Information). In the first region, 123−203 °C, it lost all of the crystallization water (3.5% obsd; 3.7% calcd). Upon further heating, the material lost weight continuously. From 211 to 301 °C, the TGA trace showed a sharp decline to give a weight loss of 38.8%, corresponding to the loss of organic moieties. A subsequently moderate release of the ligand occurred at 301−586 °C. The second and third steps lost four bpp molecules per formula unit together (51.3% obsd; 52.9% calcd). The total weight loss of 54.8% is in good accordance with the calculated value of 56.6%.

In summary, we have prepared and characterized a new eight-connected self-catenated coordination net in which bimetallic $\{Cu_4V_4O_{12}\}$ clusters act as eight-connected nodes for the first time. The successful isolation of this species not only provides an intriguing example of chemical topology but also confirms the significant potential of constructing heterometallic frameworks from polyoxometalate clusters. Appropriate choices of polyoxometalate clusters as well as spatial linkers will lead to the discovery of a large variety of new topological structures and types in the near future.

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Supporting Information Available: X-ray crystallographic data in CIF format, IR spectrum, TGA profile, and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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