Inorganic–Organic Hybrid with 3D Supramolecular Channel Assembled through C–H···O Interactions Based on the Decavanadate

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A novel compound, $[Cu(2,2'\text{-bipy})_2]_2[H_2V_{10}O_{28}]\cdot(2,2'\text{-bipy})\cdot H_2O$ (**1**) has been synthesized and characterized by elemental analyses, IR, UV, and single crystal X-ray diffraction. Compound **1** is made up of supramolecular layers of polyoxoanion-supported copper complexes pillared by individual $[H_2V_{10}O_{28}]^{4-}$ clusters via weak C–H···O hydrogen-bonding interactions forming a three-dimensional microporous framework with two types of channels, and the "guest" bipyridine molecules reside in the channels.

Inorganic–organic hybrid materials have become a subject of general interest because of not only their intriguing structural diversity but also their potential applications in catalysis, biochemical analysis, medicinal chemistry, and materials science.[1–4] Polyoxometalates (POMs), as a kind of significant rich-oxygen clusters, which have been used as molecular blocks in the construction of supramolecular compounds,[5] have become a focus of contemporary POM chemistry because of their novel and divers topologies and special applications in host–guest chemistry, shape-selective catalysis, absorption, electrical-conductive, magnetic, and photosensitive materials.[6–8] One of the important targets in the preparation of supramolecular assemblies is to establish the possible connections between organic and/or inorganic molecular fragments on the basis of various intermolecular interactions. While the connectivity between the POM clusters may result from direct condensation to form oxo-bridged arrays, in the case of POMs we have most generally achieved linkage through secondary transition metal coordination compounds acting as bridging ligands. Consequently, these materials are related to general efforts to construct specific architectures from molecular building blocks. Therefore, we can have POMs surface-modified with M^{II}–organonitrogen as a supermolecular synthon, which is a structural unit within a supermolecule which can be formed or assembled by intermolecular interactions. The various intermolecular interactions provide the driving force for the development of strategies for the design of novel supramolecular assemblies. In the interesting molecular assembling process, supramolecuar construction may be achieved not only by strong hydrogen bonds such O–H···O and N–H···O but also by weak C–H···O bonds. C–H···O hydrogen bond has been utilized in crystal engineering and supramolecular design.[9] It is hoped that the POMs surface-modified with M^{II}–organonitrogen allow the creation of new supramolecular networks through weak C–H···O bonds. Moreover, the supermolecular synthon we chose have the possibility of forming C–H···O bonds and no other directional interaction are preferable choices for supramolecular construction. The absence of O–H···O and N–H···O-forming functional groups is an advantage.

Herein, we report a novel supramolecular arrays with channel frameworks assembled through C–H···O hydrogen bonds based on the decavanadate $[Cu(2,2'\text{-bipy})_2]_2[H_2V_{10}O_{28}]\cdot(2,2'\text{-bipy})\cdot H_2O$.[10] Compound **1** possesses a novel three-dimensional microporous framework with a channel formed by hydrogen-bonding interactions between the oxygen atoms of the $[H_2V_{10}O_{28}]^{4-}$ polyoxoanions and copper-2,2′-bipy complexes, containing the "guest" 2,2′-bipy molecules residing in the channel.

The single crystal X-ray diffraction analysis[11] shows that compound **1** is made up of $[H_2V_{10}O_{28}]^{4-}$ polyoxoanion-supported copper-2,2′-bipy complexes as cations, $[H_2V_{10}O_{28}]^{4-}$ cluster as anions, dissociated 2,2′-bipy molecules and lattice water molecule (see Figure 1). The centrosymmetric polyanion consists of five independent $[VO_6]$, sharing edges, and has approximate D_{2h} symmetry. The bond lengths and angles of the decavanadate anion show a similar trend to those found in the literature.[12] The asymmetric unit in the crystal structure of **1** consists of one crystallographically independent monovacant lacunary Lindqvist anion. Two monovacant lacunary Lindqvist anions linked through sharing two $[VO_6]$ make up of the decavanadate anion. In the structure of **1**, the decavanadate anion as a bidentate ligand coordinates to two $[Cu(2,2'\text{-bipy})_2]^{2+}$ complex fragments to form a polyoxoanion-supported complex through the bridge oxygen atoms of two opposite $[VO_6]$ octahedral.

There is only one crystallization-independent copper(II), which exhibits distorted trigonal bipyramidal geometry. The equatorial plane is defined by the oxo-bridge to the vanadium core and a nitrogen donor from each bipyridine ligand, while the axial positions are occupied by the remaining nitrogen donors. The copper sites occupy opposite termini of the vanadium oxide oblate. The Cu–N bond lengths vary from 1.972(5) to 2.082(6) Å. The Cu–O bond length is 2.044(4) Å.

The most interesting feature of compound **1** is that its 3D

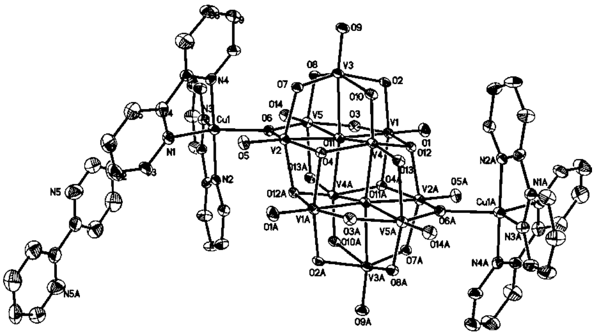

Figure 1. ORTEP drawing of compound **1** with thermal ellipsoids at 30%. Water molecules are omitted for clarity.

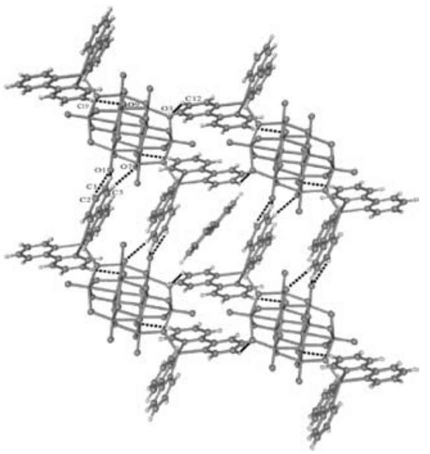

Figure 2. Ball–stick representation of the 3D supramolecular channel of **1** viewing along the *a* axis. Water molecules are omitted for clarity.

supramolecular network assembled through C–H···O hydrogen bonds, the dimensions of the two types channels are, respectively, ca. 6.0 × 5.0 Å and 15 × 7.0 Å along the a direction (Figure 2). Dissociated bipyridine molecules occupied the bigger channels. The 3D supramolecular framework may be best described as supramolecular layers of polyoxoanion-supported copper complexes pillared by individual $[H_2V_{10}O_{28}]^{4-}$ clusters via intermolecular C–H···O hydrogen-bonding interactions. It is believed that the extensive hydrogen-bonding interactions play an important role in stabilizing the 3D supramolecular framework. From Figure 2, it can be seen that hydrogen bonds are formed between C–H groups of bipyridine in the $[Cu(2,2'\text{-bipy})_2]^{2+}$ complex cations and oxygen atoms from decavanadate anions, with C–H···O distances in the range of 2.372–2.680 Å. To our best knowledge, compound **1** represents the first example of a channel-containing 3D supramolecular architecture assembled through weak C–H···O hydrogen-bonding interactions based on the copper coordination complexes and decavanadate anions.

The UV–vis spectroscopy displays two intense absorption bands at 260 and 685 nm. The higher energy band at 260 nm can be attributed to O → V charge transfer of decavanadate, and band at 685 nm may be attributed to d–d transition of distorted trigonal bipyramidal Cu^{2+}.[13] The charge transfers of N → Cu and O → Cu in 300–400 nm were not observed because of intense tail of O → V charge transfer.

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10 Preparation of **1**: The starting materials $K_2[H_4V_{10}O_{28}]\cdot 7H_2O$ (0.5 mmol), $Cu(NO_3)_3\cdot 6H_2O$ (0.5 mmol), 2,2′-bipy (1 mmol), and H_2O (9.0 mL) in a molar ration 1:1:2:1000 were mixed. The resulting suspension was stirred for 1 h, with sufficient HNO_3 to adjust the pH to 4.5, sealed in a 20 mL Teflon-lined reactor and heated at 160 °C for four days. Then, the autoclave was cooled at 6 °C/h to room temperature. Blue block crystals of compound **1** were filtered, washed with water, and dried at ambient temperature (yield 51%, based on vanadium). Anal. Calcd for $C_{50}H_{44}N_{10}O_{29}V_{10}Cu_2$ (1885.44): C, 31.85; H, 2.35; N, 7.43; Cu, 6.74; V, 27.02%. Found: C, 31.75; H, 2.20, N, 7.63; V, 27.23; Cu, 6.58%. IR (KBr pellets, ν/cm^{-1}): 1613(s), 1470(m), 1442(m), 1394(w), 1017(m), 962(s), 883(vs), 840(s), 719(m), and 664(w).

11 Crystal data for **1**: $C_{50}H_{44}N_{10}O_{29}V_{10}Cu_2$, $M_r = 1885.44$, Triclinic, $a = 10.006(5)$, $b = 13.046(6)$, $c = 13.085(6)$ Å, $V = 1545.72(12)$ Å^3, $T = 293(2)$ K, space group $P\bar{1}$, $Z = 2$, $\mu = 1.320\ \text{mm}^{-1}$, 5394 reflections measured, 455 independent ($R_{\text{int}} = 0.0286$). $R_1 = 0.0766(I > 2\sigma(I))$, $WR_2 = 0.1452$ (all data). CCDC: 619516.

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