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A polyoxometallate-templated coordination polymer: synthesis and crystal structure of $[Cu_3(4,4'\text{-bipy})_5(MeCN)_2]PW_{12}O_{40}\cdot 2C_6H_5CN$

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Received (in Columbia, USA) 11th August 2001, Accepted 6th November 2001
First published as an Advance Article on the web 9th January 2002

The spherical phosphotungstate ion, $PW_{12}O_{40}^{3-}$, has been used as a non-coordinating anionic template for the construction of a novel, three-dimensional Cu(I) coordination polymer.

The design and construction of porous coodination polymers containing transition metal ions bridged by multitopic ligands has become the object of much current study due to their potential as molecular sieves and catalysts,[1] as well as the possibility of tailoring magnetic interactions between the metal centers.[2] We[3] and others[4] have shown recently that the extended structures of several cationic coordination networks are dependent on the identity of the non-coordinating anion included in the intercrystalline voids.

Polyoxometallates[5] (POMs) are large oxoanions of Group VI (and more rarely Group V) elements, exemplified by the ubiquitous Keggin structure, first prepared as $PMo_{12}O_{40}^{3-}$ in 1826 by Berzelius. The nickname 'heteropoly blues' alludes to the dramatic (and reversible) color change that occurs upon reduction.[6] This visible response to electro- or photo-chemical stimuli has inspired their use in electrochromic devices and their stability in a variety of oxidation states has prompted their use as catalysts for alkene epoxidation[7] and other transformations.[8] Several successful strategies have been developed to integrate POMs into hybrid solid-state materials, including ion-exchange into vinylpyridine-styrene co-polymers,[9] intercalation into layered double hydroxides[10] and incorporation into inorganic–organic hybrid charge-transfer salts.[11] Most recently, *covalent* tethering of $Mo_6O_{19}^{2-}$ derivatives onto a styrene polymer,[12] as well as into a crystalline Cu(II)-coordination network has been realized.[13]

Here we report the incorporation of a polyoxometallate ion as a non-coordinating anion *around* which a three-dimensional Cu(I)-4,4′-bipyridine (bipy) network is constructed. Not only does this introduce one of the largest non-coordinating anions to date in coordination polymer structures, but also creates opportunities to use the redox properties of the *anion* (as opposed to the framework) to carry out chemical reactions within the intercrystalline voids, avoiding disruption of the framework topology and crystallinity.

Reaction of 4,4′-bipyridine in benzonitrile with $[Cu(MeCN)_4]_3PW_{12}O_{40}$† in acetonitrile afforded dark-orange blocky crystals of the title compound, **1**, after 4 days. Single crystal X-ray analysis of these crystals‡ revealed a huge unit cell that contains three unique Cu(I) cations. Each displays a distrorted tetrahedral coordination sphere, but one, Cu(2), is bonded to *four* bridging bipy ligands, while the others, Cu(1) and Cu(3), are coordinated to *three* bipy ligands and *one* terminal MeCN ligand as shown in Fig. 1.

All of the bipy ligands bridge to additional copper atoms forming a very complicated array based on a pentagonal motif. The $PW_{12}O_{40}^{3-}$ anion is not coordinated to the any of the copper atoms, though there are several CH···O interactions between the metal–organic framework and the POM in the range of 2.4–2.7 Å. Fig. 2 shows the polyoxometallate well surrounded by one of these pentagonal units comprised of one Cu(1), two Cu(2) and two Cu(3) centers. The centroid of the five corner copper atoms lies only 2.1 Å above the P atom at the center of the anion. The two molecules of benzonitrile are incorporated above and below the plane of the pentagon, in relatively close proximity to the polyoxometallate (N···O *ca.* 4 Å).

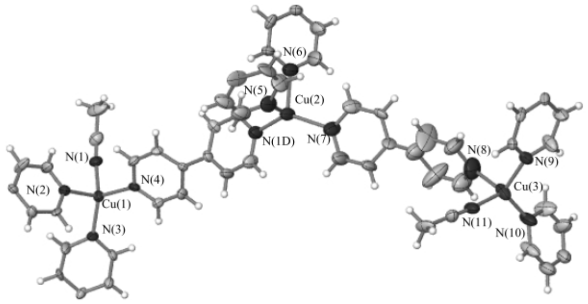


Fig. 1 ORTEP drawing of the three unique Cu(I) coordination spheres in **1** with a partial numbering scheme. All non-hydrogen atoms are shown as 50% thermal ellipsoids. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 1.96(1), Cu(1)–N(2) 1.97(1), Cu(1)–N(4) 2.15(1), Cu(2)–N(4), Cu(2)–N(1D) 1.93(1), Cu(2)–N(6) 2.13(1), Cu(3)–N(9) 1.98(1), Cu(3)–N(11) 1.98(1), N(1)–Cu(1)–N(4) 96.3(6); N(2)–Cu(1)–N(3) 116.1(5), N(6)–Cu(2)–N(7) 105.4(5), N(5)–Cu(2)–N(6) 95.3(6), N(8)–Cu(3)–N(11) 100.4(5), N(9)–Cu(3)–N(10) 101.6(5).

The pentagonal cavities are not isolated; the bipy ligands protruding from four of the five corners (only one pyridyl ring shown in Fig. 2) link to other copper atoms in neighboring pentagons creating a ribbon structure shown running left-to-right in the center of Fig. 3(a). The pentagonal ribbons are extended laterally by the bridging bipyridine from the fifth corner and form ellipical cavities on both sides of the ribbon. The connectivity is remarkably similar to the layered structure found in $[Cu(bipy)_{1.5}(PPh_3)]BF_4$,[14] though a crucial difference arises in the elliptical 8-rings: in **1** they 'miss' closing by *ca* 7.5 Å as indicated by the arrows in Fig. 3(a)! This 'defect' is a

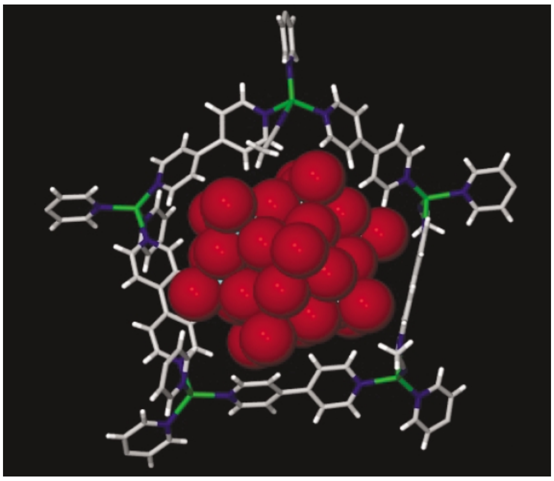
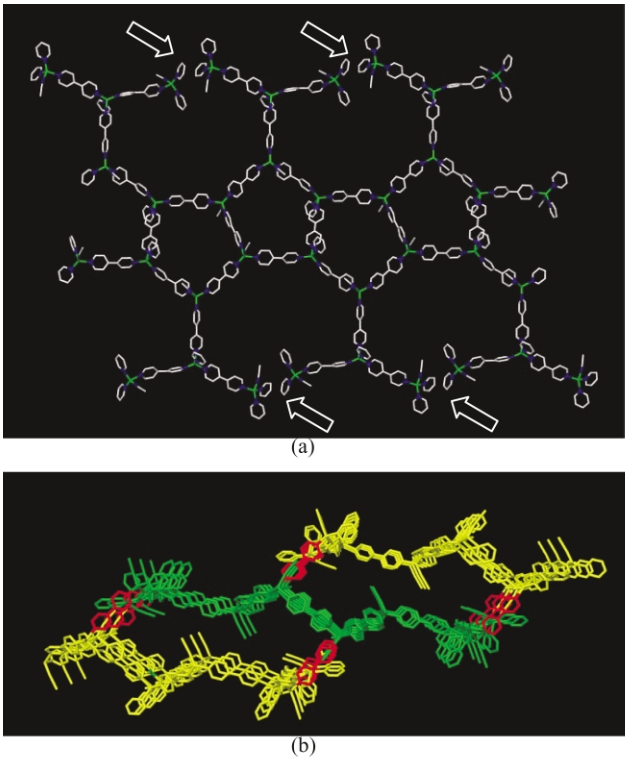


Fig. 2 Stick representation of one pentagonal cavity (Cu: green, N: blue, C: grey and H: white) encircling a POM anion shown as space filling spheres (O: red). Cu–Cu distances are in the range 11.0–11.3 Å and the Cu–Cu–Cu angles (93.6–105.0°) are all significantly narrower than the 108° angles found in regular pentagons. The nitrobenzene molecules have been omitted for clarity.

DOI: 10.1039/b107305b



(a)

(b)

Fig. 3 (a) Stick diagram of one 'layer' in **1**. The color scheme is identical to Fig. 2. The gaps described in the text are shown by the white arrows. (b) Side view of three layers (the layer shown in (a) is in green, neighboring ones in yellow) with the red bipy ligands connecting the layers in the third dimension.

consequence of the anomolously wide N–Cu–N angles around the exterior of the 8-rings allowed by the less sterically demanding MeCN ligands (as compared to PPh_3) coordinated to Cu(2) (123.9°) and Cu(3) (118.2°).

Another important structural feature results from the fourth ligands coordinated to the copper centers around each pentagon in **1**: Three of the five are *terminal* MeCN ligands, but the other two are *bridging* bipy ligands. Given the different connectivities is difficult to predict *a priori* the dimensionality of the network. Linked *tridentate* centers favor layered structures, while *four-connected* centers usually result in three-dimensional frameworks. The topology of **1** is in fact intermediate between these two possibilities. That fourth bipyridine on Cu(1) links the corrugated 'layers' shown in Fig. 3(a) to neigboring layers leading to a three-dimensional open framework as shown in Fig. 3(b).

In terms of synthetic strategy, this procedure is the reverse of that used in preparing microporous[15] and mesoporous[16] aluminosilicates, where inorganic monomeric anions are condensed around organic cations of varying shapes and sizes in order to template various open-framework topologies. The present case uses the inorganic moiety to act as the template around which the organic (or metal organic) framework is condensed. Current studies are focused on elucidating the solid-state electrochemistry of these new materials.

We are grateful to the National Science Foundation for generous funding of this work in the form of a CAREER Award (DMR-9733341) to S. W. K.

Notes and references

† $[Cu(MeCN)_4]_3PW_{12}O_{40}$ was prepared as a polycrystalline orange powder from Cu_2O and $H_3PW_{12}O_{40}$ by a variation of the method of Kubas.[17] Anal. (Calc.) for $Cu_3C_8N_4H_{12}PW_{12}O_{40}$: C, 8.97 (8.09); N, 4.87 (4.72); H, 1.13 (1.02), O; 17.67 (17.97). Anal. (Calc.) for **1** C, 19.74 (19.64); N, 4.70 (4.85), H, 1.29, (1.30), O, 15.47, (15.52).

‡ Crystal structure determination for compound **1**: *Crystal data*: $Cu_3C_{68}H_{56}N_{14}PW_{12}O_{40}$, M = 4092.5, monoclinic, space group $C2/c$, a = 51.552(2), b = 14.1894(6), c = 34.430(1) Å, β = 130.980(1)°, V = 19013.4(1) Å^3, T = 173(1) K, Z = 8, μ(Mo-Kα = 15.21 mm^{-1}, 67086 reflections measured, 20810 unique (R_{int} = 0.072), 13123 observed with $I > 2\sigma(I)$ which were used in all refinements. One of the bipyridine rings displayed some disorder, and was modelled in two different orientations (further details of the refinements provided in the ESI). The final $R(F)$ was 0.0512 for observed data.

CCDC reference number 172599.

See http://www.rsc.org/suppdata/cc/b1/b107305b/ for crystallographic data in CIF or other electronic format.

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