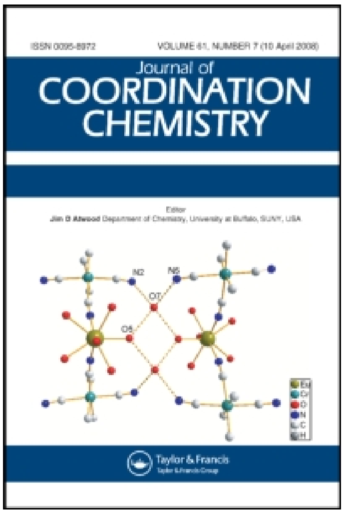

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Lu, Ying , Wang, Enbo , Xu, Xinxin and Ma, Ying(2007) 'A new grid network based on diphosphopentamolybdate cluster supported transition metal complexes', Journal of Coordination Chemistry, 60: 1, 53 — 60

To link to this Article: DOI: 10.1080/00958970600773887

URL: http://dx.doi.org/10.1080/00958970600773887

Journal of Coordination Chemistry
Vol. 60, No. 1, 10 January 2007, 53–60

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A new grid network based on diphosphopentamolybdate cluster supported transition metal complexes

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(*Received 12 October 2005; in final form 19 January 2006*)

A new grid architecture built from diphosphopentamolybdate supported copper-imidazole, $[\{Cu^{II}(im)_4\}_2\{H_2Mo_5P_2O_{23}\}]\cdot 3H_2O\cdot (im)$ (**1**) (im = imidazole), is reported. The structure of **1** features a 2-D grid network built by the interconnection of bisupporting diphosphopentamolybdate clusters, $[\{Cu^{II}(im)_4\}_2\{H_2Mo_5P_2O_{23}\}]$; free water molecules and imidazole ligands fill the void of the crystal lattice. Crystal data for compound **1**: Orthorhombic, space group *Pnma*, $a = 14.598(3)$ Å, $b = 21.059(4)$ Å, $c = 16.609(3)$ Å, $\alpha = \beta = \gamma = 90°$; $V = 5106.1$ Å^3; $Z = 4$.

Keywords: Polyoxomolybdate; Crystal structure; Grid network; Supramolecular architecture; Supported copper complex

1. Introduction

Polyoxometalates (POMs) [1] as building blocks to create solid-state materials has attracted continuous interest for material scientists and biochemists due to vast compositional range and structural diversity, as well as their potential applications in many interdisciplinary areas [2]. A traditional method developed for the linkage of POM building blocks focused on integration of transition metal complexes or coordination polymers for coupling [3]. Several successful strategies have been developed to prepare extended transition metal complex bridged polyoxoanion structures. Zubieta's group employed organoamine-ligated transition metal complexes as bridging moieties linking polyoxomolybdate clusters into one- and two-dimensional (1- and 2-D) networks [4–6]; Khan and co-workers have produced a series of novel three-dimensional (3-D) framework materials based on well-defined polyoxovanadate clusters $\{V_{18}O_{42}(XO_4)\}$ (X = S, V, Cl) through the linking of $M(H_2O)$ (M = Fe, Co, Mn, Zn) units [7–9]; Niu *et al.* have been concentrating on the isolation of 1-D structure, extending Keggin-type polyanions *via* metal-complexes [10, 11]; Xu's group reported a series of 2- and 3-D frameworks constructed from bicapped Keggin clusters [12, 13].

We have been working on assemblies of polyoxometalate clusters into multi-dimensional structures by the linkage of transition metal (mainly d-block element)

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2007 Taylor & Francis
DOI: 10.1080/00958970600773887

complexes [14–17], and exploiting their linking propensity with metal ions to obtain extended structures of new materials. As a continuation of the hydrothermal synthesis of biphosphopentamolybdate $[H_xMo_5P_2O_{23}]^{(6-x)-}$ $(x = 0, 1, 2)$ derivatives [18], we are trying to construct diphosphopentamolybdate supported transition metal complexes [19] and, if possible, move into extended architectures as building blocks of rational design. In this article, we report the hydrothermal synthesis and crystal structure of a novel grid network built from new bisupporting polyoxometalate clusters: $[\{Cu^{II}(im)_4\}_2\{H_2Mo_5P_2O_{23}\}] \cdot 3H_2O \cdot (im)$ (**1**) (im = imidazole).

2. Experimental

2.1. *Synthesis and characterization*

Synthesis of $[\{Cu^{II}(im)_4\}_2\{H_2Mo_5P_2O_{23}\}] \cdot 3H_2O \cdot (im)$. A mixture of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, H_3PO_4, $Cu(MeCO_2)_2 \cdot H_2O$, imidazole and H_2O (10 mL) in the molar ratio of 4 : 4 : 1 : 1 : 550 was stirred for 20 min in air. The mixture was then transferred to a Teflon-lined autoclave (20 mL) and kept at 160°C for five days. After slow cooling to room temperature, blue block-like crystals were filtered off, washed with distilled water and dried in a desiccator at room temperature to give a yield of 60% based on Mo. The ICP analysis showed that compound **1** contained 28.44% Mo, 7.28% Cu and 3.35% P (Calcd: Mo, 28.13; Cu, 7.45; P, 3.63%). The elemental analysis found: C, 19.64; H, 2.72; N, 13.95 (Calcd: C, 19.01; H, 2.60; N, 14.78%).

Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Mo, Cu and P were determined by a Leeman inductively coupled plasma (ICP) spectrometer. The infrared spectrum was obtained on an Alpha Centaurt FT/IR spectrometer with pressed KBr pellets in the 4000–400 cm^{-1} region. A Perkin-Elmer TGA7 thermogravimetric analyzer was used to obtain the TGA curve in N_2 at a rate of 10°C min^{-1}.

2.2. *Single-crystal X-ray diffraction*

A blue single crystal of **1** was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyanoacrylate (super glue) adhesive. Single-crystal structure determination by X-ray diffraction was performed on a R-axis RAPID IP diffractometer equipped with a normal focus, 18 kW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 200 mA. Data processing was accomplished with the RAXWISH processing program. An empirical absorption correction was applied. The structure was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXL 97 software [20]. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to nitrogen atoms and carbon atoms were fixed in ideal positions, while the hydrogen atoms attached to water molecules were not located except those attached to OW1. Further details of the X-ray structural analysis are given in table 1. Selected bond lengths are listed in table 2.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{27}H_{44}Cu_2Mo_5N_{18}O_{26}P_2$
Formula weight	1705.52
Crystal system	Orthorhombic
Space group	*Pnma*
Unit cell dimensions (Å)	
a	14.598(3)
b	21.059(4)
c	16.609(3)
Volume (Å^3)	5106.1(18)
Z	4
Reflections collected	46,130
Independent reflections	5994 ($R_{int} = 0.0406$)
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	$R_1^a = 0.0347$, $wR_2^b = 0.0890$
R indices (all data)	$R_1^a = 0.0428$, $wR_2^b = 0.0930$

$^a R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$.
$^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected bond lengths (Å) for **1**.

Mo(1)–O(4)	1.706(3)	Mo(1)–O(11)	1.9265(17)
Mo(1)–O(6)	1.718(3)	Mo(1)–O(8)	2.222(3)
Mo(1)–O(9)	1.912(3)	Mo(1)–O(13)	2.384(2)
Mo(2)–O(2)	1.687(3)	Mo(2)–O(1A)	2.036(6)
Mo(2)–O(7)	1.699(3)	Mo(2)–O(14)	2.220(5)
Mo(2)–O(1)	1.859(6)	Mo(2)–O(8)	2.332(2)
Mo(2)–O(9)	1.911(3)	Mo(2)–O(15)	2.357(5)
Mo(3)–O(12)	1.705(5)	Mo(3)–O(1A)	2.009(6)
Mo(3)–O(3)	1.726(4)	Mo(3)–O(10)	2.257(4)
Mo(3)–O(1)#1	1.779(6)	Mo(3)–O(14)#1	2.386(5)
Mo(3)–O(1)	1.779(6)	Mo(3)–O(14)	2.386(5)
Mo(3)–O(1A)#1	2.009(6)	Cu(1)–N(7)	1.987(3)
Cu(1)–N(3)	1.989(3)	Cu(1)–N(2)	2.021(4)
Cu(1)–N(5)	2.010(4)	Cu(1)–O(7)	2.408(3)
P(1)–O(14)	1.519(5)	P(1)–O(13)	1.529(4)
P(1)–O(14)#1	1.519(5)	P(1)–O(16)#1	1.570(5)
P(1)–O(15)#1	1.525(5)	P(1)–O(16)	1.570(5)
P(1)–O(15)	1.525(5)	P(2)–O(5)	1.506(4)
P(2)–O(10)	1.523(4)	P(2)–O(8)	1.552(2)
P(2)–O(8)#1	1.552(2)	O(11)–Mo(1)#1	1.9265(17)
O(13)–Mo(1)#1	2.384(2)		

Symmetry transformations used to generate equivalent atoms, #1: x, $-y + 1/2$, z.

3. Results and discussions

3.1. *Synthesis*

The isolation of compound **1** depended on hydrothermal techniques. Hydrothermal synthesis has proved a particularly useful technique in the preparation of inorganic–organic hybrid materials [21]. In the hydrothermal environment, the reduced viscosity of the solvent results in enhanced rates of solvent extraction of solids and crystal growth from solution. Furthermore, since solubility problems can be minimized, a variety of organic and inorganic precursors can be introduced. However, hydrothermal synthesis is still a relatively complex process because many factors can influence the outcome, such as the type of initial reactants, starting concentrations, pH values, reaction time and temperature [3]. By plenty of parallel experiments, it was found that starting materials play a crucial role in the isolation of **1**. First, the molybdenum source in this reaction must be heptamolybdate. If the heptamolybdate was replaced by simple sodium molybdate, only a large amount of blue slurry formed. This may be because heptamolybdate can release molybdenum slowly, favor the formation of the final product. Secondly, the organic species is significant. In the structure of **1**, the organic molecules extended into the cores of the grid network. Therefore, the dimensions of the ligands must be important for the preparation of the products, and also, the remaining uncoordinated N donors of the imidazole ligands were involved in forming extended hydrogen bonding interactions with the diphosphopentamolybdate cluster. No crystals were found if the reaction under similar conditions used pyridine in place of imidazole though imidazole in the structure of **1** has a similar coordination to pyridine. If $Cu(MeCO_2)_2 \cdot H_2O$ were replaced by $Zn(MeCO_2)_2 \cdot 2H_2O$, $Ni(MeCO_2)_2 \cdot 4H_2O$ or $Co(MeCO_2)_2 \cdot 4H_2O$ in a similar hydrothermal reaction for the synthesis of compound **1**, we could not obtain the expected structures, showing the importance of divalent transition metal. Cu(II) tends to adopt square-pyramidal geometry owing to Jahn–Teller effects whereas Zn(II), Ni(II) and Co(II) favor octahedral geometry. In addition, the pH value must be in the range of 3–4 to obtain crystallized product.

3.2. *Description of structure*

The diphosphopentamolybdate cluster in **1** can be described as a ring of five distorted MoO_6 octahedra with two PO_4 tetrahedra capping each side (the oxygen atoms of $P(1)O_4$ tetrahedra in this structure are a little disordered as often encountered in the central PO_4 tetrahedra of Keggin type polyanions [22]). Each phosphate subunit shares three oxo-groups with the molybdate ring. In turn, one of these oxo-groups adopts the μ_2-bridging mode, linking one molybdenum site and the phosphorus, and the other two adopt μ_3-bridging mode, linking two molybdenum sites and the phosphorus. In **1**, the average Mo–O distances are 1.708 Å for terminal oxygen, 1.914 Å for O bonded to two Mo atoms, 2.318 Å for O bonded to two Mo atoms and one P atom, 2.307 Å for O bonded to one Mo atom and one P atom. P–O distances vary between 1.506 and 1.570 Å, average 1.535 Å. The valence sum calculations [23] give values 5.74 for Mo(1) (2×), 6.28 for Mo(2) (2×), 6.26 for Mo(3), 4.99 for P(1), 5.02 for P(2), 1.34 for O(5) and 1.13 for O(16). The calculated results reveal that in the structure of **1**, all the Mo centers are +6, both of the P sites are +5 and two O atoms are protonated for charge balance. Each $[H_2Mo_5P_2O_{23}]^{4-}$ cluster anion is linked to two equal copper fragments $\{Cu(im)_4\}^{2+}$ through two terminal O donors of $\{Mo(2)O_4\}$ forming a bisupported complex cluster. The crystallographically independent Cu atom is in the center of a Jahn–Teller distorted square pyramid which is defined by four N donors from four different imidazole ligands with Cu–N distances ranging from 1.987 to 2.021 Å and an O atom from the diphosphopentamolybdate cluster (Cu–O 2.408 Å). The N–Cu–O angles are in the range of 84.09°–99.34°, indicating that the copper site resides in a roughly square-pyramidal environment (see figure 1).

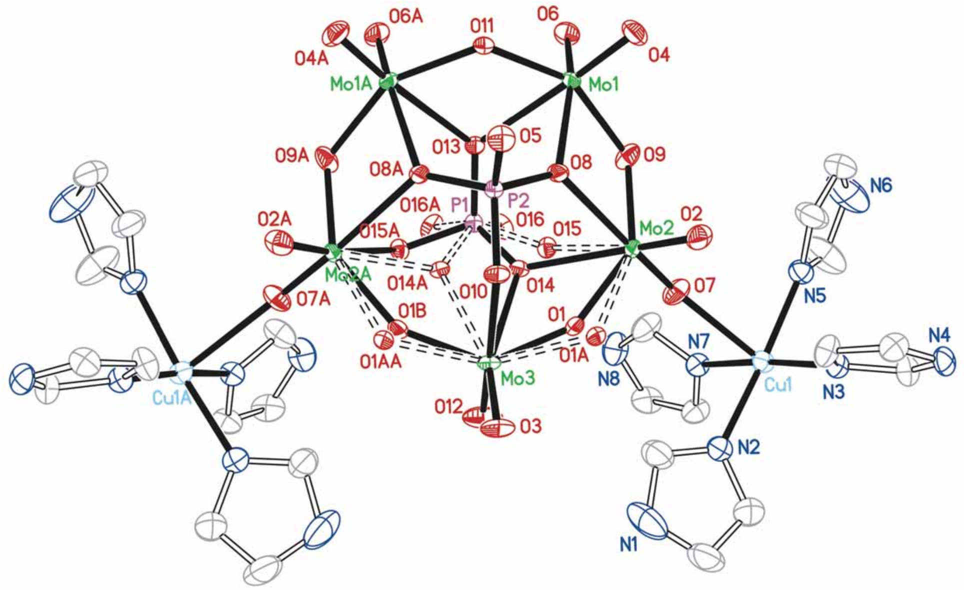

Figure 1. ORTEP drawing of the basic building block of **1** with thermal ellipsoids at 30% probability. For the sake of clarity, guest molecules (free water molecules and imidazole ligands) and all the hydrogen atoms are omitted.

Each bisupported diphosphopentamolybdate cluster links to four neighboring $[H_2Mo_5P_2O_{23}]^{4-}$ moieties *via* the bonding of its two Cu atoms and two terminal O donors of $\{MoO_6\}$ to the terminal O atoms and square-pyramidal Cu sites on adjacent clusters, respectively, with Cu–O bond length of 2.745 Å generating a uniform 2-D grid network. The copper–oxygen distance is long as previously reported in an Anderson anion supported copper complex [24]. Taking into consideration these weaker Cu $\cdots$ O contacts, the entire structure may be described as an extended framework constructed from diphosphopentamolybdate clusters attached by $Cu(im)_4$ complex linkages (figure 2). In addition, there are extensive hydrogen-bond contacts between the N atoms from one of the four coordinated imidazole ligands and O atoms from the $\{PO_4\}$ tetrahedra (typical hydrogen bonding interaction N $\cdots$ H $\cdots$ O 2.729 Å defined by N–O distance) located on adjacent networks, extending into a 3-D supramolecular structure (figure 3). Free water molecules and imidazole ligands act as space-filling constituents filling in the void of the crystal lattice.

3.3. *FT-IR spectroscopy and TG analyses*

The IR spectrum of **1** shows several bands in the range 2848–3339 cm^{-1} associated with the lattice water molecules and a series of bands in the 1263–1542 cm^{-1} region associated with the imidazole. The compound also possesses bands within 1000–1100 cm^{-1} attributed to ν(P–O) and characteristic bands at 910, 752, 673, 576, 532 cm^{-1} attributed to ν(Mo=O) and ν(Mo–O–Mo).

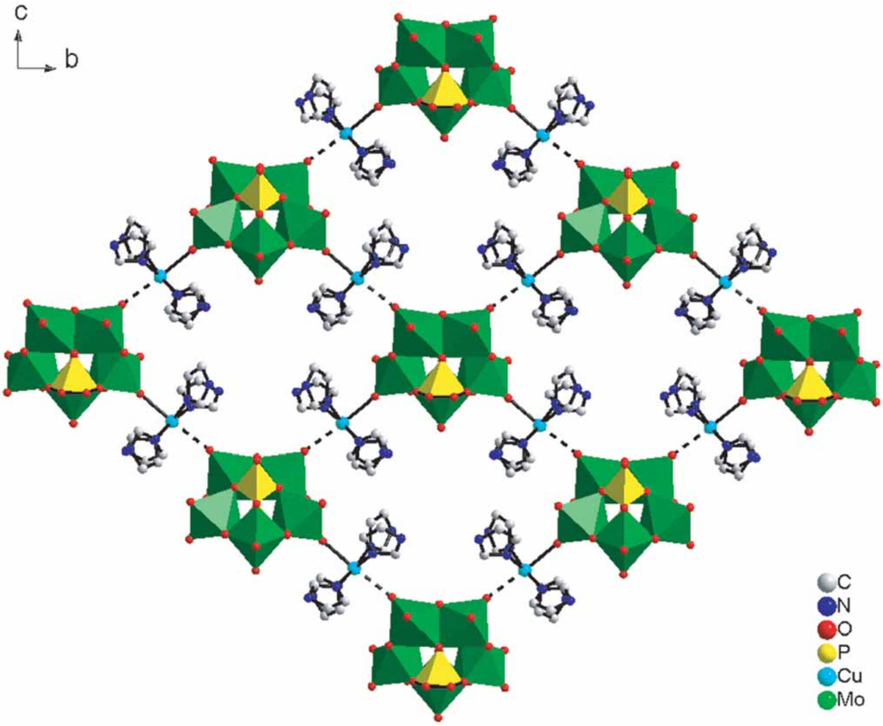

Figure 2. A view of the two-dimensional grid architecture of **1**.

Thermogravimetric analysis (TGA) was performed in air at a heating rate of 10°C min^{-1} on polycrystalline samples of **1**. A first weight loss of 3.3% occurred between 55–110°C, corresponding to three water molecules (Calcd 3.2%). In the range of 250 to 310°C, a second weight loss of 3.7% is observed corresponding to one free im molecule (Calcd 4.0%). Between 355 and 545°C, a loss of 33.4% in weight is detected in agreement with the departure of eight coordinated im ligands and the removal of one H_2O from $2HPO_4$ (Calcd 32.9%). Above 545°C and up to 700°C, no further weight loss is observed. The final product was found to be amorphous by powder X-ray diffraction.

3.4. *Discussion*

Organic species possessing relatively high coordination numbers, small volume, and versatile coordination behavior, allow networks with considerable voids in the structures in combination with polyanion clusters. The imidazole ligand utilized in this work showed interesting properties in constructing extended structures with transition metals, and is a candidate for formation of supramolecular interactions for hydrogen bonding receptors or donors, important for stabilization of the structure.

The structures also depend on the coordination preference of the oxo-groups on the polyanion surfaces together with the metal–organic linkages formed in the self-assembly processes. For example, polyanions with highly symmetric structures meet the

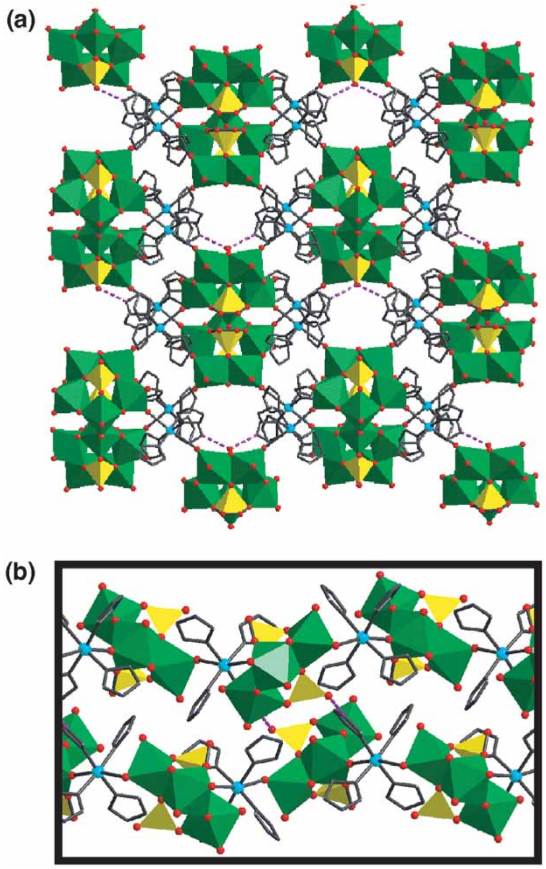

Figure 3. The 3-D framework of **1**, exhibiting the linkage of hydrogen bonds along (a) *a* axis and (b) *b* axis of the interlamellar region.

coordination abilities of metal complexes in different directions to form extended structures. That is why structures based on simple Linquist-, Anderson-, or Keggin-type anions are widely explored. In contrast, successful exploration of extended structures based on substituted or supported polyanion clusters and kinds of low symmetric moieties, is less documented. In this sense, structural characterization of metal oxo-clusters is even more interesting when they support or attach transition metal complexes.

4. Conclusions

We have synthesized a novel grid architecture constructed from bisupporting polyoxometalate compounds formed by diphosphopentamolybdate and copper-imidazole complex fragments, $[\{Cu^{II}(im)_4\}_2\{H_2Mo_5P_2O_{23}\}]\cdot 3H_2O\cdot(im)$ (**1**). In the structure of **1**, bisupporting polyoxometalate clusters connect to each other *via* the terminal O donors and the uncoordinated sites on copper centers to form grid layers, and the free water molecules and imidazole ligands fill in the voids of the crystal lattice. This work shows that the hydrothermal technique is a powerful method for synthesis of interesting architectures based on polyoxometalate subunits.

Supplementary material

Crystallographic data for the structures in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC-271626. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgement

The authors thank the National Natural Science Foundation of China (20171011) for financial support.

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