

An unprecedented extended architecture constructed from a 2-D interpenetrating cationic coordination framework templated by $\text{SiW}_{12}\text{O}_{40}^{4-}$ anion

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Abstract

A novel inorganic-organic hybrid compound based on polyoxometalates (POMs) and organic ligand formulated as $[\text{Cu}_2(\text{bpp})_4(\text{H}_2\text{O})_2](\text{SiW}_{12}\text{O}_{40}) \cdot 6\text{H}_2\text{O}$ (**1**) [bpp = 1,3-bis(4-pyridyl)propane], was hydrothermally synthesized and structurally characterized by elemental analysis, single-crystal X-ray diffraction analysis, IR, TG, and cyclic voltammetry. Crystal data for **1**: Orthorhombic, $Pbcn$, $a = 23.0085(19) \text{ \AA}$, $b = 14.6379(12) \text{ \AA}$, $c = 23.6226(19) \text{ \AA}$, $V = 7956.0(11) \text{ \AA}^3$, $Z = 4$, $D_c = 3.315 \text{ g cm}^{-3}$, and $R(\text{final}) = 0.0826$. X-ray diffraction study reveals that compound **1** was the first interpenetrating network of 2-D metal-organic cationic coordination framework $[\text{Cu}_2(\text{bpp})_4(\text{H}_2\text{O})_2]_n^{4n+}$, in which Keggin-type anions $\text{SiW}_{12}\text{O}_{40}^{4-}$ has been used as a non-coordinating anionic template. The electrochemical property of **1**-bulk modified carbon paste electrode (**1**-CPE) has been studied, and the results indicate that **1**-CPE has good electrocatalytic activities toward the reduction of nitrite in 1 M H_2SO_4 aqueous solution.

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Keywords: Polyoxometalates; Template; Interpenetrating network; Crystal structure; Electrochemical property

1. Introduction

The design and construction of infinite high-dimensional (especially two- and three-dimensional) metal-organic frameworks (MOFs) are currently of great interest in the field of crystal engineering, not only due to their intriguing structural features, but also their extensive theoretical and potential applications in molecular adsorption, catalysis, electronic-conductive, optical and magnetic materials [1–3]. Among these MOFs, the entangled structure, in which two or more infinite networks interpenetrate each other, is an attractive structural feature and has been widely researched [4–6]. Two comprehensive reviews of interpenetration have been reported by Robson and Batten [7,8], in which the most investigated type of entanglement has been included. Ongoing important research in this field has been directed

toward the design and synthesis of novel entangled networks [9,10].

On the other hand, polyoxometalates (POMs) as a unique class of metal-oxide clusters, have recently been employed as inorganic building blocks for the construction of numerous new structural types with fascinating topological beauty and the associated multitude of properties [11–13]. In the past decades, several successful strategies have been developed to integrate POMs into hybrid solid-state materials [14–16]. However, owing to the large number of potential coordination sites, the design and synthesis of the new POM-based compounds are mainly depended on the coordination abilities of the POMs to produce POM-supported metal compounds [17,18] and metal complexes bridged polyoxoanions extended structures [19,20]. Recently, Keller [15,21], Zubieta [22,23] and others [24,25] have developed new synthetic approaches and obtained several extended structures of cationic coordination networks in which the non-coordinating POM-anions were included in the intercrystalline voids as

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templates. Furthermore, Müller et al. have reported huge inorganic cage hosts templated by various POMs [26,27].

However, up to now, no reports have been made on the combination of these two interesting fields to prepare interpenetrating networks based on POMs template. Therefore, it is still a current challenge to design and synthesize POM-templated interpenetrating MOFs. It is well-known that one of the important factors for the construction of interpenetrating MOFs is the formation of large pores or cavities existing in the infinite networks, and thus the use of long organic bridging ligands is often regarded as an effective strategy for the construction of such interpenetrating MOFs [28,29]. So the flexible long bridging ligand *bpp* (*bpp* = 1,3-bis(4-pyridyl)propane) was introduced and expected to obtain a high-dimensional structure with large pores or undulated layers, which may have a tendency to form networks with interpenetrating character. In this paper, we report the synthesis and structure of the compound $[Cu_2(bpp)_4(H_2O)_2](SiW_{12}O_{40}) \cdot 6H_2O$ (**1**), which represents the first 2-D interpenetrating cationic MOFs templated by Keggin-type anions. Moreover, the electrochemical and electrocatalytic properties of **1** are investigated.

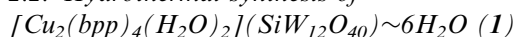
2. Experimental

2.1. Materials and instrumentation

Ligand *bpp* was commercially obtained from Aldrich and used without further purification. POM $H_4SiW_{12}O_{40} \cdot xH_2O$ was synthesized by the literature method [30]. All other reagents were of reagent grade.

FT-IR spectra (KBr pellets) were taken on a Magna FT-IR 560 spectrometer and the elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C elemental analyzer. The electrochemical experiments were carried out using a CHI 440 Electrochemical Quartz Crystal Microbalance. A conventional three-electrode cell was used at room temperature. The modified electrode was used as working electrode. A SCE and a platinum wire were used as reference and auxiliary electrodes, respectively.

2.2. Hydrothermal synthesis of



A mixture of $H_4SiW_{12}O_{40} \cdot xH_2O$, $CuCl_2 \cdot 2H_2O$, *bpp*, ethanol and H_2O in a molar ratio of 1:2:1:34:390 was stirred for half an hour in air. Then the pH was adjusted to 7.0 by diluted $NH_3 \cdot H_2O$. Then the mixture was transferred to a Teflon-lined autoclave and kept at 120 °C for 4 days. Blue crystals **1** were obtained when cooled to room temperature (yield: ca. 40% based on Cu). Anal. Calc. for $Cu_2C_{52}N_8H_{72}SiW_{12}O_{50}$: C, 15.73; N, 2.82; H, 1.83%. Found: C, 15.85; N, 2.74; H, 1.71%. IR (KBr pellet, cm^{-1}): 3453 (s), 3065 (w), 2920 (w), 2855 (w), 2355 (m), 1606 (s), 1560 (w), 1508 (m), 1428 (m), 1225 (w), 1067 (w), 1008 (w), 969 (s), 916 (vs), 791 (vs), 607 (w), 522 (m).

2.3. X-ray crystallographic study

Crystallographic data for **1** was collected at 293(2) K on a Bruker Smart 1000 CCD diffractometer with Mo $K\alpha$ (λ 0.71073 Å) by ω scan mode. The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [31]. Metal atoms in the complex were located from the *E*-maps, and other non-hydrogen atoms were located from successive difference Fourier maps and refined with anisotropic thermal parameters on F^2 . The hydrogen atoms of the ligand were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors.

A summary of crystal data and structure refinements for compound **1** is provided in Table 1. Selected bond lengths and angles are listed in Table S1. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 642469. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223336 033; e-mail: deposit@ccdc.cam.ac.uk).

2.4. Preparation of **1**-bulk modified carbon paste electrode (**1**-CPE)

The **1**-CPE was fabricated as follows: 0.5 g graphite powder and 0.035 g compound **1** were mixed and ground

Table 1
Crystal data and structure refinement summary for Compound **1**

Empirical formula	$C_{52}H_{72}Cu_2N_8O_{50}SiW_{12}$
Formula weight	3970.55
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pbcn
<i>a</i> (Å)	23.0085(19)
<i>b</i> (Å)	14.6379(12)
<i>c</i> (Å)	23.6226(19)
Volume (Å ³)	7956.0(11)
<i>Z</i>	4
<i>D</i> _{calc} (g/cm ³)	3.315
Absorption coefficient (mm ⁻¹)	17.913
<i>F</i> (000)	7200
Crystal size (mm)	0.26 × 0.24 × 0.22
θ Range (°)	1.86–25.00
Range of <i>h, k, l</i>	–27/18, –15/17, –26/28
Reflections collected	37076
Independent reflections	6813 (<i>R</i> _{int} = 0.0615)
Data/restraints/parameters	6813/312/557
Goodness-of-fit on <i>F</i> ²	1.087
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ^a = 0.0826, <i>wR</i> ^b = 0.2401
<i>R</i> indices (all data)	<i>R</i> ^a = 0.0906, <i>wR</i> ^b = 0.2467
Largest diff. peak and hole (e Å ⁻³)	2.990 and –2.130

^a*R*₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$.

^b*wR*₂ = $\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$.

together by agate mortar and pestle for approximately 20 min to achieve an even, dry mixture; to the mixture 0.20 ml paraffin oil was added and stirred with a glass rod; then the homogenized mixture was used to pack 3 mm inner diameter glass tubes to a length of 0.8 cm. The electrical contact was established with the copper stick, and the surface of the 1-CPE was wiped with weighing paper.

3. Results and discussion

3.1. Description of crystal structure

Single crystal X-ray analysis revealed **1** is an extended interpenetrating network involving 2-D metal–organic coordination frameworks $[\text{Cu}_2(\text{bpp})_4(\text{H}_2\text{O})_2]_n^{4n+}$, in which the POM $\text{SiW}_{12}\text{O}_{40}^{4-}$ anions were used as templates. The building unit of **1** contains two crystallographically independent Cu(II) cations, one $\text{SiW}_{12}\text{O}_{40}^{4-}$ anion, four *bpp* ligands, two coordinated water molecules and other six disordered water molecules. Each Cu(II) is coordinated by four nitrogen atoms (Cu(1)–N 1.99(2)–2.05(2) Å) of four *bpp* ligands, and one oxygen atom (Cu(1)–O(1W) 2.54(3) Å) of a coordinated water molecule to give a distorted square pyramidal geometry (Fig. S1a). The connection of alternate Cu atoms and *bpp* ligands forms a unique 2-D grid-like cationic framework with Cu...Cu distances ca. 12.15 and 13.64 Å, respectively, as shown in Fig. 1. $\text{SiW}_{12}\text{O}_{40}^{4-}$ anions in **1** were the classical Keggin-type heteropolyoxoanion (Fig. S1b), the W–O bond distances

fall in the ranges 1.64(2)–1.73(3), 1.80(3)–1.97(3) and 2.32(3)–2.44(3) Å, and the mean values are 1.68(3), 1.89(3) and 2.38(3) Å, respectively. The mean values of the $W\text{--}O_t$ and $W\text{--}O_{e/c}$ distances are shorter than that of the literature [32], and the mean value of the $W\text{--}O_a$ distances is somewhat longer than that of the literature [32].

The most interesting feature of **1** is that these 2-D frameworks are stacked together to generate an interpenetrating porous network, as shown in Fig. 2. The dihedral angle between the interpenetrating layers is 64.8° , the spacing between the parallel layers was 12.3 Å. In the network, $\text{SiW}_{12}\text{O}_{40}^{4-}$ anions as templates are not coordinated to copper atoms. Fig. 3 shows the POM anion $\text{SiW}_{12}\text{O}_{40}^{4-}$ well surrounded by one porous cavity comprised of eight Cu(II) centers from four different layers (and Fig. S2). As shown in Fig. 4, these MOF sheets are stacked together along the crystallographic *c* axis exactly to construct large cubic-like channels, the channels possess approximate dimensions of 12.3×13.6 Å and are occupied by $\text{SiW}_{12}\text{O}_{40}^{4-}$ clusters.

The formation of 2-D interpenetrating MOFs depends on not only the coordination geometry of the metal centers but also the nature of the anions and the bridging ligands. Compared with the simple anions, POMs are more suitable as inorganic templates in the MOFs [33], because of their relatively large volume, higher negative charges. The longer ligands may tend to form larger voids, then the more likely constructs interpenetrating structures [34]. So in compound **1**, the presence of POM-anions and flexible long *bpp* ligands play a crucial role in generating the unusual framework structure.

3.2. IR spectra

In the compound **1**, all W and Cu centers exhibit the +6 and +2 oxidation states, respectively, based on charge balance consideration and bond valence sum calculations [35]. In the IR spectrum of **1** (Fig. S3), strong peaks at

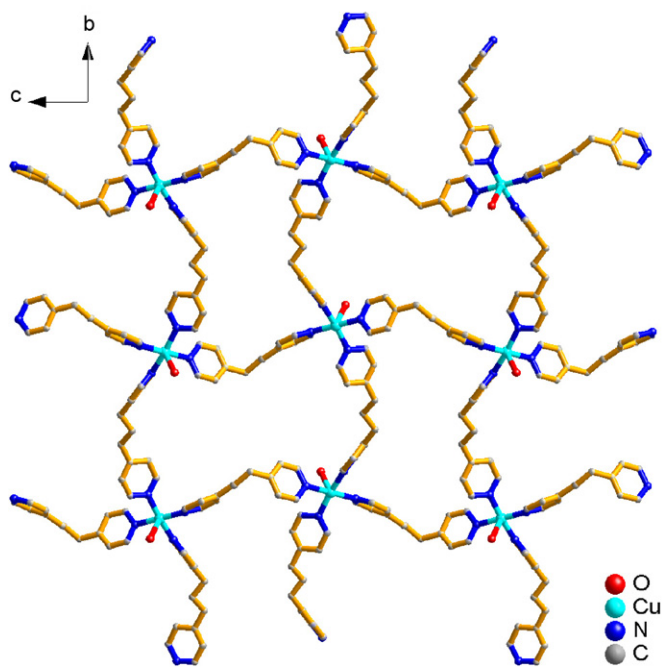


Fig. 1. Ball-and-stick representation of the 2-D grid-like metal–organic coordination cationic framework $[\text{Cu}_2(\text{bpp})_4(\text{H}_2\text{O})_2]_n^{4n+}$ of compound **1**. All H atoms and POM anions and lattice water molecules have been omitted for clarity.

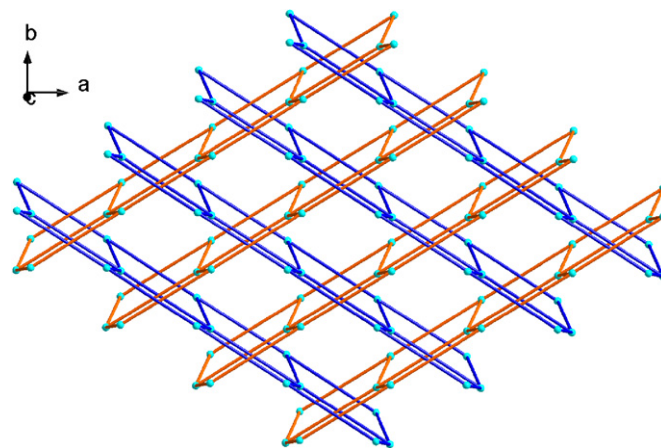


Fig. 2. Schematic representations of topologies observed in the network of interpenetrating layers.

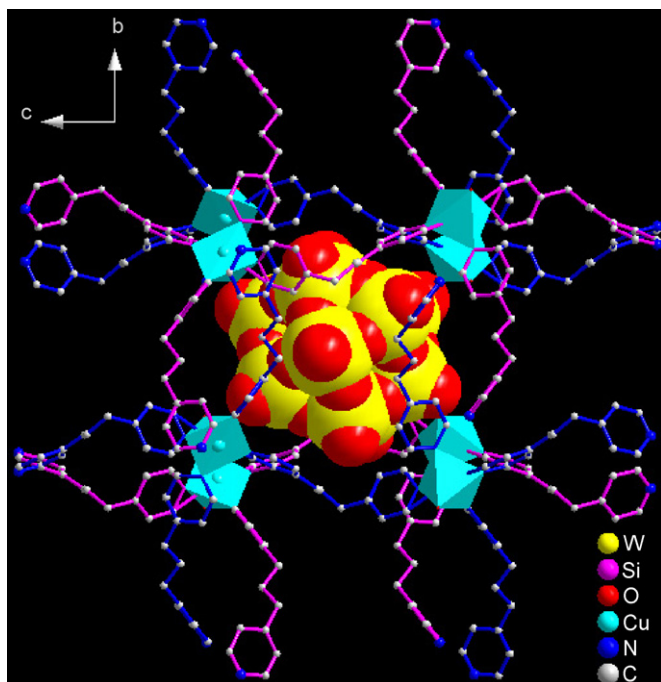


Fig. 3. Space-filling view of the POM anion sitting in one cavity constructed from the interpenetrating 2-D metal–organic networks. All H atoms and lattice water molecules have been omitted for clarity.

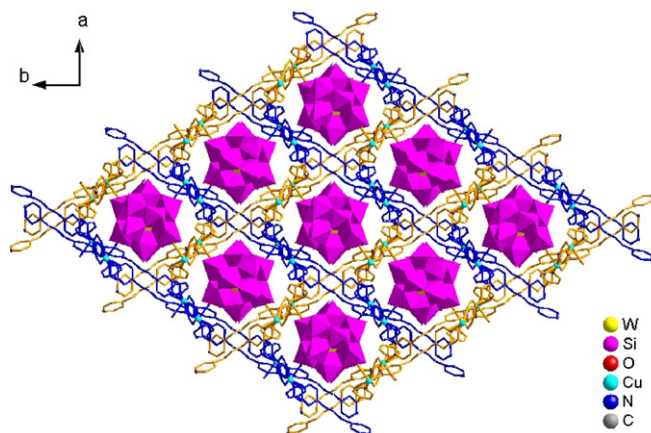


Fig. 4. Packing diagram of **1** viewed down the *c*-axis. Stick representation of the cubic-like channels based on interpenetrating $[\text{Cu}_2(\text{bpp})_4(\text{H}_2\text{O})_2]_n^{4n+}$ framework encircling POM anions shown in a polyhedral representation.

1066, 973, 918, 787 cm^{-1} are due to the $\nu_{\text{as}}(\text{Si}-\text{O}_a)$, $\nu_{\text{as}}(\text{W}-\text{O}_t)$, $\nu_{\text{as}}(\text{W}-\text{O}_e-\text{W})$ and $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W})$ vibrations, respectively. The bands at 1612, 1556, 1426 and 1197 cm^{-1} are assigned to *bpp* ligands.

3.3. TG analysis

The TG curve of compound **1** exhibits two weight-loss steps in the temperature range of 30–800 °C (Fig. S4). The continuous weight loss step from 60 to 255 °C is attributed

to the loss of all lattice and coordinated water molecules. The weight loss is about 3.4%, in correspondence with the calculated value of 3.7%. Based on the TG and elemental analyses, ca. 6 water molecules should be in the crystal structure, thus, these water molecules were included in the molecular formula directly. The weight-loss step after 255 °C is attributed to the oxidation of ligands *bpp* and the decomposition of $\text{SiW}_{12}\text{O}_{40}^{4-}$. The total weight loss is about 23.8%, in the accordance with the calculated value of 24.4%.

3.4. Voltammetric behavior

Among those important properties of POMs, the abilities to undergo reversible multi-electron redox processes [36] endow them with very attraction in electrochemical and electrocatalytic research [37]. To study the redox property of **1**, **1**-bulk-modified carbon paste electrode (**1**-CPE) was fabricated as the working electrode owing to the inorganic–organic hybrid of POMs prepared by hydrothermal reaction being of insolubility in water and poor solubility in common organic solvent. The voltammetric behavior of **1**-CPE in the 1 M H_2SO_4 aqueous solution at the scan rate of 80 mV s^{-1} was recorded (Fig. S5), exhibiting two reversible redox peaks in the potential range of -700 to -100 mV, attributable to the $\text{SiW}_{12}\text{O}_{40}^{4-}$ polyanions [37]. When the scan rate was varied from 10 to 130 mV s^{-1} , the cathodic peak currents and the corresponding anodic peak currents increase simultaneously (Fig. S6). The peak potentials changed slightly: the cathodic peak potentials shifted to the negative direction and the corresponding anodic peak potentials shifted to positive direction with increasing scan rates. This might be because the hybrid materials are solid and the electron exchanging rate between the graphite and the hybrid materials is decreased to some extent. At scan rates lower than 130 mV s^{-1} , the peak currents were proportional to the scan rate (see the insert of Fig. S6), which indicates the redox process of **1**-CPE is surface-controlled. In the experiment, **1**-CPE shows high stability. The remarkable stability of the **1**-CPE can be ascribed primarily to the insolubility of the hybrid material, avoiding the loss of the modifier during measurements. When the potential range is maintained at -700 to -100 mV, it is stable over 800 cycles at a rate of 100 mV s^{-1} and the current response remained almost unchanged. When the **1**-CPE was stored at room temperature for at least one month, the current response decreased only 8% and could be renewed by squeezing a little carbon paste out of the tube.

The electrocatalytic reduction of nitrite in 1 M H_2SO_4 aqueous solution was investigated at the **1**-CPE, as shown in Fig. 5. It is well known that direct electroreduction of nitrite ion requires a large overpotential at most electrode surfaces and no obvious response was observed at a bare CPE. Our results indicate that **1**-CPE has good electrocatalytic activity toward the reduction of nitrite. With the addition of nitrite, both reduction peak currents increase

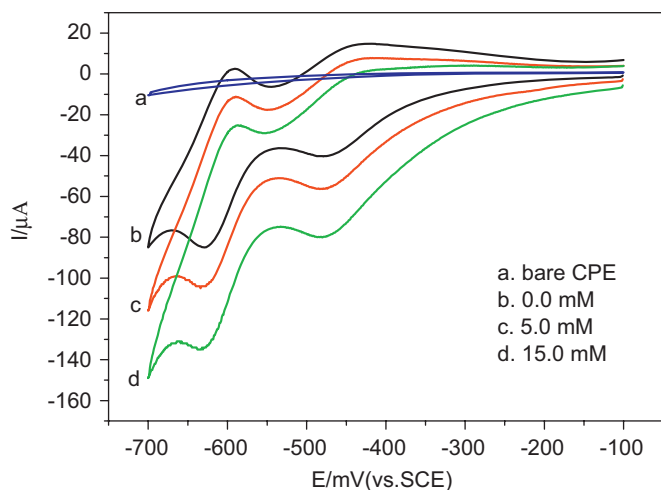


Fig. 5. Cyclic voltammogram of the **1**-CPE in the 1 M H₂SO₄ aqueous solution containing 0.0, 5.0, 15.0 mM KNO₂ and a bare CPE in 10 mM KNO₂ + 1 M H₂SO₄ solution. Potentials vs. SCE. Scan rate: 100 mV s⁻¹.

markedly while the corresponding oxidation peak currents decrease markedly, suggesting that the reduction of nitrite is mediated by the reduced species of SiW₁₂O₄₀⁴⁻ in compound **1**. We have also note that high scan rate (100 mV s⁻¹) has been used to register the electrocatalytic reduction of nitrite and obtained noticeable catalytic currents, which indicates the reduction of nitrite at the **1**-CPE is fast. The high electrocatalytic activity is probably due to the interpenetrating network structural feature of **1** that stabilized the Keggin-ions SiW₁₂O₄₀⁴⁻ in the compound.

4. Conclusions

We have successfully obtained the first extended interpenetrating network based on 2-D MOF, in which POM anions play the role of template. Our work provides a probability for the POMs to be used as template in the interpenetrating network. If the Keggin-anion templates could be successfully removed or substituted by small anions without collapse of the host framework, an actual porous material will be obtained. Further investigations of this new hybrid material in factual application are currently underway.

Acknowledgments

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Appendix A. Supplementary materials

X-ray crystallographic files for compound **1** in CIF format, TG spectrum, and IR spectrum. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2007.12.029.

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