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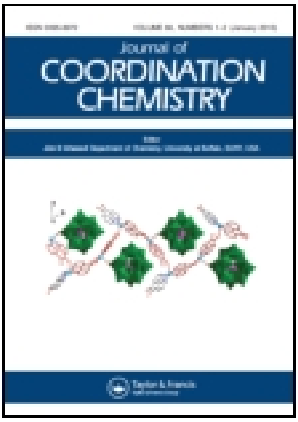

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A new compound constructed from Keggin anions and Cu-5,6-diamino-1,10-phenanthroline complexes: synthesis, structure, and characterization

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A new inorganic–organic hybrid based on polyoxometalate, $[Cu_2(daphen)_2(H_2O)_4(PW_{11}W^{V}O_{40})] \cdot 6H_2O$ (**1**) (daphen = 5,6-diamino-1,10-phenanthroline), was synthesized hydrothermally and characterized by single-crystal X-ray diffraction, elemental analysis, infrared spectroscopy, and thermal analysis. Single-crystal X-ray diffraction analysis reveals that in **1** the Keggin anion $[PW_{12}O_{40}]^{4-}$ is tetradentate, linking four Cu(II)-daphen fragments with its four terminal oxygen atoms in a plane; Cu^{2+} is coordinated by two terminal oxygen atoms of two $[PW_{12}O_{40}]^{4-}$ anions, two water molecules, and two nitrogen atoms of the phen ring of a daphen, forming a polymeric layer. The 3-D architecture of the compound is further formed *via* hydrogen bonds between these layers. The daphen is bidentate chelating and does not participate in formation of hydrogen bonds. Redox of **1** was examined.

Keywords: Polyoxometalate; Phenanthroline derivative; Supramolecular compound; 2-D structure; Hydrogen-bonding

1. Introduction

Much attention has been paid to rational design of organic–inorganic hybrid materials based on polyoxometalates (POMs) for their diversity of structures and potential applications in catalysis, medicine, sorption, magnetism, and photochemistry [1–3]. POMs with Keggin structures are an outstanding class of inorganic components for building hybrid materials *via* coordination covalent bonds and intermolecular forces. The coordination covalent bonds create a stable multi-dimensional framework and hydrogen bonds are the main interaction in forming supramolecular architectures with versatile organic ligands or metal complex moieties [4–9].

Synthesis of hybrid materials based on POMs is important for obtaining a stable multi-dimensional framework. Hydrothermal and conventional syntheses are effective for growth of crystals of compounds based on POMs [10–12]. Under hydrothermal

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conditions, reduced viscosity of water enhances diffusion [13] so that solubility of materials is increased and a variety of precursors with low solubility in water may be introduced into the reaction system. Generally the syntheses of organic–inorganic hybrid materials including organic components insoluble in water are carried out with the hydrothermal method [14–16].

The structure and coordination ability of organic components are vital for constructing multi-dimensional structures of hybrid materials. Many N-containing ligands have been used for this purpose, such as aliphatic polyammonia [17], N-heterocycles, 2,2′-/4,4′-bipyridine [18], imidazole/biimidazole [19], triazole and its derivatives [20], and 1,10-phenanthroline (phen) [21] and these ligands act either as a bridge or as a chelating reagent. Phen is unfavorable to form multi-dimensional structures [21]. Its derivative, 5,6-diamino-1,10-phenanthroline (abbreviated as daphen), is a potential bridging and double-chelating ligand if its two amino groups (ethylenediamine-like) take part in coordination to metal ions [22]. To explore the possibility of coordination of the amino groups, we took daphen as organic component but obtained a new compound $[Cu_2(daphen)_2(H_2O)_4(PW_{11}W^VO_{40})] \cdot 6H_2O$ (**1**) with 2-D structure in which the daphen is only a chelating ligand. Herein we report the synthesis and structure, thermal stability, and redox property of **1** and discuss the reason that daphen does not act as a bridging-chelating ligand.

2. Experimental

2.1. *Physical measurements*

All purchased chemicals were of reagent grade and used without purification. $H_3PW_{12}O_{40}(PW_{12})$ was synthesized according to the literature [23]. Elemental analyses (Cu, W) were performed on a Leaman inductively coupled plasma (ICP) spectrometer and that of C, H, and N were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Infrared (IR) spectra as KBr pellets were recorded on a Magna-560 FT-IR spectrophotometer from 400 to 4000 cm^{-1}. Thermal gravimetric analysis and difference thermal analysis of **1** were recorded with a Netzsch STA 449C microanalyzer in nitrogen at a heating rate of 10°C min^{-1} from 30°C to 600°C. Cyclic voltammetry measurements were carried out on a CHI 660 electrochemical workstation using a conventional three-electrode single compartment cell at room temperature. Carbon paste electrode was used as working electrode, Ag/AgCl as the reference electrode and platinum wire as the counter electrode; 1 mol L^{-1} Na_2SO_4/H_2SO_4 solution was used as electrolyte. The surface of the carbon paste electrode was polished with 0.3 mm alumina and washed with distilled water before each scan.

2.2. *Synthesis of $[Cu_2(daphen)_2(H_2O)_4(PW_{11}W^VO_{40})] \cdot 6H_2O$ (1)*

A mixture of $H_3[PW_{12}O_{40}] \cdot 20H_2O$ (0.553 g), $Cu(NO_3)_2 \cdot 2H_2O$ (0.104 g), daphen (0.02 g) and H_2O (15 mL) was stirred for 20 min in air. The pH of the mixture was adjusted to 2.54 with 1.0 mol L^{-1} NaOH aqueous solution. The final solution was then transferred to a 20 mL Teflon-lined autoclave and kept at 160°C for 4 days. The autoclave was cooled at 10°C h^{-1} to room temperature. The reaction solution was filtered and then the filtrate was kept for 48 h at ambient conditions, and blue block crystals of **1** were obtained. The yield based on W was 29%. Anal. Calcd for $C_{24}H_{36}Cu_2N_8O_{50}PW_{12}$ (**1**) ($M_r = 3599.83$): C, 8.01; H, 0.98; Cu, 3.53; N, 3.11; W, 61.29. Found (%): C, 8.13; H, 0.84; Cu, 3.27; N, 3.01; W, 60.97. Selected IR data (cm^{-1}): 3000–3500(s, b), 1701(m), 1618(m), 1578(m), 1487(w), 1432(m), 1305(w), 1096(s), 1061(w), 1022(w), 967(s), 923(s), 886(s), 749(vs), 724(s), 517(m).

2.3. *X-ray crystallography*

A blue single-crystal of **1** with dimension $0.124 \times 0.112 \times 0.104\ mm^3$ was sealed in a glass tube. Data collection was carried out on a SMART CCD diffractometer with Mo-Kα monochromated radiation ($\lambda = 0.071$ Å) at 293 K. Empirical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the *SHELXTL* crystallographic software package [24]. The positions of hydrogen atoms on carbon atoms were calculated theoretically. Crystallographic data of $C_{24}H_{36}Cu_2N_8O_{50}PW_{12}$ ($M_r = 3599.83$): monoclinic $P2(1)/n$ space group, $a = 11.6350(6)$ Å, $b = 19.6230(11)$ Å, $c = 14.7216(8)$ Å, $\beta = 106.6860(10)°$, $V = 3219.6(3)$ Å^3, $Z = 2$. $D_{calcd} = 3.725\ g\,cm^{-3}$, absorption coeff. ($\mu$) 22.119 mm^{-1}, $F(000) = 3198$, θ range = 1.78–28.20°, 7511 independent in 19,485 reflections. Goodness-of-fit on $F^2 = 1.007$, $R_1 = 0.0655$, $wR_2 = 0.1702$ [$I \geq 2\sigma(I_0)$]. $R_1 = 0.0850$, $wR_2 = 0.1828$ for all data. Selected bond lengths and angles are listed in table 1.

Table 1. Selected bond lengths (Å) and angles (°).

Bond	Length	Bond	Length	Bond	Length
W1 O12	1.699(13)	W1 O8	1.900(16)	W1 O5	1.932(14)
W1 O17	1.878(14)	W1 O19	1.910(15)	W1 O4#3	2.42(3)
W2 O21	1.696(13)	W2 O9	1.886(14)	W2 O18	1.928(15)
W2 O5	1.878(14)	W2 O11#3	1.909(14)	W2 O1#3	2.42(3)
W3 O20	1.745(17)	W3 O8#3	1.895(13)	W3 O6	1.954(15)
W3 O10	1.891(13)	W3 O7	1.922(15)	W3 O2#3	2.41(2)
W4 O22	1.668(14)	W4 O10	1.868(13)	W4 O19	1.902(15)
W4 O18	1.857(14)	W4 O15	1.876(14)	W4 O4#3	2.47(3)
W5 O13	1.669(16)	W5 O15	1.931(14)	W5 O6	1.941(15)
W5 O9#3	1.891(17)	W5 O16	1.884(18)	W5 O2#3	2.43(3)
W6 O14	1.696(16)	W6 O16	1.935(18)	W6 O17	1.921(18)
W6 O7#3	1.856(18)	W6 O11	1.931(16)	W6 O1	2.47(4)
Cu1 O4W	1.950(18)	Cu1 N4	1.989(17)	Cu1 O5W	2.000(17)
Cu1 N3	1.996(17)	Cu1 O12#4	2.380(12)	Cu1 O21	2.386(13)

Bond	Angle	Bond	Angle
W4 O19 W1	137.7(9)	W4 O10 W3	138.9(11)
W4 O18 W2	139.1(11)	W2 O9 W5#3	139.5(11)
W1 O17 W6	135.4(9)	W3#3 O8 W1	136.9(10)
W5 O16 W6	138.0(9)	W6#3 O7 W3	137.9(11)
W4 O15 W5	137.6(9)	W5 O6 W3	133.4(10)
W2 O11 W6#3	136.0(11)	W2 O5 W1	138.2(10)

Symmetry operator: #3 $-x, -y, -z$; #4 $x - 1/2, -y-1/2, z-1/2$.

3. Results and discussion

3.1. *Formation of 1*

In the synthesis of **1**, there was no crystalline product in the reaction system after hydrothermal treatment except a small amount of solid powder; so the reaction product was in solution. We let the filtrate evaporate in air and 48 h later crystals appeared. We tried obtaining **1** from the reaction of $H_3[PW_{12}O_{40}] \cdot 20H_2O$, $Cu(NO_3)_2 \cdot 2H_2O$, and daphen in aqueous solution and at same pH, but no crystalline product was obtained at temperatures $<100^\circ C$ or reflux. That is, the hydrothermal condition is essential for formation of Cu–O covalent bond in **1** with a 2-D structure. The crystallization of **1** is also affected by concentration; after the volume of the filtrate decreased **1** crystallized. Some daphen played a role of reductant resulting in reduction of one W(VI)–W(V) according to bond valence calculations [25] (Supplementary material).

3.2. *Structural description*

Compound **1** consists of one Keggin-type polyoxoanion $[PW_{12}O_{40}]^{4-}$ (PW_{12}), two Cu^{2+} complex fragments, and water molecules. PW_{12} consists of one PO_4 tetrahedron in the center of the anion and 12 WO_6 octahedra, divided into four groups as M_3O_{10}. The WO_6 octahedra in M_3O_{10} share edges with each other and the M_3O_{10} groups share oxygen atoms with the PO_4 tetrahedron. Due to orientational disorder of the polyoxoanions in the crystal the central phosphorus is at the center of a cube defined by eight oxygen atoms, each of which has half site occupancy. This kind of disorder often appears in $[XM_{12}O_{40}]^{n-}$ Keggin clusters, explained by Evans and Pope [26a] as a crystallographic result. The distances between terminal oxygen atoms and tungsten atoms in PW_{12} fall in three types (table 1): 1.669(14)–1.696(11) Å for W–O_t, 1.696(13)–1.699(13) Å for W–O_t' (O_t' links with Cu^{2+}) and 1.745(17) Å for W–O_t'' (O_t'' forms a hydrogen bond with water). The formation of hydrogen bond and coordination of O_t' to Cu^{2+} decrease the strength of W–O_t and therefore increase the W–O_t distances. Other bond lengths are consistent with those reported [26].

In **1**, two Cu^{2+} ions are crystallographically identical, coordinated by two oxygen atoms from two PW_{12} anions, two nitrogen atoms of phen of daphen and two water molecules, forming an elongated octahedron (figure 1) with two longer Cu–O(POM) bonds of 2.368(12) Å and 2.390(13) Å due to a strong Jahn–Teller distortion [27]. The PW_{12} anion connects four copper ions with its four terminal oxygen atoms in a plane (figure 1). This connection between Cu ions and PW_{12} anions creates a 2-D layer (figure 2a). The lattice water molecules are located between the layers (Supplementary material). These layers construct a 3-D supramolecular architecture through hydrogen bonds between coordinated water (Ow4) and terminal oxygen atoms (O20) of PW_{12} (figure 2b). The daphen does not adopt tetradentate-bridging coordination as expected, behaving like phen and 2,2′-bipy [18, 21]; the amino groups do not even participate in the formation of hydrogen bonds due to the direction of the ligands and the large volume of polyoxoanion. Compound **1** represents the first example of a POM-based hybrid compound that contains daphen.

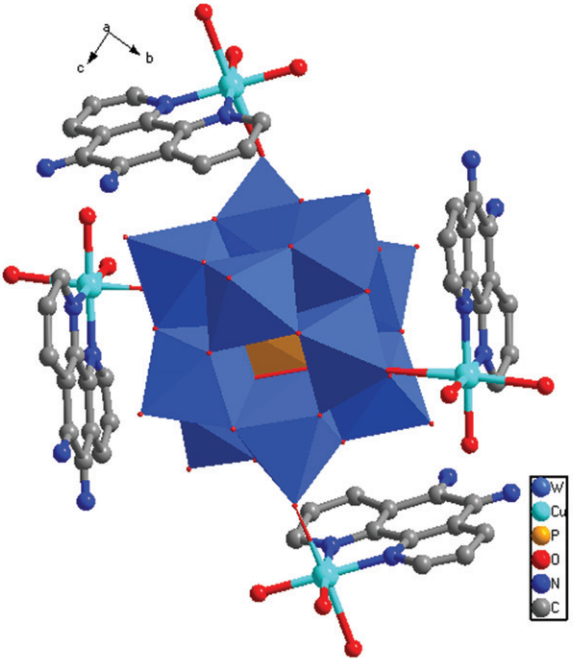

Figure 1. Coordination surroundings of Cu ion and coordination mode of $PW_{12}O_{40}^{3-}$ in **1**. The lattice water molecules and hydrogen atoms are omitted for clarity.

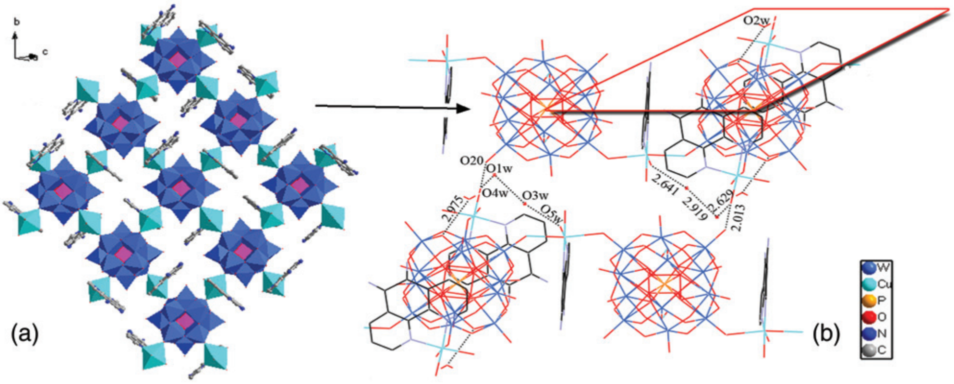

Figure 2. (a) 2-D layer and (b) hydrogen bonds between the layers of **1**. The lattice water molecules in (a) section and hydrogen atoms are omitted for clarity.

3.3. *IR spectrum*

Absorption bands in the IR spectrum of **1** (Supplementary material) may be divided into three groups. The first at 500–1100 cm^{-1} is characteristic of PW_{12} structural vibrations: 1063 cm^{-1}, 1096 cm^{-1} are ascribed to $\nu_{as}(P–O_a)$ vibration; 921 cm^{-1} and 967 cm^{-1}, typical of $\nu_{as}(W=O_d)$ vibration; and 885 and 795 cm^{-1} bands are $\nu_{as}(W–O_b)$ and $\nu_{as}(W–O_c)$ vibrations, respectively. Comparing with that of $H_3PW_{12}O_{40} \cdot 19H_2O$ [28], red shift and splitting of $\nu_{as}(W=O_d)$ band at 975 cm^{-1} are observed, from the formation of hydrogen bonds and coordination of O'_t to Cu^{2+}. The second group of bands from 1100 to 1700 cm^{-1} is vibrations of daphen, including stretches of C–N and C–C bonds, deformation vibrations of NH_2 group and water molecules. The third is a very broad plateau from 3000 to 3500 cm^{-1} formed from stretching of C–H of aromatic ring, asymmetric and symmetric stretching of N–H of NH_2 groups, and O–H of H_2O with a variety of hydrogen bonds.

3.4. *Thermal analysis*

In the TG curve of **1** (Supplementary material), a weight loss of 5.52% occurs below 200°C, attributed to loss of adsorbed, lattice, and coordinated water molecules (Calcd value for $10H_2O$: 5.02%). Three endothermic peaks in the DTA curve indicate release of three water molecules, the peak at 40°C to release of adsorbed water, the peak at 102°C to lattice, and the peak at 128°C to coordinated water. The weight loss of 11.72% between 200 and 600°C is ascribed to the release of organic molecules (Calcd value: 11.78%). The exothermic peak at 385°C indicates decomposition of daphen and other exothermic peaks correspond to formation of metal oxides. Compound **1** has low thermal stability.

3.5. *Oxidation-reduction*

To study redox of **1**, **1**-bulk-modified carbon paste electrode (**1**-CPE) was fabricated as the working electrode owing to its low solubility in water and common organic solvents. The redox of **1** was studied in 1.0 mol L^{-1} Na_2SO_4/H_2SO_4 aqueous solution at a scan rate of 60 mV s^{-1} (Supplementary material). In the potential range of +1000 to −1000 mV, two pairs of peaks (I–I′ and II–II′) with half-wave potentials $E_{1/2}$ of −555.8 and −343.7 mV ($E_{1/2} = (E_{pa} + E_{pc})/2$) are ascribed to two electron quasi-reversible redox of W(VI), similar to that of a reported analog [29]. Redox peaks III–III′ and IV–IV′ with half-wave potentials $E_{1/2}$ of +260 and +187.2 mV are ascribed to Cu^{2+} to Cu^0 through Cu^+ [29].

4. Conclusion

A potential bridging-double-chelating ligand, 5,6-diamino-1,10-phenanthroline (daphen), was used for constructing organic–inorganic compounds. Under the experimental conditions it exhibits bidentate-chelating coordination. Chelating coordination of daphen limits linkage of Cu^{2+} along six directions and, therefore, Cu^{2+} only acts as a μ_2-bridging site. Polyoxoanion is tetradentate and a hydrogen bond acceptor. Hydrothermal conditions are required for the formation of the covalent bond between oxygen and Cu in constructing the 2-D layer structure of **1**. Compound **1** represents the first example of a POM-based hybrid compound that contains daphen and a 2-D covalent-bonded layer.

Supplementary materials

Crystallographic data have been deposited with the Cambridge Crystallographic Center with a CCDC reference number of 691894 for **1**. Copy of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK; Fax: +44123336033; E-mail: deposit@ccdc.cam.ac.uk. Supplementary materials include figures and tables.

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