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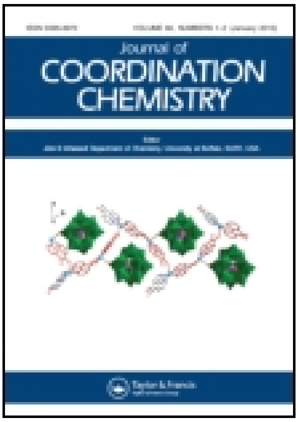

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Effect of the central metal on coordination of 1,10-phenanthroline-5,6-dione in Keggin-based hybrid compounds

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Effect of the central metal on coordination of 1,10-phenanthroline-5,6-dione in Keggin-based hybrid compounds

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Two new Keggin-based hybrid compounds, $[Cu_2(pdon)_3][PMo^{VI}{}_{11}Mo^{V}O_{40}]\cdot 3H_2O$ (**1**) and $[Mn_2Cl(H_2O)_2(pdon)_4][PMo_{12}O_{40}]\cdot 2H_2O$ (**2**) (pdon = 1, 10-phenanthroline-5,6-dione) (pdon), were synthesized under hydrothermal conditions. By using different metal ions and tuning the ratio of metal to ligand, pdon shows different coordination modes. In compound **1**, pdon with three kinds of coordination modes link Cu^{II} ions to form a 1D wave chain and Keggin-type polyanions $[PMo^{VI}{}_{11}Mo^{V}O_{40}]^{4-}$ fringe this 1D chain; hydrogen bonding interactions extend these 1D chains into a 2D supramolecular network. Compound **2** exhibits a discrete structure, in which pdon shows a single chelating coordination. Electrochemical properties of the title compounds have been investigated.

Keywords: Keggin polyoxometalate; 1,10-Phenanthroline-5,6-dione; Coordination modes; Electrochemical property

1. Introduction

Applications in gas storage, catalysis, medicine, *etc*. led to studies of inorganic–organic hybrid materials based on polyoxometalates (POMs) [1–3]. Modification of POMs by transition-metal complexes is the most effective approach to fabricate such materials [4–9]. Various 1D, 2D and 3D POM-based hybrid materials have been reported [10–15]. However, assembly is complicated and affected by subtle changes, such as reactants, pH, and reaction time [16, 17]. Thus, exploring self-assembly of POM-based hybrid materials is challenging. For examples, Tian *et al*. have investigated the effect of central-metal ion oxidation state on Keggin-based topological structures and Wei's group has studied the relationship between H-bonding and conductivity of POM-based hybrids [18, 19]. Among these influencing factors, tuning coordination modes of organonitrogen ligands is also an important question. In this work, we tune the central metal and metal-to-ligand ratios to achieve different ligand coordination and whether the whole structure would be affected. In previous reports, POM-based hybrid compounds based on 1,10-phenanthroline (phen) have been obtained [20–22]. These examples show that phen is a good candidate for construction of POM-based hybrid

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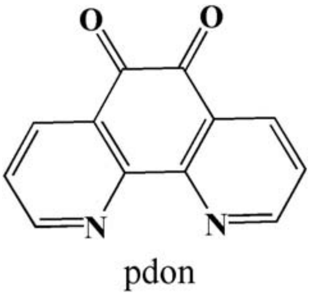

Chart 1. The pdon used in this article.

compounds. However, the two nitrogens of phen usually chelate one metal ion with a single coordination mode. Thus, in this work, we chose a phen derivative 1,10-phenanthroline-5,6-dione (pdon) as an organic moiety, which has more potential coordination sites, two N and two O donors (Chart 1), and may show various coordination modes. pdon as an organic ligand in POM-based systems has not been reported.

By changing the central metal and ratio of metal ions to ligand, we obtained two new Keggin-based hybrid compounds, $[Cu_2(pdon)_3][PMo^{VI}_{11}Mo^{V}O_{40}]\cdot 3H_2O$ (**1**) and $[Mn_2Cl(H_2O)_2(pdon)_4][PMo_{12}O_{40}]\cdot 2H_2O$ (**2**), in which pdon shows different coordination modes. Electrochemical properties of the title compounds are also reported.

2. Experimental

2.1. *Materials and general procedures*

All chemicals were reagent grade and used without purification. The pdon was synthesized according to the literature method [23]. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra (KBr pellets) were recorded on a Magna FT-IR 560 spectrometer. Thermogravimetric analyses (TGA) were carried out on a Pyris Diamond instrument in flowing N_2 with a heating rate of $10\,^{\circ}C\cdot min^{-1}$. A CHI 440 electrochemical workstation connected to a Digital-586 personal computer was used for control of the electrochemical measurement and data collection. A conventional three-electrode system was used with saturated calomel electrode as the reference electrode and a platinum wire as the counter electrode. The compounds chemically bulk-modified carbon paste electrodes (CPEs) were used as the working electrodes.

2.2. *Preparation of the title compounds*

2.2.1. Synthesis of $[Cu_2(pdon)_3][PMo^{VI}_{11}Mo^{V}O_{40}]\cdot 3H_2O$ (1). $Cu(OAc)_2\cdot H_2O$ (0.12 g, 0.60 mmol), $H_3PMo_{12}O_{40}\cdot 36H_2O$ (0.20 g, 0.08 mmol), and pdon (0.042 g, 0.20 mmol) were dissolved in 10 mL of distilled water. The pH of the mixture was adjusted with 1 M HCl solution to 3.0 and then sealed into a 20 mL Teflon-lined autoclave. After heating for 3 days at 160 °C, the reactor was slowly cooled to room temperature. Block dark green crystals of compound **1** were obtained in 39% yield (based on Mo). Elemental analysis (%) calculated for $C_{36}H_{24}Cu_2Mo_{12}N_6O_{49}P$: C, 16.40; H, 0.91; N, 3.19. Found: C, 16.43;

H, 0.89; N, 3.13. IR data (KBr pellet, cm^{-1}): 3416(s), 3234(m), 2326(s), 1618(s), 1398 (w), 1516(m), 1063(w), 961(w), 797(w), 611(s).

2.2.2. Synthesis of $[Mn_2Cl(H_2O)_2(pdon)_4][PMo_{12}O_{40}]\cdot 2H_2O$ (2). Compound **2** was prepared similarly to compound **1**, but $Mn(OAc)_2\cdot 4H_2O$ (0.049 g, 0.20 mmol) was used instead of $Cu(OAc)_2\cdot H_2O$. The pH was adjusted to 3.5 with 1 M HCl. Reddish block crystals of compound **2** were obtained in 40% yield (based on Mo). Elemental analysis (%) calculated for $C_{48}H_{32}ClMn_2Mo_{12}N_8O_{52}P$: C, 20.35; H, 1.13; N, 3.96. Found: C, 20.33; H, 1.07; N, 3.91. IR data (KBr pellet, cm^{-1}): 3418(s), 2995(m), 2359(s), 1638(s), 1576(w), 1065(w), 959(s), 799(s), 734(m).

2.2.3. Preparation of 2-CPE. The compound **2** bulk-modified carbon paste electrode (**2**-CPE) was fabricated as follows: about 0.03 g of compound **2** and 0.5 g of graphite powder were mixed and ground together by an agate mortar and pestle to achieve a uniform mixture, and then 0.18 mL of Nujol was added with stirring. The homogenized mixture was packed into a glass tube with a 3 mm inner diameter and the tube surface was wiped with weighing paper. Electrical contact was established with a copper rod through the back of the electrode.

2.2.4. X-ray crystallographic study. The crystal data for compounds **1** and **2** were collected on a Bruker Smart 1000 CCD diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å for compound **1**, $\lambda = 0.71069$ Å for compound **2**) by ω and θ scan mode at room temperature. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using the *SHELXL* package [24, 25]. All nonhydrogen atoms were refined anisotropically. Positions of hydrogens on carbons were calculated theoretically. The crystal data and structure refinements for the title compounds are summarized in table 1. Selected bond distances and angles for compounds **1** and **2** are listed in table S1 (Supplementary material). The Cambridge Crystallographic Data Center reference numbers are 885,853 (**1**) and 885,854 (**2**).

Table 1. The crystal and structure refinement data for compounds **1** and **2**.

	1	**2**
Chemical formula	$C_{36}H_{24}Cu_2Mo_{12}N_6O_{49}P$	$C_{48}H_{32}ClMn_2Mo_{12}N_8O_{52}P$
Formula weight	2633.91	2830.33
Temperature (K)	296(2)	293(2)
Wavelength (Å)	0.71073	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	*P21/c*	*P21/c*
a	15.261(2)	12.446(5)
b	22.628(3)	18.373(5)
c	22.392(3)	20.194(5)
β	127.579(7)	126.602(15)
Volume (Å^3)	6128.1(14)	3707(2)
Calculated density (Mg m^{-3}), Z	2.848, 4	2.573, 2
Independent reflection	10,694 [*R*(int) = 0.0887]	6517 [*R*(int) = 0.0486]
Goodness-of-fit on F^2	0.991	1.010
Final *R* indices [$I > 2$sigma (I)]^a	$R_1 = 0.0488$, $wR_2 = 0.0973$	$R_1 = 0.0395$, $wR_2 = 0.0800$
R indices (all data)^b	$R_1 = 0.1481$, $wR_2 = 0.1362$	$R_1 = 0.0656$, $wR_2 = 0.0867$

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

3. Results and discussion

3.1. *Structure description*

Single crystal X-ray diffraction analysis reveals that the asymmetric unit of compound **1** contains one $[PMo^{VI}_{11}Mo^{V}O_{40}]^{4-}$ (abbreviated to PMo_{12}), two crystallographically independent Cu^{II} ions, and three pdon (see figure 1). Valence sum calculations [26] show that the oxidation state of one Mo is reduced to +V and all the Cu ions are + II. In compound **1**, the Cu1 is distorted tetragonal pyramidal geometry, coordinated by two nitrogens from one pdon, two oxygens from another pdon, and one oxygen from one PMo_{12}. Cu2 exhibits a similar five-coordination with four nitrogens from two pdon and one oxygen from another pdon. The bond distances around Cu^{II} ions are 1.958(1)–2.059(1) Å for Cu–N and 1.917(9)–2.419(8) Å for Cu–O.

The pdon shows three different coordination modes in compound **1** (figure S1): (a) it only provides two nitrogens to chelate one Cu2; (b) it chelates one Cu1 with two nitrogens and an oxygen to link to Cu2; and (c) two nitrogens and two oxygens chelate Cu1 and Cu2 with all the potential coordination sites of pdon used. Besides the common chelating mode, pdon also shows single-oxygen and two-oxygen coordination modes, but very rare. The b- and c-type pdon molecules connect with Cu1 and Cu2 to form a wave-like metal-organic chain with the a-type pdon molecules pending. The Keggin-type polyanions PMo_{12} fringe the 1D chain through linking Cu1 ions (figure 2). Hydrogen bonding interactions in **1** (C11–H11A···O12 3.1813 Å, C13–H13A···O29 3.0932 Å) extend these 1D chains into a 2D supramolecular layer (figure 3).

Single crystal X-ray diffraction analysis reveals that the asymmetric unit of compound **2** contains a binuclear subunit $[Mn_2Cl(H_2O)_2(pdon)_4]^{3+}$, one PMo_{12}, and two lattice waters (see figure 4). In $[Mn_2Cl(H_2O)_2(pdon)_4]^{3+}$ (figure S2), there is one crystallographically independent manganese adopting octahedral coordination by four nitogens from two pdon, one water and one μ_2-Cl^-. The Mn–N distances are 2.248(6)–2.264(6) Å and the bond angles of N–Mn–N are 73.2(2)–172.2(2)°. In the binuclear subunit, pdon shows a single chelating coordination. As shown in figure 5, the binuclear metal-organic subunits pack to form a 1D channel along the *a* axis. The channel is occupied by nanosized PMo_{12}. Furthermore, the existence of discrete waters may enhance the stability of the whole structure by offering abundant hydrogen bonding interactions (C2–H2A···O5 3.1082 Å, C8–H8A···O20 3.0104 Å and C4–H4A···O11 3.1573 Å).

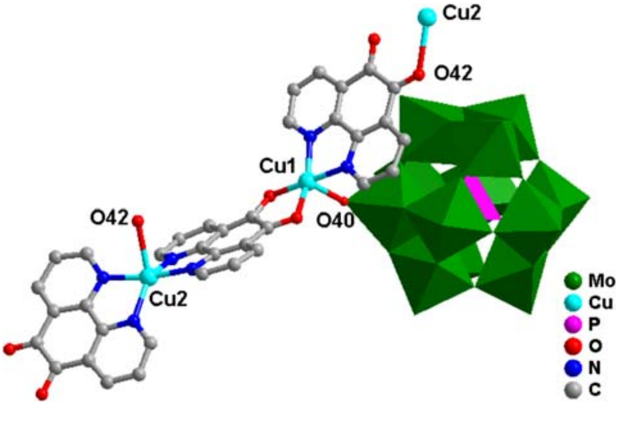

Figure 1. The asymmetric unit of compound **1** (all hydrogens and lattice waters are omitted for clarity).

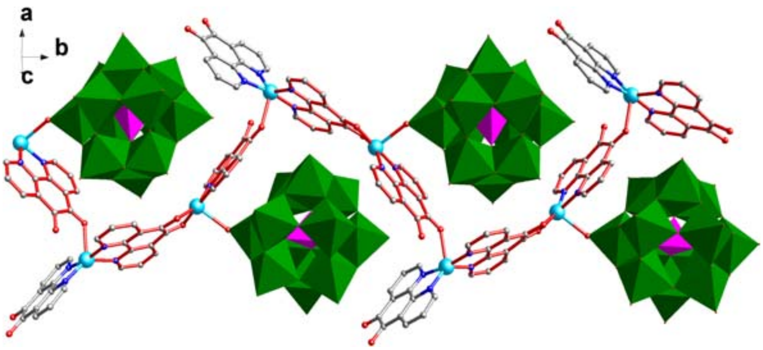

Figure 2. The 1D chain in compound **1**. Red: the b- and c-type pdon.

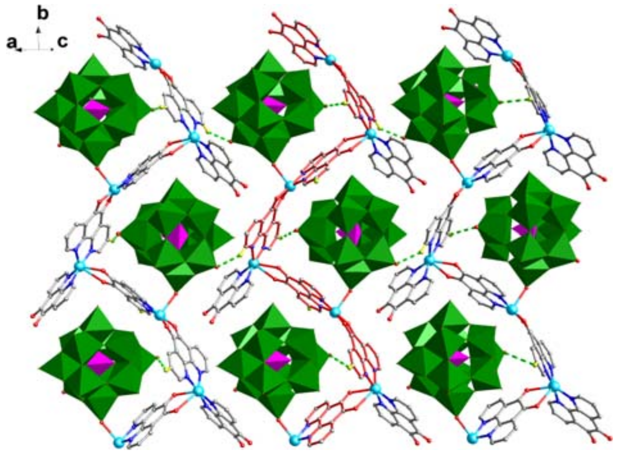

Figure 3. The 2D supramolecular network in compound **1**. Green-dotted line: hydrogen bonding interactions.

As described above, when $Cu(OAc)_2 \cdot H_2O$ was used as the central metal and the ratio of metal to ligand set to 3 : 1 in the synthesis of compound **1**, pdon shows three different coordination modes in which some oxygens from carbonyl coordinate with Cu^{II}. As a result, a 1D chain structure was obtained. Unfortunately, at the same metal-to-ligand ratio, no crystal was obtained by changing the central metal ion under the above conditions. When $Mn(OAc)_2 \cdot 4H_2O$ was employed and the ratio of metal to ligand is 1 : 1, the pdon only exhibits a single chelating coordination mode and a discrete structure was constructed. Using the same metal ion, no crystal was obtained by tuning metal-to-ligand ratio. Thus, we speculate that the central metal ions and ratio of M/L has a synergetic influence on coordination modes of pdon in the title compounds and affect the structures.

3.2. *TGA*

TGA were performed under N_2 with a heating rate of 10 °C min^{-1} from 25–750 °C, as shown in figure S3. There are two obvious weight loss steps in both compounds, ascribed

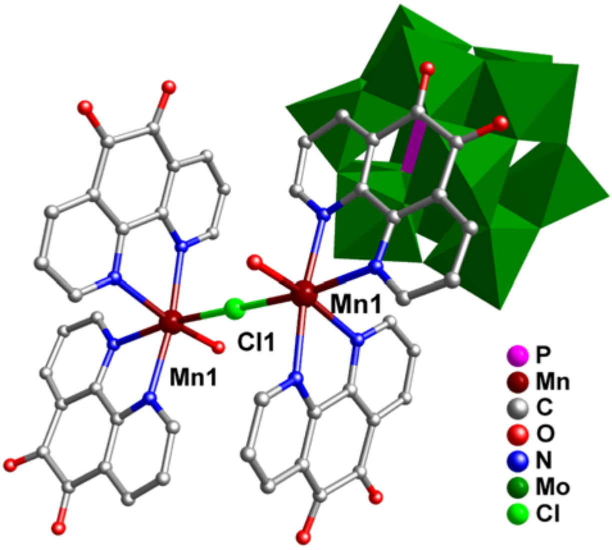

Figure 4. The asymmetric unit of compound **2** (all hydrogens and lattice waters are omitted for clarity).

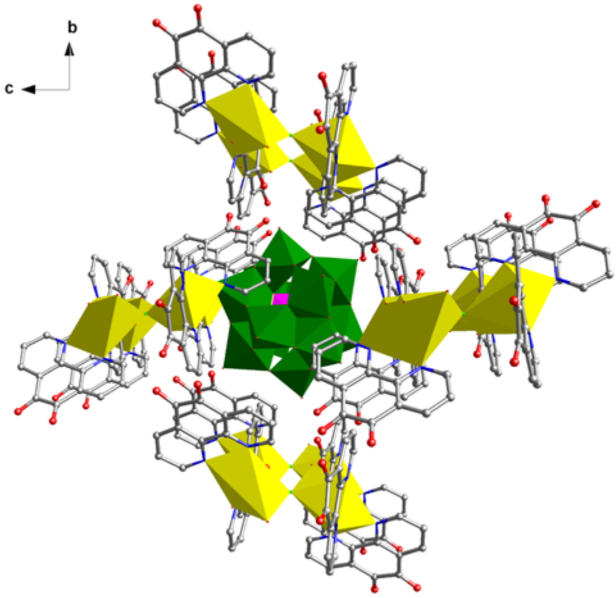

Figure 5. The 3D packing diagram along the *a* axis of compound **2**.

to loss of water and organic ligands, respectively, between 50–120 °C of 2.28% (calcd. 2.05%) and 415–570 °C of 24.01% (calcd. 23.91%) for compound **1**, while between 60–130 °C of 2.41% (calcd. 2.54%) and 390–560 °C of 30.01% (calcd. 29.67%) for compound **2**.

3.3. *Electrochemical behavior of 2-CPE in aqueous electrolyte*

The ability of POMs to undergo reversible multi-electron redox processes makes them attractive for electrocatalytic research [27]. To study the redox properties of compounds **1** and **2**, bulk-modified CPEs were fabricated as the working electrode owing to the insolubility in water and poor solubility in common organic solvents of these POM-based hybrids prepared under hydrothermal reactions. The redox properties were investigated in 0.1 M H_2SO_4 aqueous solution. Considering that there are only some slight potential shifts of the redox peaks between compounds **1** and **2**, **2**-CPE has been taken as an example of their electrochemical properties.

Figure 6 shows the cyclic voltammetric behavior of **2**-CPE in a 0.1 M H_2SO_4 aqueous solution. There are three reversible redox peaks from +760 to −120 mV, attributable to PMo_{12} [28]. The mean peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ are +366, +203 and −38 mV (scan rate: 200 mV s^{-1}). As can be seen from figure S4, with increasing scan rates, the cathodic peak potentials shift to the negative direction and the corresponding anodic peak potentials shift to the positive direction. The peak currents are proportional to the scan rates indicating that the redox process of **2-**CPE is surface controlled.

Direct electroreduction of nitrite requires a large overpotential at most electrode surfaces [29]. Therefore, no obvious response is observed at a bare CPE. However, **2**–CPE displays good electrocatalytic activity toward the reduction of nitrite in 0.1 M H_2SO_4 aqueous solution in the potential range from +760 to −120 mV. As shown in figure 7, with the addition of nitrite, all the reduction peak currents increase markedly while the corresponding oxidation peak currents decrease, suggesting that the reduction of nitrite is mediated by reduced PMo_{12} in **2**.

4. Conclusion

Two new Keggin-type polyanion complexes have been obtained by using pdon under hydrothermal conditions. In compound **1,** pdon exhibits three coordination modes by using two nitrogens and two oxygen donors. Compound **1** shows a 1D chain fringed by PMo_{12}.

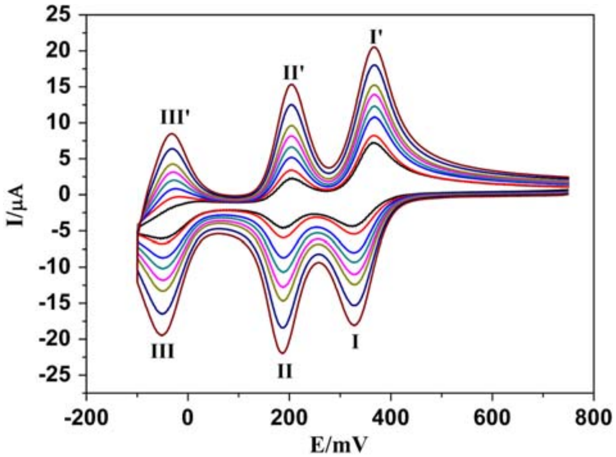

Figure 6. Cyclic voltammograms of **2**-CPE in a 0.1 M H_2SO_4 aqueous solution at different scan rates (from inner to outer: 180, 200, 250, 300, 350, 400, 450, and 500 mV s^{-1}).

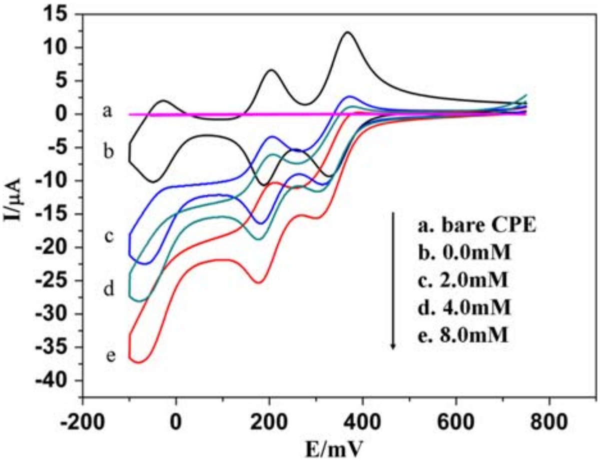

Figure 7. Cyclic voltammograms of **2**-CPE in 0.1 M H_2SO_4 aqueous solution containing 0.0–8.0 mM KNO_2 and a bare CPE in a 4.0 mM $KNO_2 + 0.1$ M H_2SO_4 solution.
Scan rate: 200 mV s^{-1}.

The pdon in compound **2** exhibits a single chelating coordination mode by using only two nitrogens. Compound **2** shows a discrete structure containing a binuclear subunit $[Mn_2Cl(H_2O)_2(pdon)_4]^{3+}$. Owing to the difference of central metal ions and M/L ratio in compounds **1** and **2**, pdon shows different coordination and distinct structures of compounds **1** and **2**. This work indicates that central metal and ratio plays an important and synergetic role in construction of different POM-based hybrid compounds. Further study on self-assembly processes is underway.

Supplementary material

Table of selected bond lengths and angles, structure figures, TG and CV curves for the title compounds.

Acknowledgments

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