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Unprecedented $^1/_\infty[\beta\text{-}Mo_8O_{26}]^{4-}$ polymeric chains and four novel organic–inorganic hybrids based on Mo–POMs and azaheterocycles templates

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ABSTRACT

Four novel organic–inorganic hybrid materials based on Mo–POMs and organic templates, namely [DEB] $[\beta\text{-}Mo_8O_{26}]$ $[NH_4]_2$ (1), [BMIM] $[\beta\text{-}Mo_8O_{26}]_{0.5}\cdot H_2O$ (2), [BMIM] $[1D\text{-}Mo_8O_{26}]_{0.5}$ (3) and $\{3D\text{-}[Cu(DIE)_2]$ $[1D\text{-}Mo_8O_{26}]_{0.5}\}_\infty$ (4) [DEB= 1,1′-diethyl-4,4′-bipyridinium, BMIM=1,1′-bis(1-methylimidazolium)methylene, DIE=1,2-diimidazoloethane] have been hydrothermally synthesized and characterized by elemental analyses, IR spectroscopy, thermal gravimetric analysis(TGA) and single-crystal X-ray diffraction. Both compounds 1 and 2 are POMs-based supramolecular compounds consisted of independent $[\beta\text{-}Mo_8O_{26}]^{4-}$ anions and $[DEB]^{2+}$ or $[BMIM]^{2+}$ organic cations. Compound 3 is the first external template example of Mo–POMs-based supramolecular network incorporated with novel $^1/_\infty[\beta\text{-}Mo_8O_{26}]^{4-}$ polymeric chains. Compound 4 is a rare supramolecular structure that contains octamolybdate $^1/_\infty[\beta\text{-}Mo_8O_{26}]^{4-}$ polymeric chains interconnected via DIE ligands to form a 3D net. Moreover, it was indicated that these polyacid compounds had definite catalytic activities on the probe reaction of acetaldehyde oxidation to acetic acid with H_2O_2.

1. Introduction

The intelligent choice of inorganic and organic building blocks to yield organic–inorganic hybrid compounds had attracted considerable interest for the purpose of creating functional polymeric materials that endow both advantages of inorganic and organic entities [1]. In recent years, the rational design and assembly of organic–inorganic hybrid materials based on polyoxometalates (POM) building blocks is of great interest, not only in terms of structural diversity but also because of potential applications for catalysis, gas-sorption, magnetism, electrical conductivity, photochemistry [2–5]. Polyoxometalates (POMs), as one kind of significant metal oxide clusters with nanosizes and abundant topologies had been employed as inorganic building blocks for the construction of supramolecular arrays with various organic components [6,7]. Octamolybdates(Mo_8) are a subclass of the POM family and have been extensively studied due to their diverse structures and intriguing properties. To date, eight isomeric forms of octamolybdates have been prepared, that is, the α-, β-, γ-, δ-, ε-, ζ-, η-, and θ-isomers [8–10]. In addition, materials based on $^1/_\infty[Mo_8O_{26}]^{4-}$ polymeric chains had been observed in some literature due to their diverse structures and intriguing properties [11,12]. Many research efforts have been focused on the assembly of polyoxometalates with transition metal-organic units or organoammonium cations (OACs) as organic templates with the structure-directing and charge-compensating functions to form extended metal-organic hybrid materials [13–15]. Most significantly, the structural information from the organic template can be imprinted on the final supramolecular frameworks [16]. The term template effect was first used and defined at the beginning of the sixties and a template is described as temporary or external if it is not incorporated into the end product [17a]. Recently we found that the temporary template can induce the formation of novel architectures in the cases of Mo (W)/Cu/S heterothiometallic polymeric clusters [17b].

Based on the above facts, our current goal is to clearly identify the template effect of the transition metal ions, OACs, or organic ligand on the composition and the architecture of hybrid materials. And fortunately, in this paper we chose OACs $[DEB]\cdot Br_2$ [DEB=1,1′-diethyl-4,4′-bipyridinium] and $[BMIM]\cdot Cl_2$ [BMIM=1,1′-bis(1-methylimidazolium)methylene] as templates to reacted with ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ under hydrothermal conditions to assemble two new POMs-based supramolecular compounds [DEB] $[\beta\text{-}Mo_8O_{26}]$ $[NH_4]_2$ **1** and compound [BMIM] $[\beta\text{-}Mo_8O_{26}]_{0.5}\cdot H_2O$ **2**, respectively. Based on the above mentioned experimental conditions of compound **2**, organic ligand succinic acid $(CH_2COOH)_2$ was chosen to react on $[BMIM]Cl_2$ and ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ under hydrothermal conditions to form a new 1D Mo–POMs-based supramolecular network [BMIM] $[1D\text{-}Mo_8O_{26}]_{0.5}$ **3,**

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which incorporated with the first example of $^1/_\infty[\beta\text{-}Mo_8O_{26}]^{4-}$ polymeric chains. It is interesting that compound **3** was different from compound **2** on composition and architecture due to the external template effect of succinic acid [SAD, $(CH_2COOH)_2$]. And then we also chose transition metal complex units from copper chloride $CuCl_2\cdot 2H_2O$ and organic ligand 1,2-diimidazoloethane(DIE) as templates reacted on ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ under hydrothermal conditions to assemble a novel 3D Mo–POMs-based coordination polymer $\{[Cu(DIE)_2](\beta\text{-}Mo_8O_{26})_{0.5}\}_\infty$ **4**, which also contained the rare octamolybdate $^1/_\infty[\beta\text{-}Mo_8O_{26}]^{4-}$ one-dimensional(1D) chain.

2. Experimental

2.1. Materials and methods

The dication $[DEB]^{2+}$ was prepared as the bromide salt by alkylation of 4,4′-dipyridine with 1-bromoethane (acetonitrile served as the solvent) [18]. The dication $[BMIM]^{2+}$ was prepared as the chloride salt by direct alkylation of 1-methylimidazole with dichloromethane (PEG 400 served as the solvent) [19]. 1,2-diimidazoloethane (DIE) were prepared according to the literature method [20]. Other chemicals were of reagent grade and used as purchased without further purification. The IR spectrum was recorded on a Shimazu IR435 spectrometer as KBr disk (4000–400 cm^{-1}). Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. The purity of the bulk microcrystalline materials obtained from the syntheses was checked by Powder X-ray diffraction analyses. XRPD patterns were recorded using Cu $K_\alpha 1$ radiation on a PAN analytical X'Pert PRO diffractometer. A model NETZSCHTG209 thermal analyzer was used to record simultaneous TG, DTG curves in flowing air atmosphere of 20 mL min^{-1} at a heating rate of 5 °C min^{-1} in the temperature range 0–800 °C using platinum crucibles.

2.2. Synthesis

[DEB] [β-Mo_8O_{26}] [NH_4]$_2$ (1). A mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.062 g, 0.05 mmol), $[DEB]\cdot Br_2$(0.037 g, 0.10 mmol) and H_2O(10 mL) was stirred at room temperature until it was homogeneous, and adjusted by CH_3COOH to pH=3.0–3.5. Then the mixture was sealed in an 18 mL Teflon-lined stainless steel container, which was heated to 165 °C under autogenously pressure for 4d. After slow cooling to room temperature with the rate 10 °C h^{-1}, the resulting white bulk crystals of **1** were formed. The product is not soluble in common solvents. Yield: 58%. IR (KBr, cm^{-1}): 3067(s), 1643(m), 1563(w), 1507(w), 1401(s), 1227(w), 1179(w), 946(m), 898(s), 820(m), 779(m), 664(m), 560(w).

[BMIM] [β-Mo_8O_{26}]$_{0.5}\cdot H_2O$ (2). A mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.124 g, 0.10 mmol), $[BMIM]\cdot Cl_2$(0.05 g, 0.20 mmol) and H_2O(10 mL) was stirred at room temperature until it was homogeneous, and adjusted by CH_3COOH to pH=3.0–3.5. Then the mixture was sealed in a 18 mL Teflon-lined stainless steel container, which was heated to 150 °C under autogenously pressure for 4d. After slow cooling to room temperature with the rate 10 °C h^{-1}, the resulting colorless bulk crystals of **2** were formed. The product is not soluble in common solvents. Yield: 50%. IR (KBr, cm^{-1}): 3471(s), 3100(s), 1654(m), 1618(m), 1581(m), 1547(m), 1442(s), 1331(s), 1165(s), 1110(m), 944(s), 912(s), 842(s), 773(s), 663(s), 555(m), 455(s).

[BMIM] [1D-Mo_8O_{26}]$_{0.5}$(3). A mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.124 g, 0.10 mmol), $[BMIM]\cdot Cl_2$(0.050 g, 0.20 mmol), $(CH_2COOH)_2$(0.028 g, 0.20 mmol) and H_2O(10 mL) was stirred at room temperature until it was homogeneous, and adjusted by HCl to pH=3.0–3.5. Then the mixture was sealed in an 18 mL Teflon-lined stainless steel container, which was heated to 150 °C under autogenously pressure for 4d. After slow cooling to room temperature with the rate 10 °C h^{-1}, the resulting light yellow crystals of **3** were formed. The product is not soluble in common solvents. Yield: 54%. IR (KBr, cm^{-1}): 3131(s), 3077(s), 3008(s), 1719(m), 1695(m), 1611(s), 1577(s), 1547(s), 1463(s), 1427(s), 1385(s), 1333(s), 1164(s), 1085(s) 939(s), 900(s), 854(s), 755(s), 696(s). 612(s), 599(s), 457(s).

{3D-[Cu(DIE)$_2$] [1D-Mo_8O_{26}]$_{0.5}$}$_\infty$ (4). A mixture of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.062 g, 0.05 mmol), DIE(0.024 g, 0.15 mmol), $CuCl_2\cdot 2H_2O$(0.027 g, 0.15 mmol) and H_2O(10 mL) was stirred at room temperature until it was homogeneous, and adjusted by HCl to pH=4.5. Then the mixture was sealed in an 18 mL Teflon-lined

Table 1
Crystal data and structure refinement for **1–4.**

	1	2	3	4
Formula	$C_{14}H_{26}Mo_8N_4O_{26}$	$C_9H_{16}Mo_4N_4O_{14}$	$C_9H_{14}Mo_4N_4O_{13}$	$C_{12}H_{15}CuMo_4N_6O_{13}$
Formula weight	1433.91	788.08	770.00	898.60
Cryst syst	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a/(Å)	7.8318(5)	10.4630(10)	9.7842(7)	9.7574(10)
b/(Å)	10.2443(4)	10.7400(8)	10.2539(7)	10.3858(10)
c/(Å)	11.2329(5)	18.3383(13)	11.4123(8)	12.2784(12)
α/(deg)	99.156(4)	96.767(6)	112.350(7)	102.790(2)
β/(deg)	96.466(5)	99.435(7)	109.734(6)	111.648(2)
γ/(deg)	107.587(5)	98.926(7)	98.946(6)	97.361(2)
vol/(Å$^{3)}$	835.71(8)	1986.4(3)	942.25(11)	1097.19(19)
Z	1	4	2	2
D_c (g cm^{-3})	2.849	2.635	2.714	2.720
μ ($mm^{-1)}$	3.004	2.547	2.677	3.257
F(000)	682	1512	736	860
Rflns collected	13,413	13,036	7,822	7,154
Unique rflns	3414	7374	3848	4248
R_{int}	0.0255	0.0215	0.0312	0.0524
GOF	1.099	1.077	1.045	0.932
R_1[a] ($I>2\delta(I)$)	0.0180	0.0271	0.0268	0.0443
wR_2[a] (all data)	0.0452	0.0562	0.0589	0.0946
$\Delta\rho$max/$\Delta\rho$min(e Å^{-3})	0.412/−0.366	0.0467/−0.499	0.603/−0.635	0.964/−1.108

[a] $R_1=||Fo|-|Fc||/|Fo|$; $wR_2=[\ w(Fo^2-Fc^2)^2/\ w(Fo^2)^2]^{1/2}$.