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Synthesis and characterization of two new extended structures based on Anderson-type polyoxoanions

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Abstract

Two new chain-like polymers, $(C_6H_5NO_2)_2Na_2[(C_6H_5NO_2)_2NaCrMo_6H_6O_{24}]$ **1** and $(C_6H_5NO_2)_2[(H_2O)_6DyCrMo_6H_6O_{24}]\cdot 4H_2O$ **2**, have been synthesized and characterized by elemental analyses, IR, TG, and single crystal X-ray diffraction. Compound **1** is built up of $[CrMo_6H_6O_{24}]^{3-}$ cluster as the structural motif covalently linked by sodium-pyridine-3-carboxylic acid fragments to yield unprecedented one-dimensional chains, which are further in close contact forming a three-dimensional supramolecular framework via extensive hydrogen-bonding interactions among polyoxoanions, coordinated pyridine-3-carboxylic acid ligands and dissociated pyridine-3-carboxylic acid molecules. Compound **2** exhibits one-dimensional chain structure constructed from $[CrMo_6H_6O_{24}]^{3-}$ building blocks and dysprosium cations, and adjacent chains are further pillared by free pyridine-4-carboxylic acid molecules to form an unusual two-dimensional supramolecular layer via hydrogen-bonding interactions.

Keywords: Extended structures; Anderson-type polyoxoanions; Sodium-organic complexes; Dysprosium cations

1. Introduction

Polyoxometalates (POMs) [1–3], as early transition metal oxide clusters, exhibit many properties that make them attractive for applications in catalysis, separation, materials science and medicine. An intriguing area in this field is the construction of extended solid materials based on POMs building blocks and metal cations/metal-organic coordination complexes owing to the remarkable features of metal oxide surfaces and the diversities in the geometric topology [4–7]. To date, many examples of extended architectures in which well-characterized POMs, such as Keggin [8], Wells-Dawson [9], Silverton [10] and Lindquist [11] type polyoxoanions serve as the building blocks have been successfully reported. However, in contrast, the role of Anderson-type polyoxoanions as the inorganic building units to construct such extended frameworks has not been so extensively studied [12,13]. Therefore, the rational design and synthesis of extended architectures based on this kind of polyoxometalate and versatile metal ions or their coordination complexes are of intense interest and one of great challenges in current synthetic chemistry.

In comparison with a number of the polyoxoanion-based solid materials structurally modified by the d-block transition metal elements, s-block and f-block elements as the linkers have been paid much less attention in assisting the self-assembly of POMs building blocks [14,15], although their compounds may possess potential applications in many fields. Moreover, we choose the pyridine-3-carboxylic acid molecule and pyridine-4-carboxylic acid molecule as the organic components because they can act as not only hydrogen-bonding accepters and hydrogen-bonding donors, but also monodentate ligands. Hence, our current synthetic strategy is to acquire new extended compounds constructed from Anderson-type polyoxoanions with s-block and f-block ions as linkers in the presence of organic ligands.

In this paper, we report two novel chain-like arrays based on Anderson-type polyoxoanions, $(C_6H_5NO_2)_2Na_2[(C_6H_5\ NO_2)_2NaCrMo_6H_6O_{24}]$ **1** and $(C_6H_5NO_2)_2[(H_2O)_6DyCrMo_6H_6O_{24}]\cdot 4H_2O$ **2**. Compound **1** is built up of $[CrMo_6H_6O_{24}]^{3-}$ cluster as the structural motif covalently linked by sodium-pyridine-3-carboxylic acid fragments to yield unprecedented one-dimensional (1D) chains, which are further in close contact forming three-dimensional (3D)

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supramolecular networks via extensive hydrogen-bonding interactions. To the best of our knowledge, compound **1** represents the first example of one-dimensional assemblies based on Anderson-type POMs and sodium (I) coordination complexes. The structure of compound **2** is constructed from linking of the $[CrMo_6H_6O_{24}]^{3-}$ clusters and dysprosium cations into zigzag chains.

2. Experimental section

2.1. Materials and methods

All chemicals were commercially purchased and used without further purification. $Na_3[CrMo_6H_6O_{24}]\cdot 8H_2O$ was synthesized according to the literature [16] and characterized by IR spectrum and TG analysis. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer; Cr, Mo, Na and Dy were analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FT/IR Spectrophotometer using KBr pellets. TG analyses were performed on a Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}.

2.2. Syntheses

2.2.1. $(C_6H_5NO_2)_2Na_2[(C_6H_5NO_2)_2NaCrMo_6H_6O_{24}]$ 1

Pyridine-3-carboxylic acid (0.246 g, 2 mmol) and $NaClO_4\cdot H_2O$ (0.140 g, 1 mmol) were orderly added to the 50 mL water solution of $Na_3[CrMo_6H_6O_{24}]\cdot 8H_2O$ (1.230 g, 1 mmol). The mixture was refluxed for 1 h at 80 °C. The filtrate was kept for one month at ambient conditions, then purple block crystals of compound **1** were isolated in about 20% yield (based on Mo). Anal. Calcd for **1**: Cr, 3.29; Mo, 36.45; Na, 4.37; C, 18.24; N, 3.55; H, 1.65 (%). Found: Cr, 3.46; Mo, 36.19; Na, 4.21; C, 18.43; N, 3.78; H, 1.77 (%). FTIR data (cm^{-1}): 3497(w), 3423(w), 3137(m), 3103(m), 3051(m), 1910(w), 1715(m), 1631(m), 1601(m), 1563(m), 1459(w), 1420(w), 1392(s), 1275(m), 1107(w), 995(w), 926(s), 894(vs), 823(w), 822(w), 759(w), 735(w), 689(m), 643(vs), 620(s), 541(m) and 418(m).

2.2.2. $(C_6H_5NO_2)_2[(H_2O)_6DyCrMo_6H_6O_{24}]\cdot 4H_2O$ 2

Pyridine-4-carboxylic acid (0.246 g, 2 mmol) and $Dy(ClO_4)_3$ (0.411 g, 1 mmol) were orderly added to the 50 mL water solution of $Na_3[CrMo_6H_6O_{24}]\cdot 8H_2O$ (1.230 g, 1 mmol). The filtrate was kept for three weeks at ambient conditions, then purple block crystals of compound **2** were isolated in about 35% yield (based on Dy). Anal. Calcd for **2**: Cr, 3.24; Mo, 35.83; Dy, 10.11; C, 8.96; N, 1.74; H, 2.24 (%). Found: Cr, 3.44; Mo, 35.90; Dy, 9.82; C 8.79; N, 1.85; H, 2.42 (%). FTIR data (cm^{-1}): 3324(s), 3097 (s), 2090(w), 2008(w), 1641(w), 1621(m), 1567(m), 1515(w), 1394(s), 1262(w), 1148(w), 1060(w), 1010(w), 945(s), 918(vs), 895(s), 832(w), 775(w), 647(vs), 537(m) and 411(m).

Table 1
Crystal data and structure refinement for **1** and **2**

Complex	**1**	**2**
Chemical formula	$C_{24}H_{26}CrMo_6N_4Na_3O_{32}$	$C_{12}H_{36}CrDyMo_6N_2O_{38}$
Formula weight	1579.10	1606.57
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a (Å)	22.045(4)	18.276(4)
b (Å)	9.4640(19)	12.549(3)
c (Å)	21.088(4)	17.822(4)
β (°)	98.56(3)	103.90(3)
V ($Å^3$)	4350.9(15)	3967.7(14)
Z	4	4
Dc (g/cm^3)	2.411	2.689
μ (mm^{-1})	2.054	4.074
R_{int}	0.0410	0.0400
GOF on F^2	1.007	1.096
$R1^a$	0.0487	0.0516
w$R2^b$	0.1293	0.1000
$R1$ (all data)	0.0692	0.0726
$wR2$ (all data)	0.1400	0.1069

[a] $R_1 = \Sigma||F_0| - |F_C||/\Sigma|F_0|$.
[b] $wR_2 = \sum[w(F_0^2 - F_C^2)^2]/\sum[w(F_0^2)^2]^{1/2}$.

2.3. X-ray crystallography

A purple single crystal of **1** with dimensions of 0.25×0.20×0.11 mm was fixed to the end of a glass capillary. The data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα ($\lambda=0.71073$ Å) at 293 K in the range of $2.35<\theta<27.47°$. Empirical absorption correction was applied. A total of 9222 (4972 unique, $R_{int}=0.0410$) reflections were measured ($-28\leq h\leq 28$, $-12\leq k\leq 12$, $-27\leq l\leq 27$). A purple single crystal of **2** with dimensions of 0.11×0.10×0.08 mm was fixed to the end of a glass capillary. The data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα ($\lambda=0.71073$ Å) at 293 K in the range of $2.17<\theta<27.48°$. Empirical absorption correction was applied. A total of

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Mo(1)–O(4)	1.913(4)	Mo(2)–O(10)	1.712(4)
Mo(1)–O(1)	2.267(4)	Cr(1)–O(1)	1.964(4)
Mo(1)–O(7)	1.716(4)	Cr(1)–O(2)	1.982(4)
Mo(1)–O(2)	2.328(4)	Cr(1)–O(3)	1.987(4)
Mo(3)–O(12)	1.703(5)	Na(1)–O(7)	2.531(4)
Mo(3)–O(11)	1.719(5)	Na(1)–O(11)#1	2.382(6)
Mo(3)–O(6)	1.963(4)	Na(1)–O(13)	2.476(6)
O(1)–Cr(1)–O(1)#1	180.0(2)	O(1)#1–Cr(1)–O(3)#1	96.92(17)
O(1)–Cr(1)–O(3)#1	83.08(17)	O(8)–Mo(1)–O(1)	161.8(2)
O(11)#1–Na(1)–O(7)	80.49(16)	O(4)–Mo(1)–O(1)	73.42(16)
O(7)–Na(1)–O(7)#3	154.3(3)	O(8)–Mo(1)–O(4)	97.5(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y+2$, $-z$ #3 $-x$, y, $-z+1/2$.