

Rapid Communication

Self-assembly of polyoxometalate clusters into a 3-D heterometallic framework via covalent bonding: synthesis, structure and characterization of $\text{Na}_4[\text{Nd}_8(\text{dipic})_{12}(\text{H}_2\text{O})_9][\text{Mo}_8\text{O}_{26}] \cdot 8\text{H}_2\text{O}$

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Abstract

An unprecedented hybrid solid obtained by self-assembly of octamolybdate clusters into a three-dimensional alkali metal modified neodymium-organic heterometallic framework is described. Crystal data: monoclinic, space group $P2_1/n$, $a = 21.868(4) \text{ \AA}$, $b = 13.039(3) \text{ \AA}$, $c = 22.479(5) \text{ \AA}$, $\beta = 98.90(3)^\circ$; $V = 6332(2) \text{ \AA}^3$; $Z = 2$, $R(\text{final}) = 0.0474$. The data were collected on a Rigaku R-AXIS RAPID IP diffractometer at 293 K using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) and oscillation scans technique in the range of $1.98^\circ < \theta < 27.48^\circ$.

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1. Introduction

Crystal engineering of inorganic-organic hybrid materials is realizable by, the so-called “building-block” concept, self-assembly of polyoxometalate (POM) [1] clusters into multi-dimensional network structures [2–8]. These solid-state materials have captured considerable research attention because of their distinctive topological structures and versatile applications in given fields, especially in the area of catalysis and intercalation chemistry [9,10]. Most research contributions have been done by Zubieta and co-workers through designed assembly of molybdenum oxide clusters into transition metal coordination networks [4–5,8]. However, hybrid solid materials based on $4f$ metal-organic frameworks and polymolybdate building blocks, which are expected to be of notable uses as luminescent probes, NMR shift agents, and magnetic resonance imaging agent [11–14], are still awfully rare [15,16]. Even though, the numbered

reported examples only possess supramolecular or one-dimensional architectures, and few of them were found to have high-dimensional (two- [15] or three-dimensional) structures on the basis of rational design, which are supposed to be topologically and functionally interesting. In fact, the successful isolation of hybrid rare-earth-POM-based (REPB) solids still remains a synthetic challenge not only because of the difficulties in controlling the synergistic interactions between organic and inorganic chemical compositions [17,18], but also in exploring appropriate POM building blocks and lanthanide complex linkages. Our current research aim is the creative synthesis of the desired novel REPB solids by solving these exigent problems below concerned with the design of high-dimensional REPB materials: (a) the variable and large coordination numbers of $4f$ metals make it less predictable to design rational lanthanide complexes or polymers to construct target REPB products; (b) low stereochemical preferences of $4f$ metals limit their selective linkage with POM building blocks; (c) the ratio between coordination numbers and volume of the organic components, which directly affect the

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extension of polymeric structures, along with their coordination fashions are key factors for the integration of lanthanide-organic units and POM moieties; and (d) an advanced view of charge balance is also necessary.

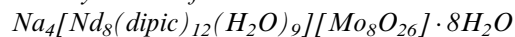
On the basis of the aforementioned points, a noticeable multi-dentate ligand, pyridine-2,6-dicarboxylic anion (dipic²⁻), which has recently shown interesting properties in constructing extended structures with 4f metals [19,20], seized our attention. It possesses relatively high coordination numbers, small volume, and versatile coordination behavior, which can cause appreciable extra-framework volume of new porous 3-D network [19,20] fitting for accommodating POM clusters. Besides, taking into account the negative charges of dipic ligands and POM units, alkali metal salts were considered as excellent candidates because those alkali metals can be introduced into the crystal structure either as counter cations or by incorporating into the polymer skeleton to achieve charge balance. By the introduction of this distinctive polycarboxylic ligand via hydrothermal technology, we got a novel 3-D hybrid REPB solid, Na₄[Nd₈(dipic)₁₂(H₂O)₉][Mo₈O₂₆]·8H₂O **1**, which features a cationic 3-D heterometallic framework accommodating anionic octamolybdate clusters. To the best of our knowledge, this is the first example that POM clusters are integrated into a 3-D lanthanide-organic framework via covalent bonding.

2. Experimental section

2.1. General procedures

All chemicals purchased were of reagent grade and used without further purification. The hydrothermal reactions were performed in 18 ml Teflon-lined stainless steel vessels under autogenous pressure with a filling capacity of approximately 60%. Distilled water was used in the reactions. Elemental analyses (C and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. Mo and Nd were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectrum was recorded in the range 400–4000 cm⁻¹ on an Alpha Centaur FT/IR spectrophotometer using KBr pellets. TG analysis was performed on Pyres Diamond TG/DTA in flowing N₂ with a heating rate of 10 °C min⁻¹. X-ray powder diffraction (XRPD) patterns were recorded on a Siemens D5005 diffractometer with CuKα (λ = 1.5418 Å) radiation.

2.2. Synthesis of



Compound **1** was originally obtained by a typical one-pot hydrothermal reaction from the mixture of Na₂MoO₄·2H₂O, Nd₂O₃, pyridine-2,6-dicarboxylic

acid, NaCl, and H₂O with a molar ratio of 2:1:2:1:555 under autogenous pressure at 120 °C for five days. After cooling to room temperature, the colorless rod-like crystals of **1** were collected as a monophasic product (about 63% yield on Mo). Anal. Calcd for C₈₄H₇₂Mo₈N₁₂Na₄Nd₈O₉₂: C, 21.31; N, 3.55; Nd, 24.37; Mo, 16.21 (%). Found: C, 21.41; N, 2.93; Nd, 24.69; Mo, 16.47 (%). The experimental and simulated X-ray powder diffraction (XRPD) patterns (see Fig. S1) of **1** are nearly identical, indicating the phase purity of the bulk product. By plenty of parallel experiments, it was found that the reaction temperatures, and the pH values are key factors for the successful isolation of **1**. When reactions were carried out at temperatures higher or lower than 10 °C and 120 °C, or the pH values were not approximately to 3.0, we could not get the final product. However, the reaction time plays a less important role that was proven by some successful reactions with heating time between 4 and 6 d.

2.3. X-ray crystallography

The data were collected on a Rigaku R-AXIS RAPID IP diffractometer at 293 K using graphite-monochromated MoKα radiation (λ = 0.71073 Å) and oscillation scans technique in the range of 1.98° < θ < 27.48°. Empirical absorption correction was applied. A total of 20605 (13177 unique, R_{int} = 0.0629) reflections were measured. The structure was solved by direct methods using the program SHELXS-97 [21] and refined by full-matrix least-squares methods on F² using the SHELXL-97 [22] program package. All of the non-hydrogen atoms were refined anisotropically. Positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions. Structure solution and refinement based on 13177 independent reflections gave R₁ (wR₂) = 0.0474 (0.1167). A summary of the crystallographic data and structural determination for compound **1** is provided in Table 1. Selected bond lengths and angles are listed in Table 2.

3. Results and discussion

The crystal structure [23] of **1** is assembled from a sodium incorporated neodymium-organic heterometallic framework covalently attached by octamolybdate clusters (Scheme 1). The octamolybdate cluster in **1** is the well-known β-{Mo₈O₂₆}⁴⁻ cluster (Fig. 1).¹ There are four crystallographically independent neodymium sites and two unique sodium positions in the asymmetric unit. Nd(1) atom, residing in a tricapped triprismatic geometry, linking to one nitrogen donor from a dipic ligand and six carboxyl oxygen atoms, a terminal aqua ligand, and a μ₂-O atom bridged with a octamolybdate cluster. The monocapped square

antiprismatic coordination environment about the Nd(2) atom is defined by two nitrogen donors and six oxygen donors, and one μ_3 -O atom from an octamolybdate cluster. Nd(3) atom bonds to one nitrogen donor, six carboxyl oxygen donors and two aqua ligands forming a tricapped triprismatic coordination environment. The Nd(4) atom is coordinated to two nitrogen

donors, five carboxyl oxygen atoms, and two aqua ligands to finish its tricapped triprismatic coordination geometry. The two crystallographically independent sodium sites are occupied by a $\{\text{Na}(1)\text{O}_6\}$ octahedron and a $\{\text{Na}(2)\text{O}_5\}$ square pyramid. There are also six crystallographically independent dipic ligands adopting four different coordination modes (Fig. S2).

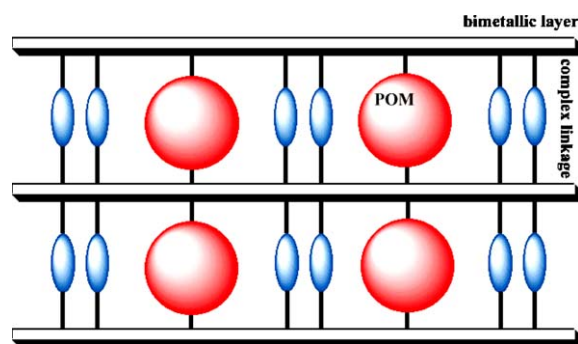
The heterometallic scaffolding can be divided into two parts, namely, the layered bimetallic subunits and the pillaring fragments. The former contain two types of “S” shaped chains constructed from alternative $\{\text{NdNO}_8\}$ and $\{\text{NaO}_6\}$ polyhedra (for one type) or $\{\text{NdNO}_8\}$ and $\{\text{NaO}_5\}$ moieties (for the other) in corner- or edge-sharing modes, which are further

Table 1
Crystal data and structure refinement for compound 1

Empirical formula	$\text{C}_{84}\text{H}_{72}\text{Mo}_8\text{N}_{12}\text{Na}_4\text{Nd}_8\text{O}_{92}$
Formula weight	4734.92
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
<i>a</i> (Å)	21.868(4)
<i>b</i> (Å)	13.039(3)
<i>c</i> (Å)	22.479(5)
β (degree)	98.90(3)
Volume (Å ³)	6332(2)
Z	2
Reflections collected	20605
Independent reflections	13177 ($R_{\text{int}} = 0.0629$)
Goodness-of-fit on F^2	1.066
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1^a = 0.0478$, $wR_2^b = 0.1247$
Indices (all data)	$R_1^a = 0.0658$, $wR_2^b = 0.1320$

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$



Scheme 1. Schematic representation of the 3-D framework of 1.

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

Na(1)–O(19)#1	2.344(6)	Na(2)–O(15)	2.370(6)
Na(1)–O(5)#1	2.429(6)	Na(2)–OW3	2.437(7)
Nd(1)–O(2)#1	2.375(5)	Nd(2)–O(5)	2.507(5)
Nd(1)–N(1)	2.596(6)	Nd(2)–N(3)	2.633(6)
Nd(1)–O(25)	2.620(5)	Nd(2)–O(30)	2.683(5)
Nd(1)–OW1	2.627(6)	Nd(2)–Na(2)#4	3.940(4)
Nd(4)–O(4)#3	2.413(5)	Nd(3)–O(13)	2.494(5)
Nd(4)–O(17)	2.521(6)	Nd(3)–O(18)#5	2.397(5)
Nd(4)–OW5A	2.577(19)	Nd(3)–N(4)	2.560(6)
Nd(4)–N(6)	2.597(7)	Nd(3)–OW2	2.668(15)
Mo(1)–O(28)	1.684(5)	Mo(2)–O(32)	1.693(5)
Mo(1)–O(27)	2.383(5)	Mo(2)–O(27)	2.344(5)
Mo(3)–O(36)	1.705(6)	Mo(4)–O(26)	1.698(6)
Mo(3)–O(33)	2.005(5)	Mo(4)–O(27)	2.377(5)
O(19)#1–Na(1)–O(11)#1	106.7(2)	O(15)–Na(2)–O(9)#2	94.1(2)
O(19)#1–Na(1)–O(1)#1	93.3(2)	O(9)#2–Na(2)–O(7)#2	71.2(2)
O(20)–Nd(1)–O(25)	131.37(18)	O(24)–Nd(2)–O(11)	82.89(18)
N(1)–Nd(1)–O(25)	68.05(18)	O(7)–Nd(2)–O(14)	73.68(18)
O(2)#1–Nd(1)–OW1	70.8(2)	O(19)–Nd(4)–O(23)	68.55(19)
O(18)#5–Nd(3)–O(10)#2	73.7(2)	OW4–Nd(4)–OW5A	143.8(5)
O(16)#4–Nd(3)–O(22)#6	112.0(4)	O(32)–Mo(2)–O(31)	105.6(3)
O(28)–Mo(1)–O(25)	104.6(3)	O(31)–Mo(2)–O(33)	97.1(2)
O(25)–Mo(1)–O(30)	99.8(2)	O(26)–Mo(4)–O(35)	105.0(3)
O(36)–Mo(3)–O(29)	104.6(3)	O(35)–Mo(4)–O(34)	102.2(3)
O(35)–Mo(4)–O(37)	101.9(2)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 3/2, y - 1/2, -z + 1/2$ #2 $-x + 3/2, y + 1/2, -z - 1/2$ #4 $-x + 3/2, y - 1/2, -z - 1/2$ #5 $x - 1/2, -y + 3/2, z - 1/2$ #6 $-x + 2, -y + 2, -z$ #7 $-x + 1, -y + 1, -z$.

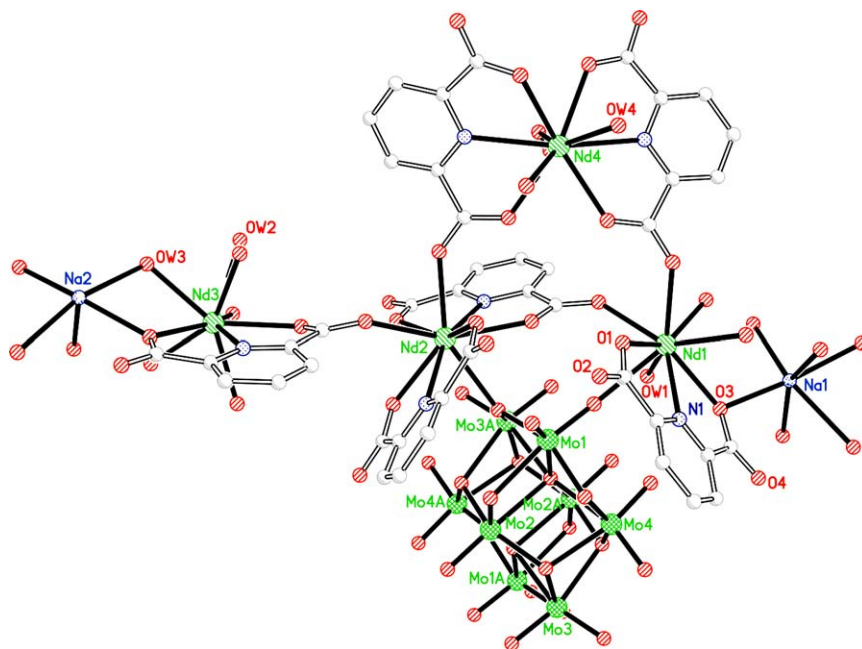


Fig. 1. The structure of the fundamental building block of compound **1**. Only parts of the atoms are labeled, and all the hydrogen atoms and the non-coordinated water molecules are omitted for clarity.

connected by $\{\text{NdN}_2\text{O}_7\}$ units through linking every other sodium atom on each “S” chain to form a bimetallic layer (Fig. 2a). Alternatively, the 2-D sheet can be considered as the aggregation of 12-membered cycles made up of six Nd atoms and six Na atoms via corner- or edge-sharing connections. Interestingly, the pyridine rings of the dipic ligands extend into the 12-membered rings or project above and below the 2-D sheets with carboxyl groups burdening all the junctures.

The extension of the 3-D bimetallic framework is realized by means of the covalent bridging of $\{\text{Nd}(4)(\text{dipic})_2\}^-$ fragments to Nd(1) and Nd(2) sites which result in a pillared coordination polymer with channels running along b axes. Although bimetallic frameworks based on $3d$ – $4f$ assemblies are often encountered, to our knowledge, such a network based on $4f$ metal and main group element is really singular. The heterometallic skeleton, as expected, contains covalently bonded alkali metal atoms becoming cationic, offering an efficacious recognition in assembling the polymer framework and POM subunits. It is also striking that these channels fall into two groups with dimensions $11.5 \text{ \AA} \times 11.7 \text{ \AA}$ and $12.5 \text{ \AA} \times 14.7 \text{ \AA}$ (defined by the separation between Nd(3) and Nd(2c), Nd(4) and Nd(4c), Nd(3) and Nd(3b), Nd4 and Nd(4e), respectively). Remarkably, the smaller channels are shut by the pyridine rings of the dipic ligands, whereas the larger “open” ones seem to remain appropriate free spaces for β - $\{\text{Mo}_8\text{O}_{26}\}^{4-}$ clusters to reside in. Thus, a 3-D network pattern with alternatively “close” and “open” channels is observed (see Fig. S3). The β - $\{\text{Mo}_8\text{O}_{26}\}^{4-}$ moieties self-assemble into the “open” channels via covalent

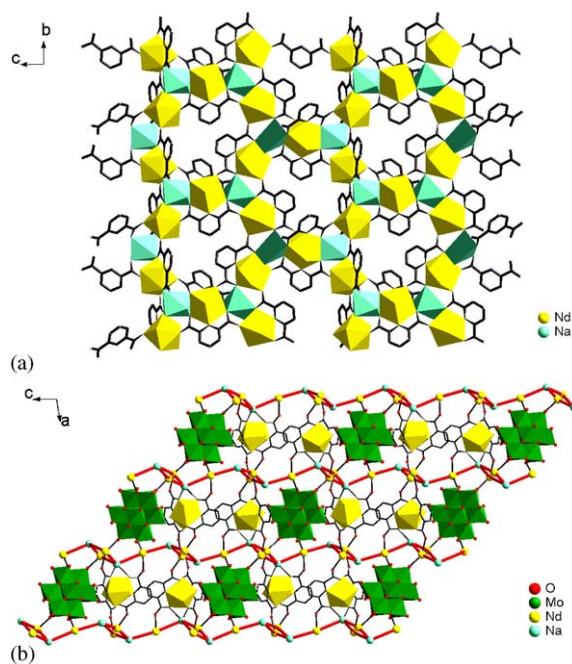


Fig. 2. (a) View of the individual 2-D bimetallic network in **1**; H atoms are omitted for clarity. (b) Projection of the 3D framework down the b axis in **1**; all the hydrogen atoms and the non-coordinated water molecules are omitted, and the 2-D layers represented in Fig. 2a are shown as bold zigzag lines for the sake of clarity.

bonding to the Nd(1) and Nd(2) sites using terminal and μ_2 -O atoms, respectively, to achieve its lodging into the framework (Fig. 2b). Dissociated water molecules fill in the whole network skeleton.

The IR spectrum (shown in Fig. S4) of **1** displayed a series of complicated bands in the range of 660–950 cm^{-1} , with distinct strong bands at 950, 935, 914, and 841 cm^{-1} , attributable to the terminal (Mo=O) and bridging (Mo–O–Mo) stretching.

Thermal gravimetric (TG) curve for **1** exhibits a three-step of mass loss in the temperature range from 30 to 800 °C, as shown in Fig. S5. The first two weight losses of 3.50% and 3.60% with slight distinction between 80 and 270 °C correspond to the dehydrating of the non-coordinated and coordinated water molecules (calc. 3.42% for each). The third mass loss of 38.23% arises from the decomposition of organic ligands and the further decomposing of the sample (calc. 37.19%). The total weight loss of 45.34% is in good accordance with the calculated value 44.03%.

In summary, we have synthesized a novel hybrid 3-D REPB material, $\text{Na}_4[\text{Nd}_8(\text{dipic})_{12}(\text{H}_2\text{O})_9][\text{Mo}_8\text{O}_{26}] \cdot 8\text{H}_2\text{O}$, which is constructed by self-assembly of $\beta\text{-}\{\text{Mo}_8\text{O}_{26}\}^{4-}$ clusters into a 3-D heterometallic framework via covalent bonding. The successful preparation of **1** opens up possibilities for the investigation of a new class of inorganic–organic hybrids based on molybdenum oxide clusters and lanthanide complexes. Future research may focus on the attempting to explore the effects of 4f metal-organic fragments and polyanion moieties on the reaction systems.

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Appendix A. Supplementary data

The online version of this article contains additional supplementary data. Please visit [doi:10.1016/j.jssc.2004.08.007](https://doi.org/10.1016/j.jssc.2004.08.007).

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