

六钨酸盐为模板的三维网状超分子化合物 [La₂(DNBA)₄(DMF)₈][W₆O₁₉]的合成和晶体结构

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Synthesis and Structure of a Hexatungstate-Templated 3D Supramolecular Network [La₂(DNBA)₄(DMF)₈][W₆O₁₉]

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Abstract: A new three-dimensional (3D) lanthanide-aromatic monocarboxylate dimer supramolecular network [La₂(DNBA)₄(DMF)₈][W₆O₁₉] (DNBA=3,5-dinitrobenzoate, DMF=dimethylformamide) was synthesized using hexatungstate anion (W₆O₁₉²⁻) as template. The crystal structure of the title compound has been determined by single-crystal X-ray diffraction. It crystallizes in triclinic, space group $P\bar{1}$ with $a=1.334\ 54(18)$ nm, $b=1.387\ 52(19)$ nm, $c=1.426\ 06(19)$ nm, $\alpha=102.189(2)^\circ$, $\beta=101.023(2)^\circ$, $\gamma=116.349(2)^\circ$, $V=2.187\ 2(5)$ nm³, $D_c=2.364$ g·cm⁻³, $Z=1$, $F(000)=1\ 453.40$. The single crystal structure reveals that two La(III) ions are bridged by four 3,5-dinitrobenzoate anions as asymmetrically bridging ligands, leading to dimeric cores, [La₂(DNBA)₄(DMF)₈]²⁺; [La₂(DNBA)₄(DMF)₈]²⁺ groups are joined together by π - π stacking interaction between the aromatic groups to form a two-dimensional grid-like network; the 2D supramolecular layers are further extended into 3D supramolecular network with a 1D box-like channels by hydrogen bonding interactions, in which hexatungstate polyanions reside. CCDC: 284694.

Key words: hexatungstate; template; 3D supramolecular network; crystal structure

0 Introduction

polyoxometalates (POMs), in addition to their importance in catalysis, biochemical separation and medicinal chemistry, play an important role for the design of new materials with novel electronic, magnetic and topological properties^[1-3]. A new area of interest is the construction of supramolecular arrays based on

POMs building blocks and various organic ligands (such as N-containing ligands, amino acids, polypeptides, tetrathiafulvalenes, organometallics and cyclopentadienyl derivatives)^[4-7]. These assemblies possess interesting one-(1D), two-(2D), and three-dimensional (3D) structures and exhibit potential applications in catalysis, medicine, and electrical-conductive and magnetic materials^[8-11]. Several successful strate-

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gies have been developed to integrate POMs into hybrid solid-state materials^[10], which are mainly based on simple material by hydrothermal methods. Most recently, POMs-templated transition metal coordination polymers have been synthesized^[12]. However, no high-dimensional rare-earth complex network encapsulating polyoxoanions has been reported yet.

Supramolecular assemblies constructed from organic and/or inorganic molecular building blocks has attracted extensive interest owing to their novel and diverse topologies and potential applications in host-guest chemistry, shape-selective catalysis, absorption, electrical-conductive, magnetic, and photosensitive materials^[13,14]. In the recent years lanthanide complexes have also attracted much attention owing to their special spectroscopic and magnetic properties, as well as their potential use as luminescent probes, NMR shift agents, magnetic resonance imaging agent and radiotherapeutic agents^[15,16]. In the hope that the combination of lanthanide complex with POMs allows the creation of new network with unique physical properties, we have reported a kind of novel hexamolybdate-templated, 3-D supramolecular network based on lanthanide dimers^[17,18]. In this paper, we continue to report a new hexatungstate-templated, 3-D supramolecular network based on lanthanum dimers building block, $[\text{La}_2(\text{DNBA})_4(\text{DMF})_8][\text{W}_6\text{O}_{19}](\text{DNBA}=3,5\text{-dinitrobenzoate}, \text{DMF}=\text{dimethylformamide})$. The title compound exhibits an interesting 3D box-like “host” network constructed from lanthanum dimers by π - π stacking and hydrogen bonding interactions, in which hexatungstate “guests” reside.

1 Experimental

1.1 Synthesis

$[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{W}_6\text{O}_{19}$ was synthesized by the method of the literature^[19] and characterized by IR spectra and ICP. 8 ml DMF solution of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{W}_6\text{O}_{19}$ (0.163 7 g) and 5 mL glacial acetic acid (HOAc) solution of 3, 5-dinitrobenzoic acid (0.106 g) were added dropwise to a stirred 5 ml ethanol (EtOH) solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.216 g) in succession. The light yellow solution was stirred at 55 °C for 2 h. The resulting solution was

filtrated and then allowed to evaporate in air at room temperature. Slow evaporation afforded light yellow crystal of the title compound. 15 % yield based on W. Elem. Anal. Calc. for $\text{C}_{52}\text{H}_{68}\text{La}_2\text{W}_6\text{N}_{16}\text{O}_{51}(\%)$: C, 20.06; H, 2.20; N, 7.20; W 35.43; La, 8.92; Found(%): C, 20.01; H, 2.16; N, 7.22; W 35.38; La 8.95; FTIR data (cm^{-1}): 310 5(w), 293 6(w), 165 2(s), 162 7(s), 158 3 (w), 154 1(s), 149 7(w), 145 9(w), 143 8(w), 140 0(m), 134 8(s), 125 1(w), 110 9(w), 981(s), 813(s), 723(s), 672(m).

1.2 Crystal structure determination

A yellow single crystal of the title compound with dimensions of 0.34 mm×0.28 mm×0.16 mm was selected for the structural analysis. Data were collected on a Bruker Smart 1000 CCD diffractometer with Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at 294(2) K in the range of $1.54^\circ<\theta<26.48^\circ$. Empirical absorption correction was applied ($8.916\ \text{mm}^{-1}$). A total of 12 457 (8 840 unique, $R_{\text{int}}=0.024\ 8$) reflections were measured.

The structure was solved by the direct method and refined by the Full-matrix least-squares on F^2 using the SHELX-97 software^[20,21]. All of the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were located by using the Fourier difference maps. The final R_1 and wR_2 was 0.036 1 and 0.126 7, respectively. A summary of the crystallographic data and structural determination for the title compound is provided in Table 1.

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Table 1 Crystal data and structure refinement details for the title compound

Empirical formula	$\text{C}_{52}\text{H}_{68}\text{La}_2\text{N}_{16}\text{O}_{51}\text{W}_6$
Formula weight	3 114.08
Crystal system	Triclinic
Space group	$P\bar{1}$
a / nm	0.133 454(18)
b / nm	0.138 752(19)
c / nm	0.142 606(19)
$\alpha / (^\circ)$	102.189(2)
$\beta / (^\circ)$	101.023(2)
$\gamma / (^\circ)$	116.349(2)
V / nm^3	2.1872(5)
Z	1
$D_{\text{calc}} / (\text{g}\cdot\text{cm}^{-3})$	2.364

Continued Table 1

μ / mm^{-1}	8.916
$F(000)$	1 458.0
Crystal size / mm	$0.34 \times 0.28 \times 0.16$
Temperature / K	294(2)
$\theta_{\min}, \theta_{\max} / (^\circ)$	1.54, 26.48
Index range	$-16 \leq h \leq 16$ $-17 \leq k \leq 17$ $-17 \leq l \leq 15$
Reflections unique	8 840 ($R_{\text{int}}=0.0248$)
$R_1^a[I > 2\sigma(I)]$	0.036 1
$wR_2^b[I > 2\sigma(I)]$	0.071 1
Goodness-of-fit on F^2	1.062

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

2 Results and discussion

2.1 Preparation of the title compound

The self-assembly reaction of $\text{La}(\text{NO}_3)_3$ with 3,5-dinitrobenzoic acid and hexatungstate at the DMF-HOAc-EtOH mixed solution is an effective route for preparation of a new rare-earth supramolecular network containing POM. The isolation of the title compound depends on the choice of ligands containing carboxylic acid and solvent system. If the 3,5-dinitrobenzoic acid was replaced by benzoic acid or sodium of terephthalic acid at the same conditions, we could not obtain the expected single crystal but only precipitate. If HOAc was not added into the reaction system, a lot of white precipitate was obtained probably due to the decomposition of polyoxoanion at neutral or basic solution.

2.2 Crystal structure of the title compound

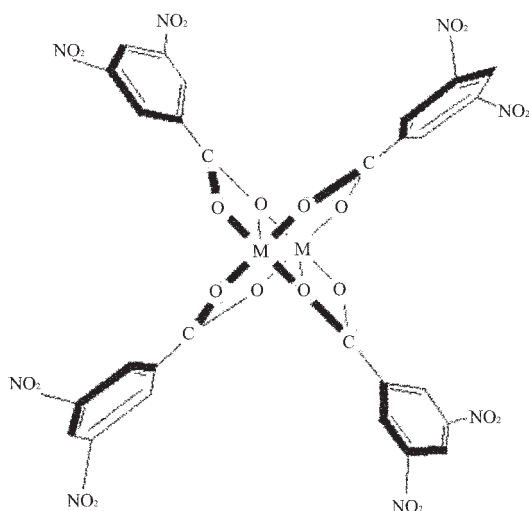
X-ray crystallography shows that the title compound consists of a lanthanum-3,5-dinitrobenzoate-dimethylformamide dimer $[\text{La}_2(\text{DNBA})_4(\text{DMF})_8]^{2+}$ cation and a polyoxoanion $\text{W}_6\text{O}_{19}^{2-}$. The polyoxoanion $\text{W}_6\text{O}_{19}^{2-}$ is the well known Lindquist structure and consists of a central oxygen atom about which are arrayed six metal atoms in an octahedral geometry. Three kinds of oxygen atoms exist in the cluster, that is, the terminal oxygen O_a , double-bridging oxygen O_b , and central oxygen O_c . Thus, the W-O bond lengths can be grouped into three sets: W- O_a 0.169 6(5)-0.170 1(5) nm, W- O_b 0.190 0(5)-0.194 2(5) nm, and W- O_c

0.231 91(4)-0.233 16(4) nm.

The lanthanum complex cation contains two La(III) centers bridged by four 3,5-dinitrobenzoate anions, leading to a dimeric $[\text{La}_2(\text{DNBA})_4(\text{DMF})_8]^{2+}$ core. The perspective view of the dimer cation together with the atomic numbering scheme is illustrated in Figure 1. Each La ion is nine-coordinate bonding to four bridging oxygen atoms and one oxygen atom of four 3,5-dinitrobenzoate units and four oxygen atoms from four DMF. The La-O distances range from 0.247 7(6) to 0.297 6(5) nm, the average La-O distance is 0.256 1 nm. It should be noted that four 3,5-dinitrobenzoate ligands can be described as two groups (I and II). Group I contains two 3,5-dinitrobenzoate ligands acting as tridentate fashion. O6 (or O6A) bridges two metal atoms (La and LaA), and O7 (or O7A) only coordinates to one metal atom La (or LaA). The distance between the bridging oxygen atom O7A and La is 0.297 6(5) nm, which is the longest distance around the La ion. Selected bond distances and angles for the complex are listed in Table 2.

The angles O7-La-O7A and La-O7-LaA are $74.9(2)^\circ$ and $105.1(2)^\circ$, respectively. Hence, it is noted the four-membered ring La-O7-LaA-O7A is obviously perfectly planar and correspondingly the two 3,5-dinitrobenzoate ligands are also in the same plane. The other two 3,5-dinitrobenzoate ligands act as bidentate fashion. O8A and O5 coordinate to La and LaA, respectively. These two ligand molecules are parallel each other. Schematic illustration of the coordination fashion of the dimer cation is shown in Scheme 1.

The most unusual structural feature of the title compound is that dimeric cation $[\text{La}_2(\text{DNBA})_4(\text{DMF})_8]^{2+}$ groups are joined together by offset π - π stacking interaction between aromatic rings along the b-axes to form a two-dimensional grid-like network, as shown in Fig.2. The close contact distance between adjacent aromatic rings is 0.35 nm along the b-axis. As is described above, each lanthanum dimer possesses four DMF molecules and four 3,5-dinitrobenzoate, and the oxygen atoms from the nitro-group of 3,5-dinitrobenzoate in one 2D layer are linked to carbon atoms from



Scheme 1 Schematic illustration of the coordination fashion of the dimer cation. The DMF molecules have been omitted for clarity

the methyl group of DMF molecules in another 2D layer through a weak hydrogen bonding interaction (Table 3).

Therefore, the 2D supramolecular layers are further extended into 3D supramolecular network with 1D box-like channels, as shown in Fig.3. The size of the box is 0.72 nm × 0.74 nm. The polyoxoanion was encapsulated inside as “guest” cluster anion and well surrounded by these “host” box-like units. Although

Chen et al. and other groups have reported related work on monomeric metal complexes that extended into 3D network via supramolecular interactions such as H-bonds and π - π stacking interactions with small anions as guests^[22,23]; Zubieta et al. have reported composite solid constructed from 1D or 3D coordination polymer matrices and molybdenum oxide subunits by hydrothermal method, in which polyoxoanions were encapsulated^[24]; Keller et al. have reported POM-tem-

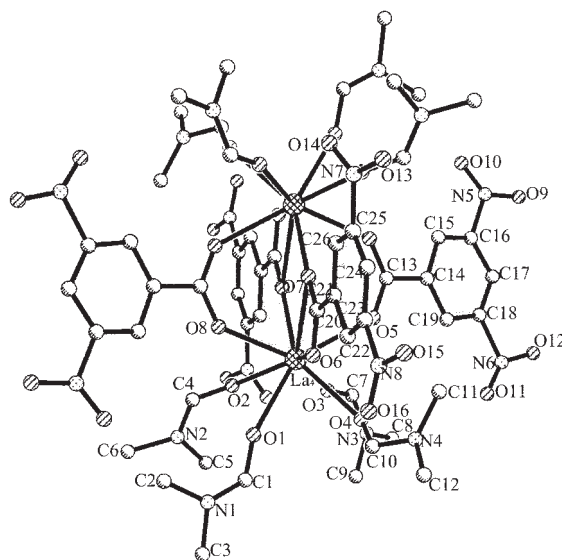


Fig.1 Structure of $[\text{La}_2(\text{DNBA})_4(\text{DMF})_8]^{2+}$ dimer cation, the hydrogen atoms are omitted for clarity

Table 2 Selected bond distances (nm) and angles ($^\circ$) for the title compound

W(1)-O(24)	0.191 7(5)	W(2)-O(19)	0.170 1(5)
W(1)-O(26)	0.233 16(4)	La(4)-O(3)	0.247 7(6)
La(4)-O(7)	0.248 6(5)	La(4)-O(5)	0.248 4(5)
La(4)-O(8)	0.249 4(5)	La(4)-O(2)	0.250 7(6)
La(4)-O(4)	0.252 8(6)	La(4)-O(6)	0.253 4(5)
La(4)-O(1)	0.256 0(6)	La(4)-O(7)#1	0.297 6(5)
La(4)-C(20)	0.311 0(7)	O(7)-C(20)#1	0.126 1(8)
O(7)-La(4)-O(2)	79.44(18)	O(7)-La(4)-O(8)	76.64(16)
O(5)-La(4)-O(8)	128.44(17)	O(7)-La(4)-O(6)	121.01(16)
O(5)-La(4)-O(6)	85.15(18)	O(8)-La(4)-O(6)	77.01(18)
O(7)-La(4)-O(7)#1	74.90(16)	O(5)-La(4)-O(7)#1	67.41(16)
O(8)-La(4)-O(7)#1	65.40(15)	O(6)-La(4)-O(7)#1	46.15(14)
La(4)-O(7)-La(4)#1	105.10(16)	O(17)-W(1)-O(25)	103.7(2)
O(25)-W(1)-O(24)	87.4(2)	O(25)-W(1)-O(21)#2	152.9(2)
O(17)-W(1)-O(26)	179.7(2)	W(3)-O(25)-W(1)	117.0(2)
W(2)-O(26)-W(2)#2	180.0	W(2)-O(26)-W(1)	89.960(14)

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

Table 3 Interatomic distances (nm) involving hydrogen-bonded atoms in the title crystal

D-H...A	$d(\text{D-H})/\text{nm}$	$d(\text{H}\cdots\text{A})/\text{nm}$	$d(\text{D}\cdots\text{A})/\text{nm}$	$\angle \text{DHA}/(^{\circ})$
C(6)-H(6A)···O(12)($x, -1+y, z$)	0.096	0.249	0.34430	170
C(11)-H(11B)···O(9)($1-x, 1-y, -z$)	0.096	0.243	0.31227	129
C(12)-H(12A)···O(11)($2-x, 1-y, -z$)	0.096	0.256	0.31628	121

plated coordination polymer^[12]. There is no report on rare-earth-carboxylate high dimensional “host” network encapsulating hexatungstate anion.

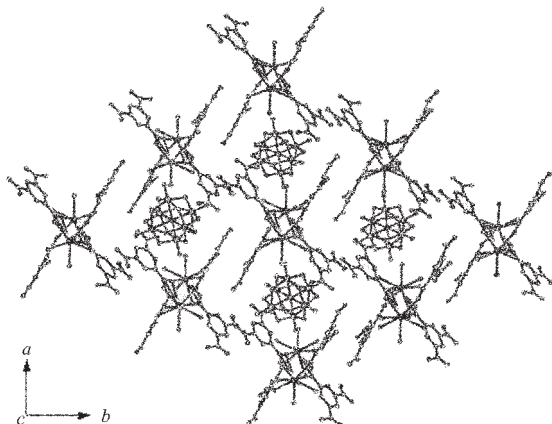


Fig.2 Ball and stick representation of grid-like cavity based on lanthanum dimers encircling $\text{W}_6\text{O}_{19}^{2-}$ anions along the a axis. The DMF molecules have been omitted for clarity

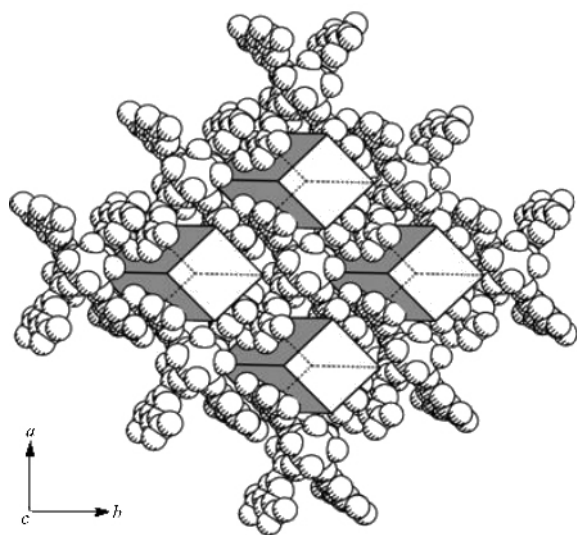


Fig.3 Space-filling diagram of the 3D “host” network and the box-like cavities of the title compound constructed from lanthanum dimers by π - π stacking interaction between aromatic rings and hydrogen bonding interaction (along a axis)

2.3 FTIR spectroscopy

In the IR spectrum of the title compound, the

characteristic peaks at 813 and 981 cm^{-1} are attributed to the $\nu(\text{W-O-W})$ and $\nu(\text{W=O})$ of the $\text{W}_6\text{O}_{19}^{2-}$ polyanions, respectively. The feature band at 1 652 cm^{-1} can be ascribed to $\nu(\text{C=O})$ of DMF. Bands in the range of 1 459~1 583 cm^{-1} are characteristic of the phenyl ring of 3,5-dinitrobenzoate. The characteristic peaks at 1 541 and 1 438 cm^{-1} are attributed to the O-C-O group of 3,5-dinitrobenzoate.

In conclusion, a new supramolecular architectures based on $\text{W}_6\text{O}_{19}^{2-}$ and lanthanum dimers building block $[\text{La}_2(\text{DNBA})_4(\text{DMF})_8][\text{W}_6\text{O}_{19}]$ (DNBA =3,5-dinitrobenzoate, DMF=dimethylformamide) have been synthesized and structurally characterized. Here $\text{W}_6\text{O}_{19}^{2-}$ act as a non-coordination template around which a 2D grid-like network is constructed by π - π stacking interaction of aromatic ring of the adjacent lanthanum complex; the 2D framework is further extended into 3D box-like network by hydrogen-bonding interaction of adjacent lanthanum complex.

References:

- [1] Pope M T. *Heteropoly and Isopoly Oxometalates*, Berlin: Springer., **1983**.
- [2] Hill C L. *Chem. Rev.*, **1998**,**98**:1~387
- [3] Pope M T, Müller A, Eds. *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*. Dordrecht, Netherlands.: Kluwer Academic Publishers, **1994**.
- [4] Peng J, Li W Z, Wang E B, et al. *J. Chem. Soc., Dalton Trans.*, **2001**:3668~3671
- [5] Mialane P, Dolbecq A, Lisnard L, et al. *Angew. Chem. Int. Ed.*, **2002**,**41**:2398~2401
- [6] Müller A, Krickemeyer E, Bogge H, et al. *Angew. Chem.*, **1998**,**110**:3567~3571
- [7] Yuan M, Li Y G, Wang E B, et al. *J. Chem. Soc., Dalton Trans.*, **2002**:2916~2920
- [8] Hölscher M, Englert U, Zibrowius B, et al. *Angew. Chem. Int. Ed.*, **1994**,**33**:2491~2493
- [9] Xu L, Lu M, Xu B B, et al. *Angew. Chem. Int. Ed.*, **2002**, **41**:4129~4132

- [10]Hagman P J, Hagman D, Zubieta J. *Angew. Chem. Int. Ed.*, **1999**,**38**:2638~2684
- [11]Coronado E, Gamenez-Saiz J R, Gomez-Garcia C J, et al. *Inorg. Chem.*, **1998**,**37**:2183~2188
- [12]Inman C, Knaust J M, Keller S W. *Chem. Commun.*, **2002**: 156~157
- [13]Robson R, Abrahams B F, Batten S R. *Supramolecular Architecture*; American Chemical Society: Washington, DC., **1992**:256
- [14]Li Y G, Zhang H, Wang E B. *New J. Chem.*, **2002**,**26**: 1619~1623
- [15]Bünzli J-C G. *Lanthanide Probes in Life, Chemical and Earth Science*, Elsevier, Amsterdam., **1989**:219
- [16]Xu J, Raymond K N. *Angew. Chem. Int. Ed.*, **2000**,**39**: 2745~2747
- [17]Wang X L, Guo Y Q, Wang E B, et al. *Inorg. Chem.*, **2003**, **42**:4135
- [18]Wang X L, Guo Y Q, Wang E B, et al. *J. Mole. Stru.*, **2004**, **691**:171~180
- [19]Hur N H, Klemperer W G, Wang R C. *Inorg. Synth.*, **1990**, **27**:77
- [20]Sheldrick G M. *SHELXS 97, Program for Crystal Structure Solution*, University of Göttingen., **1997**.
- [21]Sheldrick G M. *SHELXL 97, Program for Crystal Structure Refinement*, University of Göttingen., **1997**.
- [22]Tong M L, Lee H K, Chen X M, et al. *J. Chem. Soc., Dalton Trans.*, **1999**:3657
- [23]Roesky H W, Andruh M. *Coord. Chem. Rev.*, **2003**,**236**: 91~119
- [24]Hagman D, Zubieta C, Rose D J, et al. *Angew. Chem. Int. Ed.*, **1997**,**36**:873~876