基于柔性环己烷六酸配体的两个碱土金属配位聚合物的水热合成及结构表征

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摘要：水热反应条件下,碳酸锰和碳酸钡分别与水合环己烷六酸(H$_6$L^I·H$_2$O)(顺式椅式构型 L^I:a,e,a,e,a,e)反应生成 2 个三维的配位聚合物 [Mg$_3$(L^{II})(H$_2$O)$_6$] (**1**)和[Ba$_2$(H$_2$L^{II})(μ_2-H$_2$O)$_2$] (**2**)(反式椅式构型 L^{II}:e,e,e,e,e,e),通过元素分析和红外光谱对这 2 个配位聚合物进行了表征。X 射线单晶衍射分析表明配合物 **1** 属于三方晶系,$R\bar{3}$ 空间群,晶胞参数为：a=1.439 3(2) nm,c=1.459 7(4) nm,β=120.00°,V=2.618 7(10) nm^3,Z=18；配合物 **2** 结构属于单斜晶系,$C2/c$ 空间群,晶胞参数为：a=1.676 4(2) nm,b=0.909 5(1) nm,c=1.000 1(1) nm,β=105.991(2)°,V=1.465 9(2) nm^3,Z=4。配合物 **1** 是由反式椅式构型 L^{II}配体桥连形成的高对称性的三维配位网络。在配合物 **2** 中,顺式的 H$_6$L^{I}配体也发生构型转变并脱去部分羧基质子形成 H$_2$L^{II}配体,将 Ba 离子连接成一个具有一维孔道的三维有孔框架结构。在这 2 个配合物中,环己烷六酸配体均采取反式椅式 L^{II}构型,证明了碱土金属离子 Mg(II)及 Ba(II)在水热条件下通过配位作用可以稳定环己烷六酸配体的这种反式椅式构型。

关键词：配位聚合物；碱土金属离子；环己烷六酸；水热合成
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Hydrothermal Syntheses and Crystal Structures of Two 3D Alkaline Earth Metal Coordination Polymers with Conformation-Flexible Cyclohexane-1,2,3,4,5,6-hexacarboxylate Ligand

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Abstract: Reactions of MgCO$_3$/BaCO$_3$ and 1,2,3,4,5,6-cyclohexanehexacarboxylic acid hydrate　(H$_6$L^I·H$_2$O) (*cis*-chair conformation L^I: a,e,a,e,a,e) resulted in formation of two three-dimensional coordination polymers [Mg$_3$(L^{II})(H$_2$O)$_6$] (**1**) and [Ba$_2$(H$_2$L^{II})(μ_2-H$_2$O)$_2$] (**2**) (*trans*-chair conformation L^{II}: e,e,e,e,e,e) under hydrothermal condition and were characterized by elemental analysis and IR. X-ray diffraction crystal structure analysis shows that **1** crystallizes in trigonal system , space group $R\bar{3}$ with a=1.439 3(2) nm, c=1.459 7(4) nm, β=120.00°, V=2.618 7(10) nm^3, Z=18; and **2** crystallizes in monoclinic system, space group $C2/c$ with a=1.676 4(2) nm, b=0.909 5(1) nm, c=1.000 1(1) nm, β=105.991(2)°, V=1.465 9(2) nm^3, Z=4. Complex **1** is a highly symmetrical network bridged by the *trans*-chair conformation L^{II} ligand. In complex **2**, the *cis*-chair H$_6$L^I ligand transformed to the partly deprotoned *trans*-chair H$_2$L^{II} ligand, which bridged the Ba atoms to generate a porous 3D framework with 1D channels, which are filled with the coordinated water molecules. In the two complexes, both of the flexible cyclohexanehexacarboxylate ligands adopt the *trans*-chair conformation L^{II}, illustrating that the conformation L^{II} can be stabilized by the coordination with alkaline earth Mg(II)/Ba(II) through hydrothermal syntheses. CCDC: 755551, **1**; 755552, **2**.

Key words: coordination polymer; alkaline earth ions; cyclohexanehexacarboxylate; hydrothermal synthesis

0　Introduction

In the rational design and synthesis of metal-organic coordination polymers, rigid polycarboxylates, for example benzenepolycarboxylates and pyridinepoly-carboxylates, have been extensively employed to produce various extended structures[1-5]. Nevertheless, only a few coordination polymers based on ligands with flexible conformations have been reported so far. It is probably due to the flexibility of the ligand backbones, which makes them more difficult to predict and control the final coordination networks[6-8]. Many investigations have been focused on the flexible 1,4-cyclohexanedi-carboxylic acid (1,4-H_2chdc) for its *cis/trans*-chair conformations [6-7]. 1,2,3,4,5,6-cyclohexanehexacarboxy-lic acid (H_6L, L stands for the ligand with different conformations), which is characteristic of multiple binding sites and pH-dependent coordination fashions and has versatile flexible conformations, has attracted our great interest in studying their conformational transformations and the use in constructing metal-organic frameworks[9-13]. In our recent work on H_6L, we have observed that the starting material 1,2,3,4,5,6-cyclohexanehexacarboxylic acid hydrate ($H_6L^I \cdot H_2O$, L^I: a,e,a,e,a,e), adopting the all-*cis*-chair conformation with rich hydrogen bonds, can in situ convert to the *trans*-chair form or *cis*,*trans*-mixed-chair forms under different hydrothermal conditions. In our investigation, the L ligand in silver coordination polymers adopts the *cis*-chair conformation[9], in the transition metal coor-dination polymers such iron, cobalt, manganese and nickel adopts the *trans*-chair form[10,12], and the *cis*,*trans*-mixed-chair forms can be observed in the cadmium coordination polymers[11-12]. Meanwhile, we also trapped the intermediates in crystalline states via the coordination with the relatively reactive and catalytically active metal ion Cu(Ⅱ), and then found out the reaction mechanism with structural clues[12].

Compared to the *d*-block transition metal ions, the *s*-block alkaline earth ions size varies considerably on moving down the group, which makes a rapidly deve-loping study of these metal coordination polymers[14]. As our continuing investigation on this interesting metal-H_6L system, we employed the alkaline earth ions to react with the H_6L ligand to investigate the ligand flexible conformations. Herein, we report two alkaline earth coordination polymers, three-dimensional (3D) $[Mg_3(L^{II})(H_2O)_6]$ (**1**) and $[Ba_2(H_2L^{II})(\mu_2-H_2O)_2]$ (**2**), in both of which the L ligands adopt the trans-chair L^{II} conformation (L^{II}: e,e,e,e,e,e) (Scheme 1).
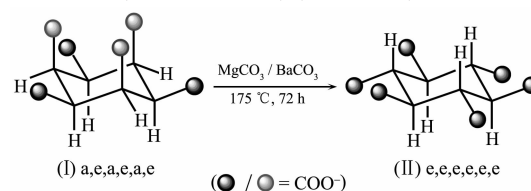
Scheme 1　Summary of hydrothermal conditions and ligand conformation transformation in the preparation of **1** and **2**

1　Experimental section

1.1　Materials and physical measurements

The starting material *cis*, *cis*, *cis*, *cis*, *cis*-1,2,3,4,5,6-cyclohexanehexacarboxylic acid hydrate ($H_6L^I \cdot H_2O$) employed was commercially available and used as received without further purification. The C and H microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FTIR spectra were recorded from KBr tablets in the range 4 000~400 cm^{-1} on a Bio-Rad FTS-7 spectrometer.

1.2　Hydrothermal synthesis

$[Mg_3(L^{II})(H_2O)_6]$ (**1**): A mixture of $H_6L^I \cdot H_2O$ (0.087 g, 0.25 mmol) and magnesium carbonate (0.063 g, 0.75 mmol) in H_2O (15 mL) were placed to a 25 mL Teflon reactor and heated in an oven to 175 ℃ for 72 h. After being cooled at a rate of *ca.* 5 ℃·h^{-1}, the colorless crystals of **1** in single phase (in *ca.* 18% yield based on H_6L^I) were obtained, isolated by filtration and washed with water. Elemental analysis calcd for $C_4H_6MgO_6$(%): C 27.55, H 3.47; found(%): C 28.22, H 3.05. IR (KBr, cm^{-1}): 3 400(s), 2 366(m), 1 620(vs), 1 574(vs), 1 420(vs), 1 384(vs), 1 258(w), 1 080(w), 1 021(w), 937(w), 760(w), 681(w), 517(w).

$[Ba_2(H_2L^{II})(\mu_2-H_2O)_2]$ (**2**): Similar to the synthesis of **1**, barium carbonate (0.145 mg, 0.75 mmol) instead of

magnesium carbonate reacted with $H_6L^I \cdot H_2O$ (0.087 g, 0.25 mmol) at 175 ℃ for 72 h. The colorless crystals of **2** in single phase (in *ca*. 10% yield based on H_6L^I) were obtained, isolated by filtration and washed with water. Elemental analysis calcd for $C_{12}H_{10}Ba_2O_{13}$(%): C 22.63, H 1.58; found(%): C 22.09, H 1.79. IR (KBr, cm^{-1}): 3 412(s), 2 908(w), 1 715(m), 1 635(vs), 1 586(s), 1 432 (vs), 1 402(s), 1 273(w), 1 071(w), 1 012(w), 935(w), 728 (w), 629(w), 566(w), 497(w).

1.3　Crystal structure determination

Data collections of complexes **1** and **2** were performed on a Bruker Smart Apex CCD diffractometer with Mo $K\alpha$ radiation (λ=0.071 073 nm) at 150(2) and 293(2) K. The raw data frames were integrated with $SAINT^+$, and the corrections were applied for Lorentz and polarization effects. Absorption correction was applied by using the multiscan program SADABS[15]. The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least-squares on F^2 using the SHELXTL program[16]. Hydrogen atoms on organic ligands were generated by the riding mode (C-H 0.093 nm). Crystal data as well as details of data collections and refinements for complexes **1** and **2** are summarized in Table 1. Selected bond distances and bond angles are listed in Table 2.

CCDC: 755551, **1**; 755552, **2**.

Table 1　Crystal data and structure parameters for 1 and 2

Identification code	**1**	**2**
Empirical formula	$C_4H_6MgO_6$	$C_{12}H_{10}Ba_2O_{13}$
Formula weight	174.40	636.88
Temperature / K	150(2)	293(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Trigonal	Monoclinic
Space group	$R\bar{3}$	$C2/c$
a / nm	1.439 3(2)	1.676 4(2)
b / nm	1.439 3(2)	0.909 5(1)
c / nm	1.459 7(4)	1.000 1(1)
β / (°)	120.00	105.991(2)
Volume / nm^3	2.618 7(10)	1.465 9(2)
Z	18	4
D_c / ($g \cdot cm^{-3}$)	1.991	2.886
Absorption coefficient / mm^{-1}	0.282	5.421
$F(000)$	1 620	1 192
Crystal size / mm	0.14×0.14×0.07	0.15×0.11×0.09
θ range for data collection / (°)	2.15~26.95	2.53~25.98
Limiting indices	$-17 \leqslant h \leqslant 16, -15 \leqslant k \leqslant 18, -18 \leqslant l \leqslant 13$	$-20 \leqslant h \leqslant 19, -11 \leqslant k \leqslant 6, -12 \leqslant l \leqslant 12$
Reflections collected	3 643	3 379
Independent reflections (R_{int})	1 249 (0.036 3)	1 411 (0.019 1)
Completeness / %	97.9	97.7
Max. and min. transmission	0.980 6 and 0.961 6	0.655 8 and 0.492 9
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1 249 / 2 / 100	1 411 / 2 / 126
Goodness-of-fit on F^2	1.085	1.013
Final R indices ($I>2\sigma(I)$)	R_1^a=0.043 0, wR_2^b=0.116 3	R_1^a=0.022 2, wR_2^b=0.050 5
R indices (all data)	R_1^a=0.052 2, wR_2^b=0.122 6	R_1^a=0.025 5, wR_2^b=0.051 9
Largest diff. peak and hole / ($e \cdot nm^{-3}$)	92, −319	735, −478

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

Table 2 Bond lengths (nm) and angles (°) for 1 and 2

1					
Mg1-O1A	0.205 7(2)	Mg1-O4B	0.207 3(2)	Mg1-O3	0.206 1(2)
Mg1-O1W	0.209 3(2)	Mg1-O2	0.206 7(2)	Mg1-O2W	0.210 7(2)
O1A-Mg1-O3	94.55(7)	O2-Mg1-O1W	88.72(7)	O1A-Mg1-O2	170.30(7)
O4B-Mg1-O1W	100.00(7)	O3-Mg1-O2	87.17(7)	O1A-Mg1-O2W	84.98(7)
O1A-Mg1-O4B	90.59(7)	O3-Mg1-O2W	86.13(7)	O3-Mg1-O4B	172.68(7)
O2-Mg1-O2W	104.67(7)	O2-Mg1-O4B	88.64(7)	O4B-Mg1-O2W	89.14(7)
O1A-Mg1-O1W	81.89(7)	O1W-Mg1-O2W	164.04(7)	O3-Mg1-O1W	85.91(7)
2					
Ba1-O3A	0.266 4(3)	Ba1-O4B	0.288 6(3)	Ba1-O1	0.279 7(3)
Ba1-O6C	0.289 2(3)	Ba1-O6B	0.281 1(3)	Ba1-O5D	0.289 4(3)
Ba1-O1W	0.281 3(1)	Ba1-O2	0.291 4(3)		
O3A-Ba1-O1	68.67(8)	O4B-Ba1-O6C	122.77(8)	O3A-Ba1-O6B	76.12(9)
O3A-Ba1-O5D	151.25(8)	O1-Ba1-O6B	124.46(8)	O1-Ba1-O5D	120.59(8)
O3A-Ba1-O1W	89.66(9)	O6B-Ba1-O5D	76.99(8)	O1-Ba1-O1W	66.25(8)
O1W-Ba1-O5D	119.10(8)	O6B-Ba1-O1W	154.99(6)	O4B-Ba1-O5D	89.41(7)
O3A-Ba1-O4B	70.25(8)	O6C-Ba1-O5D	112.62(8)	O1-Ba1-O4B	62.90(8)
O3A-Ba1-O2	113.95(8)	O6B-Ba1-O4B	65.46(7)	O1-Ba1-O2	45.37(7)
O1W-Ba1-O4B	129.09(7)	O6B-Ba1-O2	134.99(8)	O3A-Ba1-O6C	66.37(8)
O1W-Ba1-O2	69.57(6)	O1-Ba1-O6C	126.71(8)	O4B-Ba1-O2	76.80(8)
O6B-Ba1-O6C	69.27(9)	O6C-Ba1-O2	155.74(8)	O1W-Ba1-O6C	86.26(6)
O5D-Ba1-O2	79.07(8)				

Symmetry codes for **1**: A: $-y+1/3$, $x-y+2/3$, $z-1/3$; B: $y-1/3$, $-x+y+1/3$, $-z+1/3$; for **2**: A: $-x+2$, $-y+1$, $-z+1$; B: $-x+2$, y, $-z+3/2$; C: $x+1/2$, $-y+1/2$, $z-1/2$; D: $x+1/2$, $y-1/2$, z.

2 Results and discussion

2.1 Synthesis

As is well known, there are a variety of hydrothermal parameters such as time, temperature, pH value, and molar ratio of reactants, and small changes in one or more of the parameters can have a profound influence on the final reaction outcome[17-18]. Meanwhile, the metal ion size[19-20] as well as the ligand conformation[9-13] also play an important role in the construction of coordination polymers. In our previous work, three different conformations can be trapped in the cadmium coordination polymers by the Cd(II) ions, but the *cis*-chair form can only be found in the silver complexes, and the *trans*-chair form can be found in the iron, cobalt, manganese and nickel complexes[10,12]. Considering the characters of alkaline earth ions, we employed

Mg(II) and Ba(II) with different radii, attempting to trap the L ligand conformations. We carried out the reactions of MgCO$_3$/BaCO$_3$ with H$_6$L$^{\text{I}}$·H$_2$O under 175 ℃ hydrothermal conditions (Scheme 1). As a result, only the *trans*-chair L$^{\text{II}}$ *in situ* transformed from the *cis*-chair form L$^{\text{I}}$ in the starting material can be observed in the final crystal complexes **1** and **2**, which may be because L$^{\text{II}}$ is a more stable conformation according to the theoretical study[12,21] and the cation size is not suitable to trap other conformations. The resulting structures illustrated that the alkaline earth ions Mg(II) and Ba(II) can stabilize the L$^{\text{II}}$ conformation by coordination bonding in their complexes.

2.2 Structure of [Mg$_3$(L$^{\text{II}}$)(H$_2$O)$_6$] (1)

X-ray diffraction crystal structure analysis reveals that **1** crystallizes in $R\bar{3}$ space group and is isostructural to our recently reported cobalt, iron, manganese and

nickel coordination polymers[10,12]. Herein, the structure will be simply discussed. The asymmetric unit consists of one crystallographically unique Mg atom on a general position, one unique L^{II} ligand lying across a 3-fold axis transformed from the starting material cis-chair L^{I}, and two coordinated water molecules. Each Mg atom is coordinated in an octahedral geometry by four

carboxylate oxygen atoms from three L^{II} ligands and two water molecules (Mg-O 0.205 7(2)~0.210 7(2) nm, O-Mg-O 81.89(7)°~172.68(7)°). Each L^{II} ligand connects nine Mg atoms through its six carboxylate groups in a syn-anti bridging mode (Fig.1a). A 3D metal-organic framework is therefore generated by the Mg-carboxylate coordination (Fig.1b).
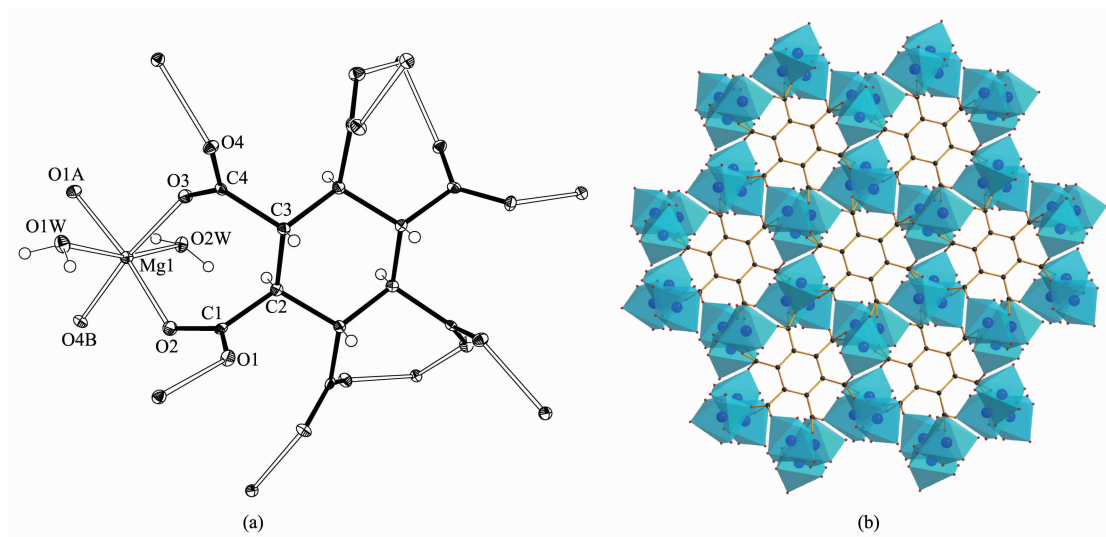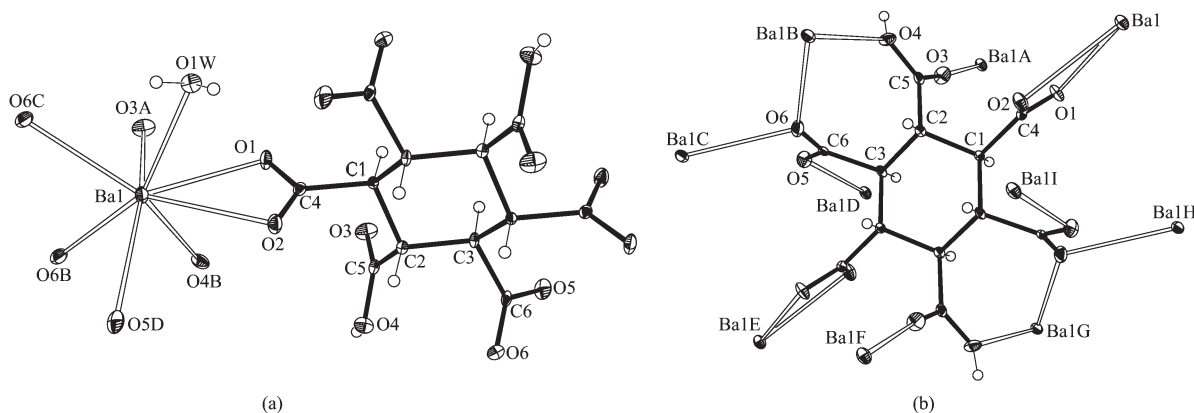

Symmetry codes: A: −y+1/3, x−y+2/3, z−1/3; B: y−1/3, −x+y+1/3, −z+1/3

Fig.1　(a) ORTEP drawing of coordination environment of the Mg atoms and the coordination mode of the L^{II} ligand (with thermal ellipsoids at 50% probability), (b) polyhedron view of the 3D coordination network along the c axis in 1

2.3　Structure of $[Ba_2(H_2L^{II})(\mu_2\text{-}H_2O)_2]$ (2)

When the bigger alkaline earth Ba(II) was used instead of Mg(II) ions, a novel 3D framework was formed in the similar reaction condition. X-ray diffraction crystal structure analysis reveals that complex **2**

contains one crystallographically unique Ba atom, one partly deprotoned H_2L^{II} ligand lying on a 2-fold axis transformed from the starting material cis-L^{I}, and one coordinated water molecule (Fig.2a). Each Ba atom adopts a heavily distorted coordination geometry,

Symmetry codes: A: −x+2, −y+1, −z+1; B: −x+2, y, −z+3/2; C: x+1/2, −y+1/2, z−1/2; D: x+1/2, y−1/2, z; E:−x+1/2, −y+1/2, −z+1; F: x−1/2, y−1/2, z; G: x−1/2, −y+1/2, z−1/2 ; H: −x+2, y, −z+1/2; I: −x+2, y, −z+1

Fig.2　(a) ORTEP drawing of coordination environment of the Ba atom, (b) coordination mode of the H_2L^{II} ligand with thermal ellipsoids at 50% probability

coordinated by seven O atoms from different L^{II} ligands and one water molecule (Ba-O 0.266 4(3)~0.291 4(3) nm, O-Ba-O 45.37(7)°~155.74(8)°). The partly deprotoned H_2L^{II} ligand adopts μ_{10}-bridging mode connecting ten Ba atoms through its six bridged μ-η^1:η^1, μ-η^1:η^2 and chelated carboxylate groups (Fig.2b).

Interestingly, two Ba atoms was bridged by two μ_2-O6 from two carboxylate groups to form a four-member ring through two Ba-O bonds with different distances 0.281 1(3) and 0.289 2(3) nm. The four-member rings are further connected to form a 1D $(COO)_2$-Ba_2-H_2O chain by the μ_2-H_2O bridges (Fig.3a). Adjacent chains are linked to generate a 3D coordination framework by the μ_{10}-H_2L^{II} ligands (Fig.3b). The 3D framework has 1D distorted quadrangular channels along the c axis filled with the coordinated water molecules (Fig.3c). In the channels, there are existing hydrogen bonds between the O atoms of carboxylate groups and coordinated
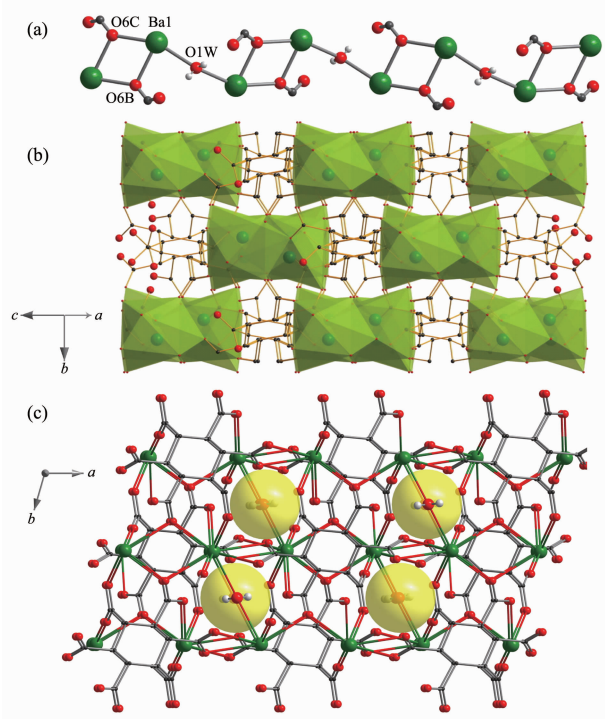
water molecules (O4···O1A 0.249 8 nm, O4−H4···O1A 176.10°; O1W···O5B 0.282 0 nm, O1W−H1W···O5B 137.34°; symmetry codes: A: x, $-y+1$, $z+1/2$; B: $x+1/2$, $-y+1/2$, $z-1/2$).

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Fig.3　(a) Perspective views of the 1D $(COO)_2$-Ba_2-H_2O chain, (b) polyhedron view of the 3D coordination framework, (c) 1D channels in the porous framework viewed along the c axis of **2**