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二维钡配位聚合物[Ba(μ_5-1,8-nap)]$_n$的水热合成、晶体结构和荧光性质

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摘要：通过水热法合成得到 1 个以 1,8-萘二酸(1,8-nap)为配体的 Ba(Ⅱ)配合物 [Ba(μ_5-1,8-nap)]$_n$ (**1**)。X 射线单晶衍射测定结果表明:配合物属于单斜晶系,空间群 $P2_1/c$。配合物最小不对称单元由 1 个九配位的钡原子和 1 个 1,8-萘二酸配体构成。每个 1,8-萘二酸配体连接五个钡原子,每个钡原子连接五个 1,8-萘二酸配体,在(100)平面上形成二维双层结构。此外,对配合物的固态荧光性质做了测定,结果显示其在紫光区有荧光发射。

关键词：钡(Ⅱ)配合物；1,8-萘二甲酸；晶体结构；水热合成；荧光
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Hydrothermal Synthesis, Crystal Structure and Luminescence Property of a 2D Ba(Ⅱ) Coordination Polymer [Ba(μ_5-1,8-nap)]$_n$

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Abstract: The title complex, [Ba(μ_5-1,8-nap)]$_n$ (**1**), was the first barium complex based on naphthalene-1,8-dicarboxylate (1,8-nap) ligand, has been synthesized by hydrothermal method. It belongs to monoclinic system with space group $P2_1/c$, a=1.551 80(7) nm, b=0.830 32(4) nm, c=0.816 72(4) nm, β=93.973(3)°, V=1.049 81(9) nm^3, D_c=2.224 g·cm^{-3}, Z=4, F(000)=664, the final R_1=0.047 9, wR_2=0.124 2. The crystal structure of complex **1** consists of a 9-coordinated Ba(Ⅱ) atom and a 1,8-nap ligand. Each 1,8-nap ligand links five Ba(Ⅱ) atoms and each Ba(Ⅱ) atom attaches to five 1,8-nap ligands to form a 2D bilayer framework along the (100) plane. The luminescence of complex **1** has also been investigated, and results reveals that it displays luminescent property in the voilet region. CCDC: 778610.

Key words: Ba(Ⅱ) complex; naphthalene-1,8-dicarboxylate; hydrothermally synthesis; luminescence property

0 Introduction

The ration design and synthesis of new metal-organic frameworks have attracted wide interest, not only because of their intriguing variety of architecture features and fascinating new topologies, but also because of their potential applications as functional solid materials in host-guest chemistry, ion exchange, fluore-scence, magnetism, and catalysis[1-5]. To build these molecular architectures, researchers often employ aromatic polycarboxylate ligand to construct coordination polymers as their versatile coordination modes and high structural stability[6-7]. At the same time, plenty of versatile and novel complexes of aromatic polycarboxylate groups containing naphthalene rings with various coordination modes have been synthesized and charac-

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terized[8-11]. Among them, naphthalene-1,8-dicarboxylic anhydride, hydrolyzed under hydrothermal condition into the naphthalene-1,8-dicarboxylate ligand (1,8-nap), caused our attention. It has two carboxyl groups that may be completely or only partly deprotonated and thus results in multiple coordination sites, which may construct structures of higher dimensions. In our previous work, the features of naphthalene-1,8-dicarboxylate have been demonstrated in several complexes which have been reported[12-14]. Herein, we wish to report the hydrothermal synthesis and crystal structure of the first barium complex with two-dimensional (2D) bilayer structure, $[Ba(\mu_5\text{-}1,8\text{-nap})]_n$ (**1**).

1 Experimental

1.1 Materials and measurements

All starting materials and solvents for syntheses were obtained commercially and used without further purification. IR spectra were recorded on an FTIR-8700 spectrometer with KBr pellets in the range of 4 000~400 cm^{-1}. Elemental analysis was performed on a PE-2400(Ⅱ) element analysis instrument. The crystal data collections were carried out on a Bruker SMART APEX-Ⅱ CCD diffractometer. Luminescence spectrum was performed on a HITACHI F-2500 Fluorescence Spectrometer in solid state at room temperature.

1.2 Synthesis of complex 1

A mixture of naphthalene-1,8-dicarboxylate anhydride (0.099 1 g, 0.5 mmol), $BaCl_2 \cdot 2H_2O$ (0.122 1 g, 0.5 mmol), Na_2CO_3 (0.053 g, 0.5 mmol) and water-ethanol (18 mL, V/V=1:1) was sealed in a 25 mL stainless-steel reactor with a Telflon liner and was heated at 433 K for 3 d. On completion of the reaction, the reactor was cooled slowly to room temperature and the mixture was filtered, giving pink single crystals suitable for X-ray analysis in yield 25%. Elemental Anal. Found (%): C, 42.21; H, 1.14. Calcd. For $C_{12}H_6BaO_4$ (%): C, 41.16; H, 1.19. IR (KBr, cm^{-1}): 3 051(w), 1 619(m), 1 557(s), 1 437(s), 1 388(m), 842(m), 784(s).

1.3 X-ray crystallography

Crystal of **1** (0.31 mm×0.18 mm×0.06 mm) was mounted on glass fiber using epoxy resin. Data collection was performed on a Bruker SMART APEX-Ⅱ CCD diffractometer (Mo $K\alpha$ radiation, λ=0.071 073 nm). The data of **1** was collected up to 2θ maximum of 55.12° using the φ-ω scan technique. Data intensity was corrected by Lorentz-polarization factors and empirical absorption. The structure was solved by direct methods and expanded with Fourier techniques. Anisotropic displacement parameters were applied to all non-hydrogen atoms in full-matrix least-squares refinements based on F^2. The hydrogen atoms were assigned with isotropic displacement factors and included in the final refinement cycles by the use of geometrical restrains. All calculations were performed with SHELX-97 package[15]. All pertinent crystallographic data for **1** is summarized in Table 1. The select bond distances and bond angles are listed in Table 2.

CCDC: 778610.

Table 1 Crystallographic data for complex 1

Formula	$C_{12}H_6BaO_4$	μ / mm^{-1}	3.78
Formula weight	351.51	F(000)	664
Temperature / K	296(2)	Crystal size / mm	0.31×0.18×0.06
Crystal system	Monoclinic	θ range / (°)	2.63~27.56
Space group	$P2_1/c$	Limiting indices	$-19 \leqslant h \leqslant 20, -10 \leqslant k \leqslant 10, -10 \leqslant l \leqslant 10$
a / nm	1.551 80(7)	Reflections collected	14 533
b / nm	0.830 32(4)	Reflections unique (R_{int})	2 410 (0.059 3)
c / nm	0.816 72(4)	Refinement method	Full-matrix least-squares on F^2
β / (°)	93.973(3)	Data / restraints / parameters	2 410 / 0 / 154
V / nm^3	1.049 81(9)	Goodness-of-fit on F^2	1.092
Z	4	R_1, wR_2 ($I>2\sigma(I)$)	0.047 9, 0.124 2
D_c / ($g \cdot cm^{-3}$)	2.224	R_1, wR_2 (all data)	0.056 3, 0.135 2

Table 2　Data of selected bond distances (nm) and bond angles (°) of the complex

Ba(1)-O(3)^{i}	0.265 8(4)	Ba(1)-O(4)^{iii}	0.274 7(4)	Ba(1)-O(1)^{i}	0.297 8(4)
Ba(1)-O(4)^{ii}	0.272 0(4)	Ba(1)-O(1)^{iv}	0.277 2(4)	Ba(1)-O(3)^{iii}	0.300 6(4)
Ba(1)-O(2)^{ii}	0.274 1(4)	Ba(1)-O(1)	0.292 8(5)	Ba(1)-O(2)	0.302 8(4)
O(3)^{i}-Ba(1)-O(4)^{ii}	118.52(12)	O(2)^{ii}-Ba(1)-O(1)	127.24(11)	O(2)^{ii}-Ba(1)-O(3)^{iii}	132.82(12)
O(3)^{i}-Ba(1)-O(2)^{ii}	76.86(12)	O(4)^{iii}-Ba(1)-O(1)	73.27(12)	O(4)^{iii}-Ba(1)-O(3)^{iii}	45.13(11)
O(4)^{ii}-Ba(1)-O(2)^{ii}	67.02(12)	O(1)^{iv}-Ba(1)-O(1)	69.62(13)	O(1)^{iv}-Ba(1)-O(3)^{iii}	131.26(11)
O(3)^{i}-Ba(1)-O(4)^{iii}	14.214(12)	O(3)^{i}-Ba(1)-O(1)^{i}	78.50(12)	O(1)-Ba(1)-O(3)^{iii}	96.98(10)
O(4)^{ii}-Ba(1)-O(4)^{iii}	98.99(12)	O(4)^{ii}-Ba(1)-O(1)^{i}	72.84(12)	O(1)^{i}-Ba(1)-O(3)^{iii}	69.36(10)
O(2)^{ii}-Ba(1)-O(4)^{iii}	126.56(13)	O(1)^{i}-Ba(1)-O(2)	58.67(12)	O(3)^{i}-Ba(1)-O(2)	80.00(12)
O(3)^{i}-Ba(1)-O(1)^{iv}	77.64(13)	O(2)^{ii}-Ba(1)-O(1)^{i}	113.17(13)	O(4)^{ii}-Ba(1)-O(2)	123.52(11)
O(4)^{ii}-Ba(1)-O(1)^{iv}	122.70(12)	O(4)^{iii}-Ba(1)-O(1)^{i}	110.37(12)	O(2)^{ii}-Ba(1)-O(2)	156.69(7)
O(2)^{ii}-Ba(1)-O(1)^{iv}	64.53(13)	O(1)^{iv}-Ba(1)-O(1)^{i}	155.85(7)	O(4)^{iii}-Ba(1)-O(2)	74.82(13)
O(4)^{iii}-Ba(1)-O(1)^{iv}	86.69(12)	O(1)-Ba(1)-O(1)^{i}	98.25(12)	O(1)^{iii}-Ba(1)-O(2)	113.04(12)
O(3)^{i}-Ba(1)-O(1)	69.00(12)	O(3)^{i}-Ba(1)-O(3)^{iii}	142.75(10)	O(1)-Ba(1)-O(2)	43.45(10)
O(4)^{ii}-Ba(1)-O(1)	165.74(10)	O(4)^{ii}-Ba(1)-O(3)^{iii}	69.65(11)	O(3)^{iii}-Ba(1)-O(2)	67.59(10)

Symmetry transformations used to generate equivalent atoms: ^{i} x, $-y+1/2$, $z+1/2$; ^{ii} $-x$, $y+1/2$, $-z+1/2$; ^{iii} $-x$, $-y$, $-z$; ^{iv} $4-x$, $-y+1$, $-z$.

2　Results and discussion

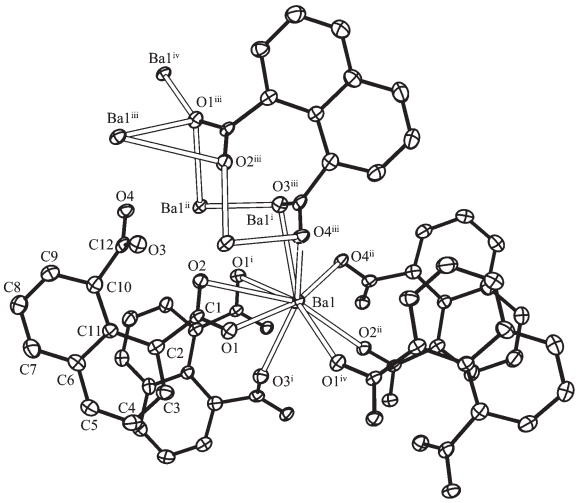
2.1　IR spectrum

The weak peaks 3 051 cm^{-1} of complex **1** are assigned to the C-H stretching vibrations. The conspicuous carboxylate stretching at 1 619, 1 557, 1 437, 1 388 cm^{-1} present two groups of the antisymmetric ν_{as}(COO$^-$) and symmetric stretching frequency ν_s(COO$^-$). The strong band appeared in the 778 cm^{-1} in **1** is ascribed to the asymmetric stretching vibration of the aromatic ring. These data clearly show the formation of the complex **1**.

2.2　Crystal structure of complex 1

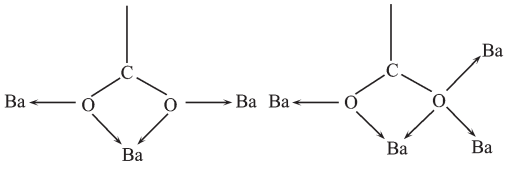
The X-ray diffraction study shows that complex **1** crystallizes in a centrosymmetric space group $P2_1/c$, and the asymmetric unit is composed of one Ba atom, one naphthalene-1,8-dicarboxylate ligand.

As shown in Fig.1, the center Ba(Ⅱ) ion is 9-coordinated to seven carboxylate groups from five 1,8-nap ligands, the Ba-O distances range from 0.265 8(4) to 0.302 8(4) nm are similar to the reported[16]. As to 1,8-nap ligand, the carboxylic groups in complex **1** are all deprotonated, in agreement with the IR spectrum, where no a absorption peak around 1 730 cm^{-1} for protonated carboxylate group is observed. Two carboxylate groups of 1,8-nap represent different coordination modes: bis-bidentate and quinquidentate (Scheme 1). As a result, the whole 1,8-nap ligand acts as μ_5-bridge



Symmetry codes: ^{i} x, $-y+1/2$, $z+1/2$; ^{ii} $-x$, $y+1/2$, $-z+1/2$; ^{iii} $-x$, $-y$, $-z$; ^{iv} $4-x$, $-y+1$, $-z$; Hydrogen atoms are omitted for clarity

Fig.1　Coordination environment of the barium atom in the complex **1** showing 30% probability ellipsoids and the atom-labeling scheme



Scheme 1　Coordination modes of the carboxylate groups in complex **1**

linking five Ba(Ⅱ) atoms.

Each 1,8-nap ligand links five Ba(Ⅱ) atoms and each Ba (Ⅱ) atom attaches to five ligands to form 1D double chains along *c* axis (Fig.2a), both consisting of 4-metal grids with the sizes of 0.453 40(4) nm×0.431 09(4) nm (Ba1-Ba1^{i}×Ba1-Ba1^{ii}). Meanwhile, naphthalene rings exist on sides of double chain, the centroids distance between adjacent naphthalene rings are 0.433 79(2), 0.404 68(2) nm, respectively. Furthermore, the 4-metal grids are extended by the carboxylate group of 1,8-nap ligands along *b* axis, form double chains (Fig.2b). The dihedral angle between the two adjacent naphthalene rings of the two adjacent chains is 0.000(178)° and the distance between their centroids is 0.830 32(4) nm, which means that the two planes are parallel but no π-π stacking interactions exists between them. As a result, such double chains are further extended by the carboxylic groups of 1,8-nap ligands running in the direction of the *b* axis and c axis to form a 2D bilayer framework along the (100) plane (Fig.3).

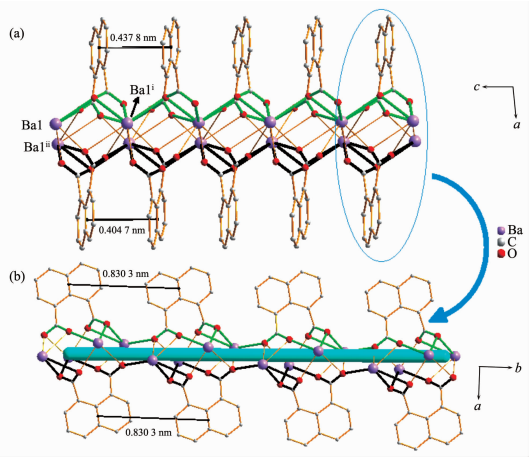
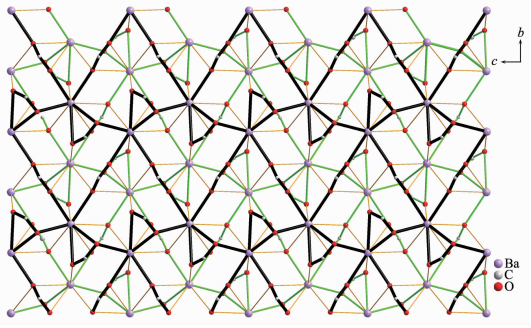


Fig.2 (a) A view of the double chains of complex **1**; (b) 4 grids along *b* axis



Naphthalene rings are omitted for clarity

Fig.3 A view of 2D bilayer framework of complex **1**

2.3 Luminescence property

The solid state luminescence spectrum of complex **1** reveals a emission maximum at approximately 409 nm in the voilet region, while a fluorescent emission band is observed at 449 nm for the naphthalene-1,8-dicarboxylate anhydride, upon excited at 339 nm (Fig.4). It is clear that the blue-shift of emission occurs in complex **1**, which is probably because of the coordination of the 1,8-nap ligand breaks the coplanar effect of the naphthalene-1,8-dicarboxylic anhydride molecule. Photoluminescence behavior is closely associated with the local environment around metal ions[13,17].

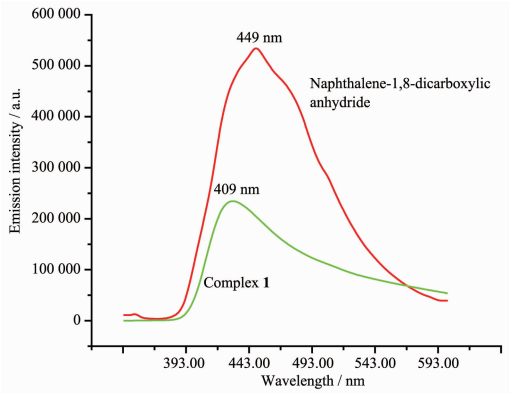


Fig.4 Fluorescence emission spectrum of complex **1** in the solid state at room temperature

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