

A 3D Ba(II) Inorganic-organic Hybrid Framework Based on 1,3,5-Benzenetricarboxylic Acid Ligand: Synthesis and Characterization^①

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ABSTRACT A three-dimensional (3D) barium complex with 1,3,5-benzenetricarboxylic acid (H₃BTC), {[Ba_{1.5}(BTC)(H₂O)]·(H₂O)}_n (**1**), was synthesized in DMF/EtOH/H₂O mixed solution under solvothermal conditions, and characterized by single-crystal X-ray diffraction, elemental analyses, IR spectra, thermogravimetric analyses, and photoluminescence measurement. In complex **1**, the 2D I²O⁰ type inorganic layer is constructed by {Ba₁O₁₀} and {Ba₂O₉} polyhedra. Moreover, the solid-state fluorescence measurement reveals a fluorescence emission band at 465 nm under 344 nm excitation, assigned to a charge-transfer transition.

Keywords: Ba(II) complex, 1,3,5-benzenetricarboxylic acid, I²O⁰ type inorganic layer, fluorescence

1 INTRODUCTION

The past decade has witnessed the rich ongoing research of the design and synthesis of metal-organic coordination compounds (MOCCs) and their potential applications as catalysis, separation, gas storage, optoelectronics, chemical sensors and membranes^[1-7]. Generally, the construction of coordination complex is seriously affected by the bewildering structure-directing factors such as the metal ions, predesigned organic linkers, solvent, pH value of the solution, temperature, counter ion with different bulk or coordination ability, the template and metal-to-ligand stoichiometry, *et. al*^[8, 9]. As we

know, more than thousands of MOCCs were published. 1,3,5-benzenetricarboxylic acid has been proved to make vital contribution to the structural and functional versatility of MOCCs^[10-12].

Meanwhile, the choice of metal ions is another important factor. Most of the research work so far is mainly focused on the incorporation of transition and rare-earth metal ions, whereas less attention is paid to the alkaline-earth ions. Recently, the main group alkaline-earth metals have been getting more and more research attention, owing to their low polarizability and various coordination modes for the construction of polymer materials featuring robust structures and interesting properties^[13].

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At last, extended inorganic hybrids with arrays of inorganic connectivity, $M-X-M$ (M = metal, X = O, Cl, N, or S) became more and more popular in inorganic-organic hybrid materials, because their metal oxides have peculiar magnetic, electronic, and optical properties. The connectivity of extended hybrid framework can be described using I^nO^m notion. I^n is the dimensionality of inorganic connectivity (metal-oxygen-metal), and O^m is the dimensionality of organic connectivity. The sum of $n + m$ is must be less than or equal to 3.5. In recent years, some hybrid frameworks with the diversity of connectivities, such as I^0O^3 , I^1O^0 , I^1O^1 , I^1O^2 , I^2O^0 , and I^2O^1 , have been reported^[14]. Therefore, rational selection of metal ions with well-defined coordination geometries and organic polycarboxylate ligands will play a key role in synthesizing coordination polymers with desired inorganic connectivity and excellent properties.

We report here a 3D Ba(II) inorganic-organic hybrid framework based on 1,3,5-benzenetricarboxylic acid, in which the 2D inorganic Ba-O-Ba layers were found. Moreover, the synthesis, characterization and fluorescent property of complex **1** were also investigated.

2 EXPERIMENTAL

2.1 Materials and methods

All reagents and solvents employed were commercially available and used as received. The structure of complex **1** was determined on a Bruker Apex II CCD diffractometer and solved by direct methods using the SHELXTL program. Elemental analyses were performed by a Vario EL analyzer. IR spectra on KBr pellets were recorded on a FTIR-8400S spectrometer in the range of 4000~400 cm^{-1} . The thermogravimetric analyses were conducted on a ZCT-A analyzer at the heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$ under N_2 atmosphere.

2.2 Synthesis of $\{[\text{Ba}_{1.5}(\text{BTC})(\text{H}_2\text{O})]\cdot(\text{H}_2\text{O})\}_n$ (**1**)

A mixture of $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ (0.1 mmol, 24 mg) and H_3BTC (0.02 mmol, 4 mg) was dissolved in

DMF/EtOH/ H_2O (2/1/1, v/v/v, 1 mL). Then the solution was sealed in a pressure-resistant glass tube, slowly heated to 75 $^\circ\text{C}$ from room temperature in 300 minutes, kept at 75 $^\circ\text{C}$ for 3000 minutes, and then slowly cooled to 30 $^\circ\text{C}$ in 500 minutes. The colorless needle-shaped crystals formed were collected and dried in air. Yield 47% based on H_3BTC . Anal. Calcd. (%) for $\text{C}_9\text{H}_7\text{Ba}_{1.5}\text{O}_{11}$ (497.16): C, 21.74; H, 1.42. Found (%): C, 21.65; H, 1.54. IR (KBr, cm^{-1}): 3388 (s), 1614 (s), 1543 (s), 1437 (s), 1367 (s), 1109 (m), 773 (m), 721 (m), 517 (w).

2.3 Data collection and structure refinement

Data collection for complex **1** (0.12mm \times 0.11mm \times 0.10mm) was performed on a Bruker Smart APEX II CCD diffractometer at 293 K by using a graphite-monochromatic $\text{MoK}\alpha$ radiation (λ = 0.71073 \AA). A total of 25844 reflections with 3315 unique ones (R_{int} = 0.0870, R_{sigma} = 0.0549) were collected in the range of $6.44 \leq 2\theta \leq 54.96^\circ$. The final R = 0.0370 ($I > 2\sigma(I)$) and wR = 0.1009 (all data). Structural solutions were performed by direct methods using SHELXS-97^[15] program and the structures were refined by full-matrix least-squares techniques with SHELXL-97^[16]. All non-hydrogen atoms were placed in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2 . The organic hydrogen atoms were geometrically generated and refined by a riding mode. The selected bond lengths and bond angles are summarized in Table 1.

3 RESULTS AND DISCUSSION

3.1 Structural description

Complex **1** belongs to orthorhombic, space group $Pbcn$ (no. 60) with a = 20.812(4), b = 6.6495(13), c = 20.865(4) \AA , V = 2887.5(10) \AA^3 , Z = 8, D_c = 2.287 g/mm^3 , M_r = 497.16, the final R = 0.0370 and wR = 0.947 with $I > 2\sigma(I)$. Complex **1** features a 3D porous framework. Interestingly, it contains a 2D Ba-O-Ba inorganic layer with BTC ligands, so the structure of **1** should be classified as I^2O^0 type. Single-crystal X-ray diffraction reveals that com-

plex **1** crystallizes in the orthorhombic system with *Pbcn* space group. The asymmetry unit of **1** contains one point five Ba(II) ions, one BTC³⁻ anion, one coordinated water molecule and one lattice water molecule. As shown in Fig. 1, Ba(1) is ten-coordinated by six carboxylate oxygen atoms (O(1), O(1^a), O(2), O(2^a), O(6^c), O(6^e)) from four individual BTC ligands and four bridging oxygen atoms (O(7), O(7^d), O(9), O(9^d)). Ba(2) is nine-coordinated by four carboxylate oxygen atoms (O(2), O(3^b), O(4^b), O(5^c)) from three different BTC

ligands, four bridging oxygen atoms (O(7), O(8), O(8^c), O(9)) and one oxygen atom (O(1w)) from coordinated water molecule (Fig. 1a). The bond lengths of Ba–O carboxylate bonds range from 0.2716(4) to 0.2952(4) nm with the mean of 0.283(4) nm and the Ba–O(1w) bond is 0.2740(4) nm, which compare well with the average values determined from those of reported Ba(II)-BTC compounds. Selected bond lengths and bond angles are listed in Table 1.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for Complex **1**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Ba(1)–O(1)	2.851(4)	Ba(1)–O(2 ^a)	2.856(4)	Ba(1)–O(6 ^b)	2.721(4)
Ba(1)–O(7)	2.896(4)	Ba(1)–O(9)	2.952(4)	Ba(2)–O(1w)	2.740(4)
Ba(2)–O(2)	2.716(3)	Ba(2)–O(3 ^d)	2.806(4)	Ba(2)–O(4 ^d)	2.944(4)
Ba(2)–O(5 ^c)	2.764(4)	Ba(2)–O(7)	2.901(4)	Ba(2)–O(8)	2.940(4)
Ba(2)–O(8 ^c)	3.035(4)	Ba(2)–O(9)	2.871(4)		
Angle	(°)	Angle	(°)	Angle	(°)
O(1)–Ba(1)–O(1 ^a)	151.47(17)	O(1 ^a)–Ba(1)–O(2 ^a)	45.50(10)	O(1)–Ba(1)–O(2 ^a)	123.89(10)
O(1 ^a)–Ba(1)–O(7 ^a)	110.10(11)	O(1 ^a)–Ba(1)–O(7)	75.92(11)	O(1 ^a)–Ba(1)–O(9)	60.58(12)
O(1)–Ba(1)–O(9)	95.45(12)	O(2)–Ba(1)–O(2 ^a)	146.21(16)	O(2)–Ba(1)–O(7 ^a)	121.12(11)
O(2)–Ba(1)–O(7)	66.52(11)	O(2)–Ba(1)–O(9 ^a)	85.97(12)	O(6 ^b)–Ba(1)–O(1 ^a)	128.71(11)
O(6 ^b)–Ba(1)–O(1)	78.24(11)	O(2)–Ba(2)–O(7)	68.24(11)	O(2)–Ba(2)–O(8)	73.61(11)
O(2)–Ba(2)–O(8 ^c)	96.09(10)	O(2)–Ba(2)–O(9)	69.57(12)	O(3 ^d)–Ba(2)–O(4 ^d)	44.92(12)
O(3 ^d)–Ba(2)–O(7)	76.33(11)	O(3 ^d)–Ba(2)–O(8 ^c)	102.19(11)	O(3 ^d)–Ba(2)–O(8)	78.26(13)
O(3 ^d)–Ba(2)–O(9)	113.59(13)	O(4 ^d)–Ba(2)–Ba(1)	148.92(8)	O(4 ^d)–Ba(2)–O(8 ^c)	57.43(10)
O(5 ^c)–Ba(2)–Ba(1)	90.55(7)	O(7)–Ba(2)–Ba(1)	40.64(7)	O(5 ^c)–Ba(2)–O(3 ^d)	141.43(13)
O(5 ^c)–Ba(2)–O(4 ^d)	119.55(11)	O(5 ^c)–Ba(2)–O(7)	130.00(10)	O(5 ^c)–Ba(2)–O(8)	131.73(10)
O(5 ^c)–Ba(2)–O(8 ^c)	72.56(10)	O(5 ^c)–Ba(2)–O(9)	66.87(11)	O(7)–Ba(2)–O(4 ^d)	110.41(11)
O(7)–Ba(2)–O(8 ^c)	144.58(12)	O(1w)–Ba(2)–Ba(1)	134.43(11)	O(1w)–Ba(2)–O(3 ^d)	73.90(14)
O(1w)–Ba(2)–O(7)	133.01(15)	O(1w)–Ba(2)–O(8 ^c)	77.65(14)	O(1w)–Ba(2)–O(9)	92.88(14)

Symmetry codes: ^a–x, y, 0.5–z; ^b–0.5+x, –0.5+y, 0.5–z; ^c0.5–x, –0.5+y, z; ^d0.5–x, 0.5–y, –0.5+z; ^e0.5–x, 0.5+y,

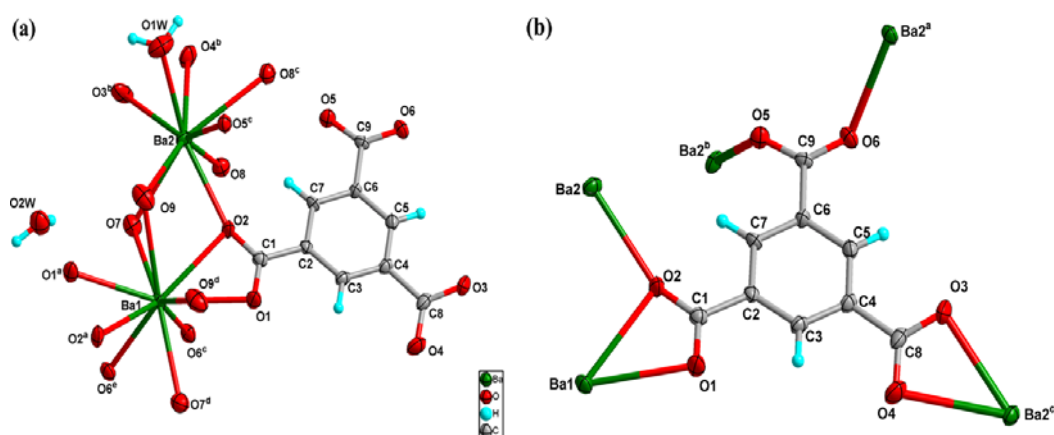


Fig. 1. (a) Coordination environment of Ba²⁺ in complex **1** (Symmetry codes: a –x, y, 0.5–z; b = 0.5–x, 0.5–y, –0.5+z; c = 0.5–x, 0.5+y, z; d = –x, y, 0.5–z; e = –0.5+x, –0.5+y, 0.5–z); (b) Coordination mode of BTC³⁻ in complex **1** (Symmetry codes: a = 0.5+x, 0.5+y, 0.5–z; b = 0.5–x, –0.5+y, z; c = 0.5–x, 0.5–y, 0.5+z)

In complex **1**, the crystallographic unique BTC^{3-} molecule adopts a $\mu_7:\eta^3\eta^2\eta^3$ coordination mode to bind five different Ba(II) ions. Three are three types of coordination modes for the carboxyl groups: (1) $\mu_2:\eta^2\eta^1$ bridging mode, (2) $\mu_2:\eta^1\eta^1$ bridging mode and (3) $\mu_1:\eta^1\eta^1$ chelating mode (Fig. 1b).

Each $\{\text{Ba}_1\text{O}_{10}\}$ polyhedron shares two surfaces, six edges and six corners with two neighboring $\{\text{Ba}_2\text{O}_9\}$ polyhedra. Each $\{\text{Ba}_2\text{O}_9\}$ polyhedron shares one surface, three edges and five corners with three neighboring $\{\text{BaO}_{10}\}$ polyhedra. Then,

these connectivities link the polyhedra into a 2D inorganic Ba–O–Ba layer (Fig. 2). Finally, the BTC^{3-} ligands link the 2D layers into a 3D inorganic-organic hybrid framework, so the structure of **1** should be classified as I^2O^0 type. Ma *et al.* reported a 3D fish-netted topological network based on Ba(II) and BTC^{3-} ligands, in which the Ba(II) ions are seven- and nine-coordinated. Yao *et al.* reported a 2D I^2O^0 type inorganic layer framework built from $\{\text{Ba}_1\text{O}_8\}$, $\{\text{Ba}_2\text{O}_9\}$ and $\{\text{Ba}_3\text{O}_8\}$ polyhedra (Fig. 3).

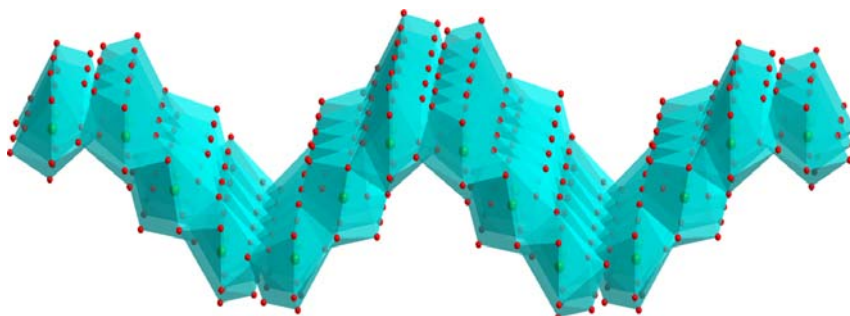


Fig. 2. 2D inorganic Ba-O-Ba layer in complex **1**

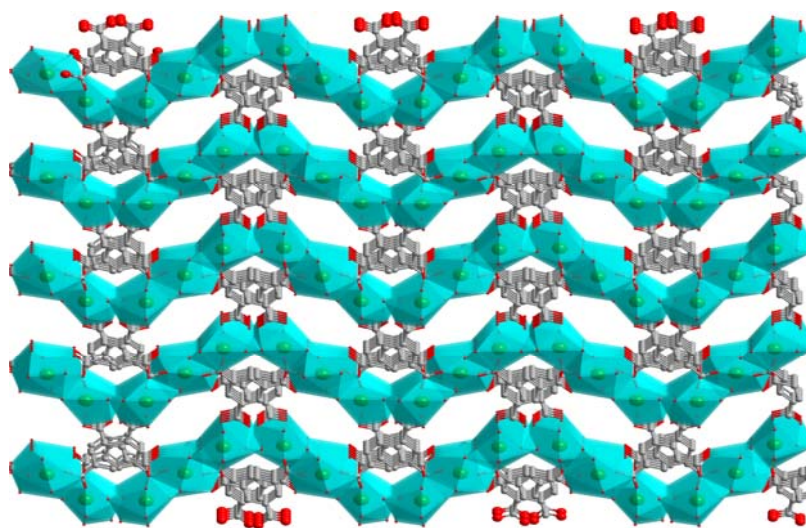


Fig. 3. 3D structure of complex **1**

3.2 IR spectrum

In the IR spectra of complex **1**, the characteristic broad peak at 3388 cm^{-1} means the coordination of water molecule. The asymmetric stretching vibration ($\nu_{\text{as}}(\text{COO}^-)$) and symmetric stretching vibration ($\nu_{\text{s}}(\text{COO}^-)$) of carboxylate groups appear at 1614, 1437 and 1543 and 1367 cm^{-1} , respectively. The $\Delta\nu$

($\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$) are 177 and 176 cm^{-1} ($< 200\text{ cm}^{-1}$) in **1**. These values indicate that the carboxylate groups coordinate in a bidentated mode^[17-20].

3.3 Thermogravimetric analyses

The thermogravimetric (TG) analyses of the title complex **1** under N_2 atmosphere at a heating rate of

$10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ were investigated in the temperature range of $25\sim 1000\text{ }^{\circ}\text{C}$ and the TG curve is shown in Fig. 4. The TG curve of **1** displays the first weight loss of 7.35% at $25\sim 116\text{ }^{\circ}\text{C}$, which corresponds to the departure of one lattice and one coordinated water molecules (Calcd. 7.24%). The dehydrated framework is stable to $571\text{ }^{\circ}\text{C}$, and then the framework begins to collapse, accompanying the release of organic ligands.

3.4 Luminescent property

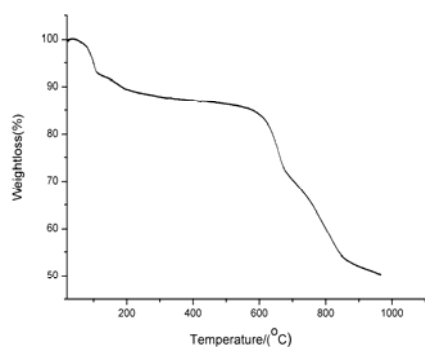


Fig. 4. TG curve of complex **1**

4 CONCLUSION

In summary, the synthesis and characterization of a 3D barium complex with 1,3,5-benzenetricarboxylic acid (H_3BTC) was described. In complex **1**,

The photoluminescent properties of free ligand and complex **1** were investigated in the solid state at room temperature (Fig. 5). The free H_3BTC shows a main emission in the visible region at 428 nm ($\lambda_{\text{excitation}} = 344\text{ nm}$), whereas complex **1** shows an emission band at 465 nm. The emission of H_3BTC was ascribed to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ electronic transitions. The emission of complex **1** can be assigned to a charge-transfer transition rather than the $\pi^* \rightarrow n$ transition of organic ligand^[10].

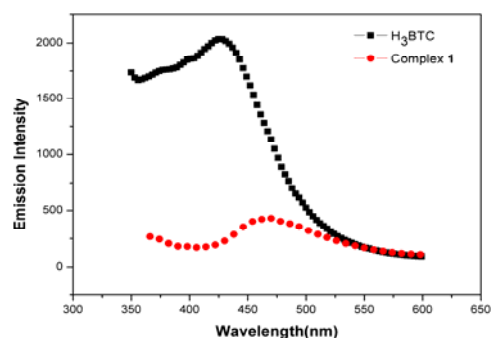


Fig. 5. Emission spectra of **1** and free ligand (H_3BTC) in the solid state at room temperature

2D I^2O^0 type inorganic layer was constructed by $\{\text{Ba}_1\text{O}_{10}\}$ and $\{\text{Ba}_2\text{O}_9\}$ polyhedra. Additionally, complex **1** reveals a fluorescence emission band at 465 nm under 344 nm excitation, which can be assigned to a charge-transfer transition.

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