

Hydrothermal synthesis, crystal structures and properties of two alkaline earth metal coordination polymers with 3D pillared open framework structures based on trifunctional aromatic ligands

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Two novel alkaline earth metal coordination polymers, $[\text{Sr}(\text{HL})(\text{H}_2\text{O})]_n$ (**1**) and $[\text{Ba}(\text{HL})(\text{H}_2\text{O})_{1.5}]_n$ (**2**) (NaH_2L = 5-sulfoisophthalic monosodium salt), have been synthesized by hydrothermal reactions. The central strontium and barium atoms have been eight- and nine-coordinate with the distorted bicapped trigonal prism and monocapped square anti-prism, respectively. The whole HL^{2-} ligands act as hexadentate linkers to generate the homometallic 3D (4, 12)-type lattice-like topologies with the nonequivalent six-connected nodes based on central metal ions. In the solid state, both **1** and **2** show blue photoluminescence with the maximum emission intensities at 398 and 471 nm upon excitation at 315 nm, respectively.

Keywords: Hydrothermal synthesis, Open framework, Crystal structure, Coordination polymer

The design and construction of metal-organic frameworks (MOFs) is one of the most active areas of materials research. This intense interest is driven by their potential applications in catalysis, magnetism, electric conductivity, and non-linear optics and for their fascinating topologies and intriguing architectures¹⁻¹⁰. One of the key steps to assemble unusual architectures is to select appropriate organic ligands containing functional coordinating groups, and rigid multidentate ligands are a good choice¹¹⁻¹³. The aromatic carboxylate ligands are frequently used for construction of MOFs, due to the diversity of the coordination modes and high structural stability, such as benzoic acid¹⁴, benzenedicarboxylate^{15,16} and 1,3,5-benzenetricarboxylate¹⁷. However, introduction of a sulfonate group into rigid carboxylate ligands may result in the formation of novel open frameworks, as the coordination of the sulfonate group may form highly flexible frameworks, which can lead to a potential for structural transformation involving a significant rearrangement of the bonds in the solid¹⁸. The sulfonate group is able to perform a wide range of coordination modes, which can result in diverse open frameworks and properties^{19,20}.

NaH_2L is considered as a multifunctional ligand, acts as a good candidate for synthesizing multifunctional MOFs. To the best of our knowledge, it has been chosen to build open frameworks owing to

the following three considerations: (i) It contains two kinds of functional groups and multiple coordination sites, which can yield high dimensional structures; (ii) It has an asymmetric geometry, which may lead to acentric crystal structures for the development of non-linear optical materials; (iii) Its rigidity can facilitate the formation of 3D pillared open frameworks.

Numerous MOFs with varied dimensions and topologies have been obtained through a judicious choice of organic ligands and metal ions²¹⁻²³. Many of the efforts have so far been devoted to the study of transition-metal-based coordination polymers. Compared to the transition metals, alkaline-earth metals are still rarely studied as building units for coordination polymers. The alkaline earth metal ions bearing large radii may exhibit different coordination geometries with diverse coordination numbers, which could provide the unique opportunity for the discovery of new coordination systems. Additionally, the relatively large radii and high affinities of Sr and Ba ions for oxygen donors, make them promising candidates for constructing coordination polymers based on multifunctional systems. A series of new Sr and Ba based coordination polymers have been reported with the diverse topologies²⁴⁻²⁶, such as the coordination polymers, $\{\text{Sr}_{1.5}(\text{ptc})\cdot 5\text{H}_2\text{O}\}_n$, $\{[\text{Ba}(\text{ptc})(\text{H}_2\text{O})][\text{Ba}(\text{ptcH}_2)(\text{H}_2\text{O})]\}_n$ (ptcH_3 = pyridine-2,4,6-tricarboxylic acid), exhibiting different dimensionality depending on

the nature of the metal ions²⁴, [Sr(5-OH-BDC)(H₂O)₄].H₂O and [Ba(5-OHBDC)(H₂O)₃] (5-OH-H₂BDC = 5-hydroxyisophthalic acid), revealing two-dimensional networks with (6, 3) topology²⁵, [Ba(Pzdc)(H₂O)]_n and [Ba(Pzdc)]_n (H₂Pzdc = 2,3-pyrazinedicarboxylic acid), showing 2D layer networks generated by one-dimensional chains containing the [Ba₂O₁₁N] units²⁶.

Herewith, we report on the hydrothermal synthesis and characterization of two alkaline earth metal coordination polymers with 3D pillared (4, 12)-type network structures constructed by HL²⁻ ligands. Accurate photoluminescent, thermogravimetric analyses, and IR measurements were performed.

Materials and Methods

All reagents were purchased from commercial sources and used without further purification. X-ray single crystal diffraction data were collected at 298(2) K from a single crystal mounted atop a glass fiber with a Bruker Apex-II diffractometer using graphite-monochromated Mo K_α (λ = 0.71073 Å) radiation. Elemental analyses were performed on a Perkin-Elmer 240C instrument. The FT-IR spectra were recorded on a Nicolette FTIR spectrometer using KBr pellets in the range of 4000–400 cm⁻¹. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 10 °C·min⁻¹ under a nitrogen atmosphere. Photoluminescence analyses were performed on a Perkin-Elmer LS55 fluorescence spectrometer.

Synthesis of compound 1

A mixture of NaH₂L (0.268 g, 1 mmol) and Sr(NO₃)₂ (0.212 g, 1 mmol) in distilled water (15 mL) was stirred at room temperature for 1 h. Afterwards, CH₃CH₂OH (5 mL) was added to the clear solution and sealed in a 25 mL Teflon lined stainless steel container, which was heated at 150 °C for 2 days. After the sample was cooled to room temperature, colorless blocked crystals were obtained (yield: 70% based on Sr). Anal. (%) Calcd.: C₈H₅O₈SSr: C, 27.52; H, 1.43. Found (%): C, 27.81; H, 1.77. IR (KBr cm⁻¹): ν(O-H) = 3546, ν(CO₂⁻) = 1700, 1608, 1400, ν(C=C) = 1560, δ(OH) = 1457, ν(SO₃²⁻) = 1280, 1240, 1116, 1064, δ(C-H) = 889, 757, ν(C-S) = 700, ν(Sr-O) = 626^{27,28}.

Synthesis of compound 2

A mixture of NaH₂L (0.268 g, 1 mmol) and Ba(NO₃)₂ (0.261 g, 1 mmol) in distilled water (15 mL) was stirred at room temperature for 1 h. Afterwards, CH₃CH₂OH (5 mL) was added to the clear solution and

sealed in a 25 mL Teflon lined stainless steel container, which was heated at 120 °C for 4 days. After the sample was cooled to room temperature, colorless blocked crystals were obtained (yield: 72% based on Ba). Anal. (%) Calcd.: C₈H₇O_{8.50}SBa: C, 23.50; H, 1.71. Found (%): C, 23.72; H, 1.95. IR (KBr cm⁻¹): ν(O-H) = 3542, ν(CO₂⁻) = 1700, 1604, ν(C=C) = 1554, 1436, δ(OH) = 1398, ν(SO₃²⁻) = 1278, 1199, 1118, 1049, δ(C-H) = 892, 771, ν(C-S) = 698, ν(Ba-O) = 626^{27,28}.

X-ray crystallographic measurement

Data collection for compounds **1-2** were carried out on a Bruker Smart CCD diffractometer equipped with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) at 298 K. Data reduction was performed with SAINT²⁹, and empirical absorption corrections were applied by the SADABS program. Structures were solved by direct methods using the SHELXS program and refined with the SHELXL program³⁰. Heavy atoms and other non-hydrogen atoms were directly obtained from a difference Fourier map. Final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F². C-bonded H atoms were placed geometrically and refined as riding model. O-bonded H atoms were placed in idealized positions and constrained to ride on their parent atoms. For compound **1**, the coordinated water molecule (O8) is disordered. For compound **2**, the sulfonate oxygen atoms (O6 and O7) and the coordinated water molecules (O8 and O9) are disordered. The atomic occupancy rate of the water atom (O9) is 0.5. Crystal data as well as details of data collection and refinement for compounds **1-2** are summarized in Table 1. Selected bond distances and bond angles are given in Table 2. Hydrogen bond lengths and bond angles are listed in Table 3.

Results and Discussion

Structure description of compound 1

Single-crystal X-ray crystallographic analysis reveals that compound **1** crystallizes in the monoclinic, space group *P2₁/n*. The asymmetry unit of compound **1** consists of one crystallographically independent strontium ion, one HL²⁻ ligand, and one coordinated water molecule, as shown in Fig. 1a. The coordination arrangement of the strontium atom is eight-coordinate with a distorted bicapped triangle prism (Fig. 1b). Its coordination sites are occupied by four oxygen atoms (O1, O2, O3 and O1^{IV}) from four carboxylate oxygen atoms, three sulfonate oxygen

Table 1 — Crystal data and structure refinement for compounds **1-2**

	1	2
Chemical formula	C ₈ H ₆ O ₈ SSr	C ₈ H ₇ O _{8.50} SBa
<i>M_r</i>	349.8	408.54
Crystal system, space group	Monoclinic, <i>P2₁/n</i>	Monoclinic, <i>P2₁/c</i>
Temperature (K)	296	298
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.196 (3), 17.360 (7), 9.065 (5)	7.4190 (6), 17.7431 (15), 9.8859 (8)
β (°)	109.548 (5)	118.003 (2)
<i>V</i> (Å ³)	1067.2 (8)	1148.98 (16)
<i>Z</i>	4	4
μ (mm ⁻¹)	5.28	3.67
Crystal size (mm)	0.27×0.25×0.22	0.21×0.17×0.10
<i>T_{min}</i> , <i>T_{max}</i>	0.330, 0.390	0.513, 0.710
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	7741, 1873, 1719	5680, 2017, 1612
<i>R_{int}</i>	0.041	0.039
(sin θ/λ) _{max} (Å ⁻¹)	0.595	0.595
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.029, 0.077, 1.06	0.034, 0.064, 1.09
No. of reflections	1873	2017
No. of parameters	172	191
No. of restraints	12	0
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.58, -0.61	0.79, -0.77

Table 2 — Selected Bond Lengths (Å) and Bond Angles (°) for compounds **1-2**

Compound 1		Compound 2					
Sr1-O6 ⁱ	2.548 (3)	Sr1-O1 ^{iv}	2.551 (3)	Ba1-O2 ⁱⁱⁱ	2.723 (4)	Ba1-O6 ⁱ	2.823 (14)
Sr1-O7 ⁱⁱ	2.516 (3)	Sr1-O2	2.646 (3)	Ba1-O8	2.753 (5)	Ba1-O1	2.849 (4)
Sr1-O8	2.580 (4)	Sr1-O3	2.662 (3)	Ba1-O5 ^{iv}	2.768 (4)	Ba1-O2	2.857 (4)
Sr1-O5	2.482 (3)	Sr1-O1	2.667 (3)	Ba1-O3 ^v	2.817 (4)	Ba1-O7 ⁱⁱ	2.866 (19)
				Ba1-O9	2.965 (10)		
O5-Sr1-O7 ⁱⁱ	97.85 (13)	O8-Sr1-O2	129.06 (15)	O2 ⁱⁱⁱ -Ba1-O8	73.71 (15)	O2 ⁱⁱⁱ -Ba1-O2	70.06 (12)
O5-Sr1-O6 ⁱⁱⁱ	152.82 (11)	O5-Sr1-O3	75.94 (11)	O2 ⁱⁱⁱ -Ba1-O5 ^{iv}	73.00 (13)	O8-Ba1-O2	110.79 (15)
O7 ⁱⁱ -Sr1-O6 ⁱⁱⁱ	80.71 (11)	O7 ⁱⁱ -Sr1-O3	79.53 (9)	O8-Ba1-O5 ^{iv}	136.38 (13)	O5 ^{iv} -Ba1-O2	83.05 (12)
O5-Sr1-O1 ^{iv}	132.86 (13)	O6 ⁱⁱⁱ -Sr1-O3	77.12 (9)	O2 ⁱⁱⁱ -Ba1-O3 ^v	153.81 (14)	O3 ^v -Ba1-O2	109.83 (11)
O7 ⁱⁱ -Sr1-O1 ^{iv}	94.92 (10)	O1 ^{iv} -Sr1-O3	151.18 (10)	O8-Ba1-O3 ^v	126.92 (14)	O6 ⁱ -Ba1-O2	108.5 (4)
O6 ⁱⁱⁱ -Sr1-O1 ^{iv}	74.07 (10)	O8-Sr1-O3	132.34 (14)	O5 ^{iv} -Ba1-O3 ^v	80.94 (12)	O1-Ba1-O2	45.18 (10)
O5-Sr1-O8	67.75 (14)	O2-Sr1-O3	67.73 (8)	O2 ⁱⁱⁱ -Ba1-O6 ⁱ	139.0 (3)	O2 ⁱⁱⁱ -Ba1-O7 ⁱⁱ	88.8 (3)
O7 ⁱⁱ -Sr1-O8	76.09 (17)	O5-Sr1-O1	92.46 (13)	O8-Ba1-O6 ⁱ	68.8 (2)	O8-Ba1-O7 ⁱⁱ	78.0 (4)
O6 ⁱⁱⁱ -Sr1-O8	136.39 (13)	O7 ⁱⁱ -Sr1-O1	163.27 (9)	O5 ^{iv} -Ba1-O6 ⁱ	147.8 (4)	O5 ^{iv} -Ba1-O7 ⁱⁱ	73.9 (4)
O1 ^{iv} -Sr1-O8	71.78 (14)	O6 ⁱⁱⁱ -Sr1-O1	96.02 (10)	O3 ^v -Ba1-O6 ⁱ	66.9 (3)	O3 ^v -Ba1-O7 ⁱⁱ	81.4 (3)
O5-Sr1-O2	77.80 (10)	O1 ^{iv} -Sr1-O1	68.49 (10)	O2 ⁱⁱⁱ -Ba1-O1	113.35 (11)	O6 ⁱ -Ba1-O7 ⁱⁱ	98.9 (3)
O7 ⁱⁱ -Sr1-O2	147.10 (8)	O8-Sr1-O1	95.91 (17)	O8-Ba1-O1	135.58 (15)	O1-Ba1-O7 ⁱⁱ	142.7 (3)
O6 ⁱⁱⁱ -Sr1-O2	88.73 (9)	O2-Sr1-O1	48.32 (8)	O5 ^{iv} -Ba1-O1	83.97 (12)	O2-Ba1-O7 ⁱⁱ	152.5 (4)
O1 ^{iv} -Sr1-O2	112.08 (9)	O3-Sr1-O1	115.93 (8)	O3 ^v -Ba1-O1	65.38 (10)	O2 ⁱⁱⁱ -Ba1-O9	85.0 (2)
				O6 ⁱ -Ba1-O1	84.0 (2)	O8-Ba1-O9	63.7 (3)
				O5 ^{iv} -Ba1-O9	138.6 (2)	O1-Ba1-O9	73.1 (3)
				O3 ^v -Ba1-O9	117.5 (2)	O2-Ba1-O9	56.3 (2)
				O6 ⁱ -Ba1-O9	64.1 (5)	O7 ⁱⁱ -Ba1-O9	141.5 (4)

Symmetry codes for compound **1**: (i) *x*-1, *y*, *z*; (ii) -*x*, -*y*, -*z*; (iii) *x*+1, *y*, *z*; (iv) -*x*+1, -*y*, -*z*+1.

Symmetry codes for compound **2**: (i) *x*, -*y*+3/2, *z*+1/2; (ii) -*x*+1, *y*-1/2, -*z*+3/2; (iii) -*x*+1, -*y*+1, -*z*+1; (iv) *x*+1, -*y*+3/2, *z*+1/2; (v) *x*+1, *y*, *z*+1.

atoms (O5, O6 and O7), and one coordinated water molecule (O8). The Sr-O bond lengths are in the range of 2.482(3) Å to 2.667(3) Å. The O-Sr-O bond angles are between 48.32(8)° and 163.27(9)°

(Table 2). These distances and angles are comparable to those observed in other reported metal carboxylate-sulfonates³¹. The whole HL²⁻ ligand acts as a μ⁶η⁶ coordination mode (Fig. 1c). In each HL²⁻ ligand, one

Table 3 — Hydrogen Bond Lengths (Å) and Bond Angles (°) for compounds 1-2

D-H...A	d(D-H)	d(H...A)	d(D...A)	DHA
Compound 1				
O8-H8B...O6 ⁱ	0.840	1.860	2.653(3)	156.00
O9-H9A...O3 ⁱⁱ	0.850	1.850	2.694(3)	174.00
O9-H9B...O7 ⁱⁱⁱ	0.840	2.170	2.953(3)	155.00
O10-H10A...O1 ^{iv}	0.890	1.770	2.661(3)	179.00
O10-H10B...O8 ⁱⁱⁱ	0.880	2.390	3.265(3)	177.00
O10-H10B...O6 ^{iv}	0.880	2.590	3.061(3)	115.00
O11-H11A...O7 ^v	0.840	1.970	2.785(3)	166.00
O11-H11B...O4 ^v	0.810	2.030	2.811(3)	161.00
Compound 2				
O8-H8A...O9 ⁱ	0.840	2.440	3.121(6)	139.00
O8-H8B...O6 ⁱⁱ	0.840	1.830	2.623(7)	157.00
O9-H9A...O3 ⁱⁱⁱ	0.840	1.830	2.670(6)	176.00
O9-H9B...O7 ^{iv}	0.840	2.120	2.911(6)	156.00
O10-H10A...O1 ^v	0.890	1.720	2.611(6)	178.00
O10-H10B...O8 ^{iv}	0.880	2.310	3.190(6)	178.00
O10-H10B...O6 ^v	0.880	2.510	2.994(6)	115.00
O11-H11A...O7 ^{vi}	0.840	1.950	2.774(5)	167.00
O11-H11B...O4 ^{vi}	0.810	2.000	2.790(5)	163.00
C6-H6...O10 ^{viii}	0.930	2.380	3.258(6)	157.00
C8-H8...O6	0.930	2.530	2.893(6)	103.00

Symmetry transformations for compound 1: (i): $1-x, 1-y, -1/2+z$; (ii): $-x, 1-y, 1/2+z$; (iii): $-1+x, y, z$; (iv): $-x, 1-y, -1/2+z$; (v): $-1/2+x, 3/2-y, z$. Symmetry transformations for compound 2: (i): $1+x, y, z$; (ii): $1-x, 1-y, -1/2+z$; (iii): $-x, 1-y, 1/2+z$; (iv): $-1+x, y, z$; (v): $-x, 1-y, -1/2+z$; (vi): $-1/2+x, 3/2-y, z$; (vii): $1/2+x, 3/2-y, 1+z$.

sulfonate group coordinates with three strontium ions in a $\mu^3 \eta^3$ coordination mode, one carboxylate group coordinates to one strontium ion by monodentate coordination, and the other carboxylate group chelates and bridges with two strontium ions.

Structure descriptin of compound 2

The X-ray crystal structure of compound 2 reveals the presence of a molecular lattice, as shown in Fig. 2a, which crystallizes in the monoclinic system, $P2_1/c$ space group. The structure consists of one barium ion, one HL^{2-} ligand, one and a half coordinated water molecules. The coordination sphere of barium ion is an O-donor atom sphere, created by two different types of ligands, namely, HL^{2-} ligand and water molecule. Each HL^{2-} ligand can employ one sulfonate group to coordinate with three barium ions through its three deprotonated hydroxides, adopt one oxygen atom (O3) of one carboxylate group to linker one barium ion, with the remaining hydroxide staying in the noncoordination form, utilize the other carboxylate group coordinates to two barium ions, adopting $\mu^2 \eta^1$ - and $\mu^1 \eta^2$ -coordination modes. In view

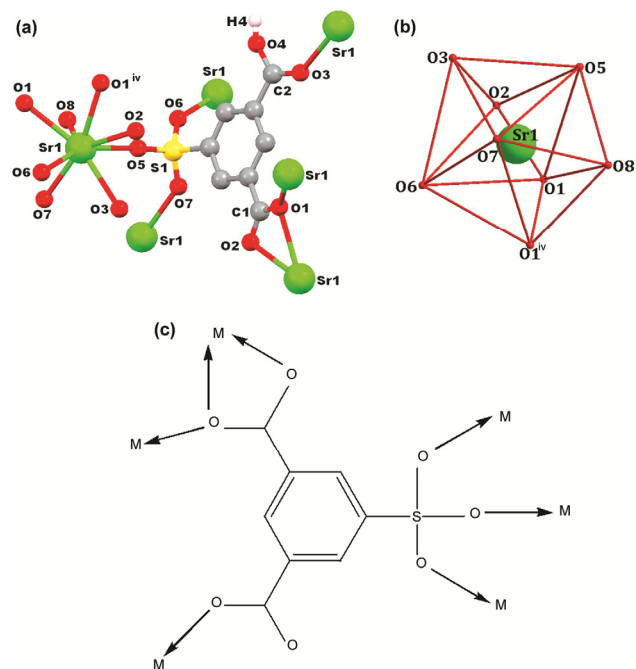


Fig. 1 — (a) The molecular structure of compound 1. The asymmetric structure unit of compound 1 with atomic labeling scheme. All hydrogen atoms, but H4 are omitted for clarity. (b) Sr1 ion exhibits a bicapped trigonal prism geometry. (c) The coordination mode of HL^{2-} ligand.

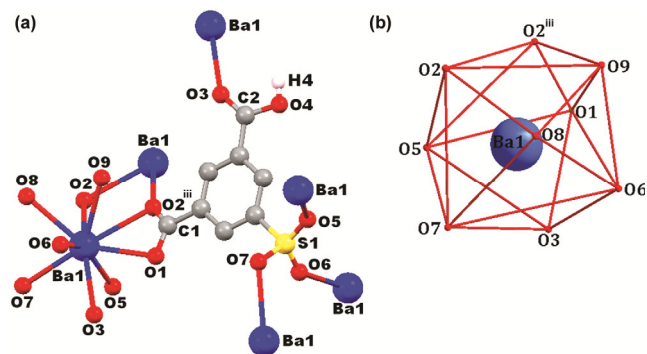


Fig. 2 — (a) The molecular structure of compound 2. The asymmetric structure unit of compound 2 with atomic labeling scheme. All hydrogen atoms, but H4 are omitted for clarity. (b) Ba1 ion exhibits a monocapped square anti-prism geometry.

of this description, the barium is nine-coordinated, and the coordination geometry can be described as a monocapped square anti-prism, as shown in Fig. 2b, where O1, O2, O3, O5, O2ⁱⁱⁱ, O6, O7 and O9 atoms can generate a square anti-prism, capped by O8 atom. The Ba-O distances are of similar length in the range of 2.723(4)–2.965(10) Å, the O-Ba-O angles are in the range of 45.18(10)–153.81(14)°, which are similar with those found in barium complexes containing O-donor ligands³². The HL^{2-} ligand in compound 2 shows the same coordination mode with that of compound 1.

The HL^{2-} ligands anchored onto the strontium and barium coordination sites are observed in compounds **1-2**, respectively. Compared compounds **1-2**, it is considered that the same coordination mode of HL^{2-} ligands in compounds **1-2** is adopted, forming the similar topological structures. However, it can reveal a different coordination mode with the ones previously observed in metal carboxylate-sulfonates^{32, 33}. As reported, one rare earth coordination polymer $[Dy(L)(H_2O)_4]$ was synthesized by hydrothermal method. In each L^{3-} anion, two carboxylate groups take the same $\mu^1-\eta^1:\eta^1$ coordination mode, the sulfonate group coordinates to one dysprosium ion by monodentate coordination. The whole ligand L^{3-} acts as a μ^3 bridge to coordinate with three different dysprosium ions, generating a wave-like two-dimensional network with (6,3) topological structure³³. The complex $[Ba_3(L)_2(H_2O)_9]\cdot H_2O$ was synthesized by hydrothermal method. In each L^{3-} ligand, the two carboxylate functions adopt $\mu^2-\eta^1:\eta^1$ -bridging and $\mu^2-\eta^2:\eta^1$ -bridging modes, respectively. The sulfonate group takes a μ^3 -coordination mode to coordinate to three different barium atoms. The ladder-like one-dimensional chains are generated by the coordination of sulfonate groups with the barium atoms, which are further connected by $\mu^2-\eta^1:\eta^1$ -bridging carboxylate functions to form wave-like two-dimensional networks. These two-dimensional networks are further linked by benzene rings to generate a three-dimensional structure³². In addition, as reported, the whole L^{3-} ligand displays other diverse coordination modes, such as $\mu^2\eta^1$, $\mu^2\eta^2$, $\mu^3\eta^2$, $\mu^3\eta^3$, $\mu^4\eta^2$, $\mu^4\eta^4$, $\mu^5\eta^4$, $\mu^5\eta^5$, $\mu^5\eta^6$, $\mu^6\eta^4$, $\mu^6\eta^5$ and $\mu^7\eta^7$, which together with the versatile coordination ability of the bridging ligand makes it adaptable to metal ions of different sizes and leads to the various topologies of the coordination networks^{27, 28, 31-35}.

The HL^{2-} ligands in compounds **1-2** exhibit the same coordination mode. Only the pillared layered structure of compound **2** is described herein in detail, as shown in Fig. 3. The barium ions are bridged by the HL^{2-} ligands through the trifunctional groups to generate a 3D network, as shown in Fig. 3a. The $\eta^3\mu^3$ -sulfonate group, $\eta^1\mu^1$ and $\eta^2\mu^2$ -carboxylate groups bridge the barium ions to form a 2D layer extending in ac plane, as shown in Fig. 3b. The layer features three types of rings. The two carboxylate oxygen atoms (O2 and O2ⁱⁱⁱ) can bridge to the two neighboring barium atoms, forming a 4-membered ring [Ba1-O2-Ba1-O2ⁱⁱⁱ], where the Ba...Ba separation is 4.57 Å. Both of sulfonate oxygen atoms (O5 and O7) bridge two neighboring barium atoms, generating an eight-membered ring [Ba1-O5-S1-O7-Ba1-O5-S1-O7]. Two sulfonate oxygen atoms

(O5 and O6) can bridge two 4-membered rings [Ba1-O2-Ba1-O2ⁱⁱⁱ], generating a 12-membered ring [Ba1-O5-S1-O6-Ba1-O2-Ba1-O5-S1-O6-Ba1-O2]. The two adjacent layers are bridged by HL^{2-} ligands to form a 3D pillared open framework structure. The distance between the adjacent layers is 8.94 Å. Up to now, a large number of pillared open frameworks have been reported, such as pillared framework $Zn_2(3,5-Pdc)_2(H_2O)_2(bipy)$ (3,5-Pdc = 3,5-pyridinecarboxylate)³⁶, POM column pillared MOF $H\{[Ag_3(3-pytz)_2(H_2O)]_2\cdot[AgSiW_{12}O_{40}]\}\cdot 2H_2O$ (3-pytz=5-(3-pyridyl)-1H-tetrazole)³⁷, pillared-layer framework $[Co_2(bpdc)_2(H_2bpz)]\cdot 2(DMF)\cdot 5(H_2O)$ (H_2bpdc = 4,4'-biphenyl dicarboxylic acid, H_2bpz = 3,3',5,5'-tetramethyl-4,4'-bipyrazole)³⁸.

To best understand the structure of the compound **2**, the topology analysis is employed. Each barium ion is coordinated to six neighboring HL^{2-} ligands, so that the barium atoms can act as 6-connected nodes. Both carboxylate oxygen atoms (O2 and O2ⁱⁱⁱ) and both sulfonate oxygen atoms (O5 and O7) can bridge two

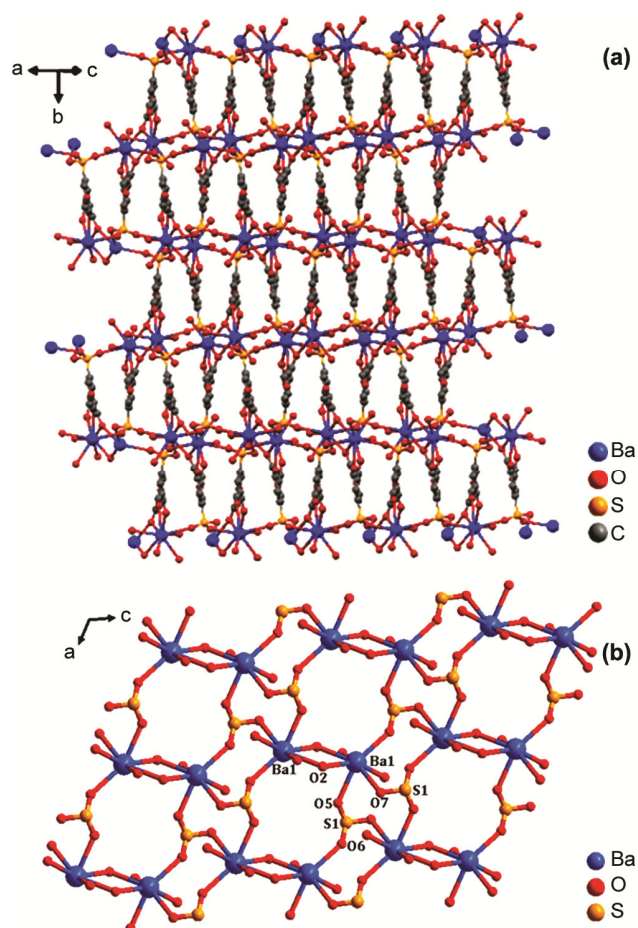


Fig. 3 — (a) The 3D pillared structure of compound **2**, and, (b) 2D layer structure along b axis.

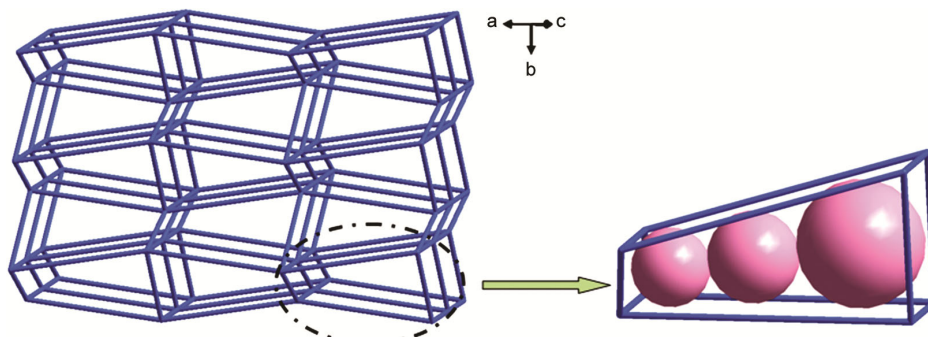


Fig. 4 — Schematic representation of the 3D (4, 12)-type topological network structure of compound 2.

barium atoms to form $[\text{Ba}_2\text{O}_2]$ and $[\text{Ba}_2\text{S}_2\text{O}_4]$ structural units, respectively, which can be simplified as the sticks. Both barium atoms can be interconnected by a pair of sulfonate oxygen atoms (O5 and O6), which can be regarded as the stick. These sticks can be formed to 2D layers in a horizontal and vertical connection with barium ions acting as connected nodes. Each HL^{2-} ligand can bridge barium atoms via one sulfonate group and two carboxylate groups, respectively. These ligands are alternately arranged into a ladder-like type in the opposite fashion, which support the layers. Such unit can be regarded as a pillared column to generate a 3D (6,12)-type pillared open framework structure, as shown in Fig. 4. The (6,12)-type open framework constructed from HL^{2-} ligands and alkaline earth metal ions has never been observed in coordination chemistry. From the description above, we can see that two factors play important roles in the formation of 3D pillared open framework structure: (i) the barium ions can provide the 6-connecting nodes; (ii) the rigid bridging linker HL^{2-} ligands play a supporting role through coordination modes.

Hydrogen bonding interactions are present in the crystal structures of compounds 1-2. Hydrogen bonding interactions are listed in Table 3. These interactions involve the coordinated water molecules, the carboxylate and sulfonate oxygens on the ligands. Collectively, the hydrogen bonds generate an extensive network, which likely contribute to the overall stability of the crystal lattices in compounds 1-2.

X-ray powder diffraction

In order to check the purity of compounds 1-2, X-ray powder diffraction patterns have been measured and compared with the simulation from the single-crystal structures. As can be seen in Fig. 5, the measured and simulated XRPD patterns for compounds 1 and 2 match well. Consequently, it can be considered that

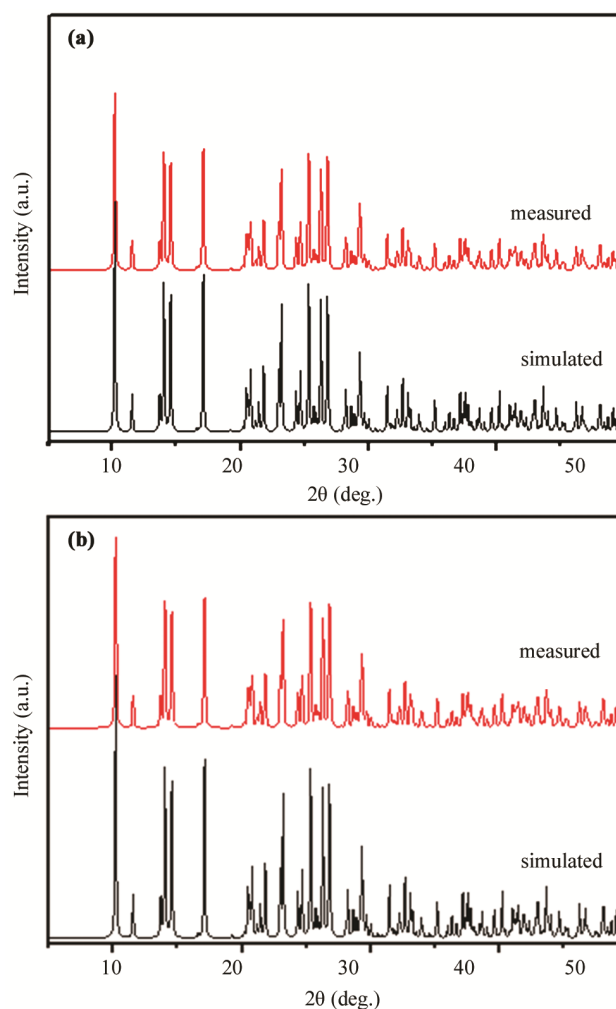


Fig. 5 — The simulated and measured PXRD patterns of (a) compounds 1, and, (b) compound 2.

the bulk of the as-prepared materials represent the pure phases of compounds 1 and 2³⁹.

Thermal analyses

The thermogravimetric diagrams of compounds 1-2 indicate three main steps of weight losses, as shown

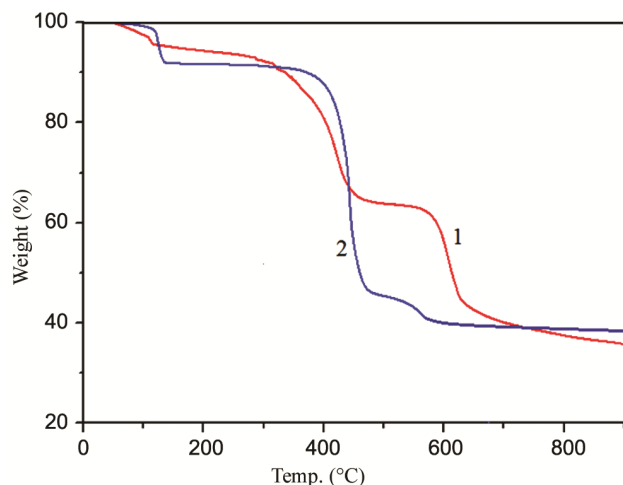


Fig. 6 — TGA curves for compounds 1-2.

in Fig. 6. The first steps are completed at 169 °C (for compound 1) and 177 °C (for compound 2), which correspond to the losses of the coordinated water molecules, respectively. The observed weight losses of 5.3% for compound 1 and 7.1% for compound 2 are in good agreement with the calculated values (5.1% for compound 1 and 6.6% for compound 2), respectively. The deaquation temperature ranges support the presence of H-bonding among the coordinated water molecules and HL^{2-} ligands. On further heating, the dehydrated compounds continue to decompose. Upto 800 °C, the total weight losses are ca. 64.2% for compound 1 and 60.7% for compound 2, respectively. It is observed that the decomposing processes are not complete due to the use of N_2 atmosphere, hence, the final products are assumed to be the mixture of metal oxides and metal sulfates²⁸.

Luminescent properties

Photoluminescent properties of alkaline earth metal compounds are not well studied as compared with those of transition metal and rare earth metal complexes, although there are reports on the photoluminescent properties of alkaline earth metal-containing materials⁴⁰. Furthermore, previous studies have shown that MOFs exhibit photoluminescent properties⁴¹. Hence, we investigated the photoluminescent properties of compounds 1-2. The room temperature solid state photoluminescent spectra of compounds 1-2 and its related ligand are presented in Fig. 7. The free ligand displays photoluminescent emission at 358 nm upon excitation at 315 nm, which may be attributed to $\pi-\pi^*$ or $n-\pi^*$ transition of the ligand. Compound 1 exhibits

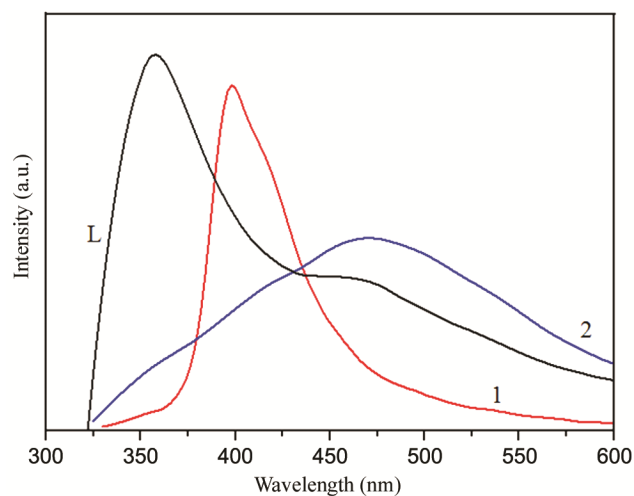


Fig. 7 — Solid-state emission spectra of NaH_2L ligand and compounds 1-2 at room temperature.

photoluminescent emission with the maximum at 398 nm, which is similar to that of the ligand under the same excitation wavelength. It is only slightly shifted toward higher wavelength (the red-shift is 40 nm), compared to the emission of free ligand. This indicates that the emission band in compound 1 arises neither from metal-to-ligand nor from ligand-to-metal charge transfer, but is probably due to $\pi-\pi^*$ intraligand fluorescence³². Compound 2 exhibits photoluminescent emission with the maximum at 471 nm upon excitation at 315 nm, which occurs at much longer wavelength (the red-shift is 113 nm) than that of the free ligand. The large bathochromic shift indicates that the aromatic rings of the ligands are effectively interacting with the metal ions. It can be assigned to the ligand-to-metal charge transfer⁴¹. The similar bathochromic shift is also observed in other metal complex with the same ligand⁴². The blue emissions of compounds 1-2 in the solid state imply that both complexes may be potentially applicable as materials for blue-light-emitting diode devices^{42,43}.

Conclusions

In conclusion, the self-assembly of the alkaline earth metal ions with HL^{2-} ligands affords two novel coordination polymers, $[Sr(HL)(H_2O)]_n$ and $[Ba(HL)(H_2O)_{1.5}]_n$. They feature 3D pillared open frameworks with unique (4, 12)-type network structures based on nonequivalent 6-connected nodes and the hexadentate bridging HL^{2-} ligands. Both compounds at room temperature exhibit blue photoluminescence with the maximum emission at 398 nm and 471 nm in the solid state, revealing the

potential application in the blue-light-emitting diode devices.

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