

基于刚性四面体含硅配体构筑的两个钴配位聚合物及其结构多样性

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摘要: 基于四齿刚性羧酸配体 $H_4L(H_4L=4,4',4'',4'''$ -silanetetrayltetrabenzoic acid) 在水热条件下合成了 2 个微孔配位聚合物, 分别是 $[CoL][NH_2(CH_3)_2] \cdot 2.25H_2O$ (**1**) 和 $[Co_3L_2]H_3O]_2 \cdot 4DMA$ (**2**) ($DMA=N,N$ -二甲基乙酰胺)。晶体结构分析表明这 2 个化合物均属于正交晶系, 晶体 **1** 的空间群是 $Pbca$, 晶胞参数是 $a=2.270\ 2(2)$ nm, $b=1.456\ 5(7)$ nm, $c=2.826\ 4(7)$ nm, 晶体 **2** 的空间群是 $Pnna$, 晶胞参数是 $a=2.698\ 2(3)$ nm, $b=2.188\ 2(2)$ nm, $c=1.382\ 1(9)$ nm。化合物 **1** 是由四面体型的单核钴和 4-连接的配体构成的 sra 拓扑的三维结构。化合物 **2** 是由三核钴 $\{Co_3(COO)_8\}$ 和 4-连接的四面体型配体构成的、带有一维孔道的双节点(4,8)-连接的 alb 三维网络结构。讨论了由 H_4L 构成的配位聚合物的结构多样性。

关键词: 配位聚合物; 晶体结构; 钴; 配体

中图分类号: O614.81²

文献标识码: A

文章编号: 1001-4861(2015)05-0981-08

DOI: 10.11862/CJIC.2015.125

Structural Diversity of Coordination Polymers Built from a Rigid Silicon-Based Tetracarboxylate Linker

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Abstract: By using a rigid tetrapodal carboxylate linker $4,4',4'',4'''$ -silanetetrayltetrabenzoic acid (H_4L), two open-framework coordination polymers, namely, $[CoL][NH_2(CH_3)_2] \cdot 2.25H_2O$ (**1**) and $[Co_3L_2]H_3O]_2 \cdot 4DMA$ (**2**) ($DMA=N,N$ -Dimethylacetamide), were solvothermally synthesized and structurally characterized. The crystal structure analyses indicate that both compounds crystallize in orthorhombic system. The unit cell parameters for compound **1** are space group $Pbca$, $a=2.270\ 2(2)$ nm, $b=1.456\ 5(7)$ nm, $c=2.826\ 4(7)$ nm, and for compound **2**, space group $Pnna$, $a=2.698\ 2(3)$ nm, $b=2.188\ 2(2)$ nm, $c=1.382\ 1(9)$ nm. Compound **1** is a 3D framework built on tetrahedral Co units and a 4-connecting ligand L to give a 4-connected sra structure. Compound **2** is a 3D 2-nodal (4,8)-connected alb network with small 1D channels built from a trinuclear $\{Co_3(COO)_8\}$ unit and a 4-connected tetrahedral L ligand. The structure diversity of H_4L -based MOFs is discussed. CCDC: 1011878, **1**; 1011879, **2**.

Key words: coordination polymer; crystal structure; cobalt; ligand

收稿日期: 2014-10-30。收修改稿日期: 2015-02-03。

国家自然科学基金(No.21471075), 973 项目(No.2011CB808704)资助。

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0 Introduction

The design and synthesis of porous metal-organic frameworks (MOFs) aiming at exploration of potential applications and fascinating topology have been a subject of intensive research during the past decade^[1-2]. The structure and property of MOFs are highly dependent on the geometry and coordination environment of the metal ions and selection of organic linkers. In most cases, the structural integrity and rigidity of the ligands remain unaltered throughout the assembly process, which could help to realize predesigned structural topology. Considerable efforts have been devoted to the synthesis of new rigid ligands. A series of rigid tetrapodal ligands such as 4,4',4'',4'''-methanetetrayltetrabenzoic acid^[3], 4',4'',4''',4''''-methanetetrayltetrakis (([1,1'-biphenyl]-4-carboxylic acid))^[4] and 4, 4', 4'', 4'''-(4, 4', 4'', 4'''-methanetetrayltetrakis(4,1-phenylene)tetra-kis(ethyne-2,1-diyl)) tetrabenzoic acid^[5] were prepared and successfully used in the construction of porous MOFs. In these MOFs, the ligands adopt a tetrahedral coordination geometry, resulting in *flu*, *pts*, *dia* and *itl* topologies with open frameworks.

Recently, several silicon-based tetrahedral ligands, *e.g.* 5, 5', 5'', 5'''-silanetetrayltetraisophthalic acid^[6] and 4,4',4'',4'''-silanetetrayltetrabenzoic acid^[7-11] (H_4L), were prepared during the course of constructing new MOFs. Compared to the carbon counterparts, these silicon-based tetracarboxylate ligands are more synthetically accessible and showed unique features such as increased bond angle flexibility at the silicon center and decreased conformational rigidity^[8], which makes them promising candidates for constructing new MOFs. Previously, we reported the construction of lanthanide metal-organic frameworks with highly-connected topology, demonstrating that H_4L is a versatile ligand in the construction of MOFs with unusual structures^[7]. As an extension to our studies, we herein report the synthesis of two open-framework coordination polymers, $[CoL][NH_2(CH_3)_2]_2 \cdot 2.25H_2O$ (**1**) and $[Co_3L_2][H_3O]_2 \cdot 4DMA$ (**2**) ($DMA=N,N$ -Dimethylacetamide), based on the rigid tetrapodal ligand H_4L ,

further showing that H_4L is a good candidate for construction of coordination polymers with diverse structures.

1 Experimental

1.1 Materials and General methods

All the chemicals except the ligand H_4L were commercially purchased and used without further purification. The ligand H_4L was synthesized according to a literature method^[7]. Elemental analyses of C, H, N were performed on an Elementar Vario MICRO Elemental Analyzer. Fourier transformed Infrared (FTIR) spectra were obtained on a Bruker Vector 22 FTIR spectrophotometer by using KBr pellets. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer thermal analyzer under nitrogen with a heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ range of $5^\circ \sim 50^\circ$ with a scan speed of $0.1^\circ \cdot \text{s}^{-1}$ on a Bruker D8 Advance instrument using a Cu $K\alpha$ radiation ($\lambda=0.154\ 056\text{ nm}$) at room temperature.

1.2 Synthesis

$[CoL][NH_2(CH_3)_2]_2 \cdot 2.25H_2O$ (**1**): A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.029 g, 0.1 mmol) and H_4L (0.025 5 g, 0.05 mmol) in 6 mL of DMA and three drops of HCl ($6\text{ mol} \cdot \text{L}^{-1}$) was sealed in an autoclave equipped with a Teflon liner (25 mL) and heated at $120\text{ }^\circ\text{C}$ for 3 days. Purple block single crystals of **1** were collected in a *ca.* 29% yield based on H_4L . Elemental analysis for $C_{32}H_{36.5}CoN_{2.0}O_{10.25}Si$, Calcd. (%): C, 54.89; H, 5.25; N, 4.00. Found(%): C, 54.94; H, 5.31; N, 4.27. IR data (KBr, cm^{-1}): 3 442(w), 2 918 (w), 1 670 (m), 1 614(s), 1 566(w), 1 507(w), 1 398(s), 1 289(w), 1 245(s), 1 173(m), 1 126(w), 989(m), 827(w), 783(s), 682(w), 618(w).

$[Co_3L_2][H_3O]_2 \cdot 4DMA$ (**2**): A mixture of $CoCl_2 \cdot 6H_2O$ (0.023 5 g, 0.1 mmol) and H_4L (0.025 5 g, 0.05 mmol) in 2 mL of H_2O , 4 mL of DMA and two drops of HCl ($6\text{ mol} \cdot \text{L}^{-1}$) was sealed in an autoclave equipped with a Teflon liner (25 mL) and heated at $120\text{ }^\circ\text{C}$ for 3 days. Purple block single crystals of **2** were collected in a *ca.* 33% yield based on H_4L . Elemental analysis for $C_{72}H_{74}Co_3N_4O_{22}Si_2$, Calcd. (%):C,

54.72; H, 4.72; N, 3.55. Found (%):C, 54.65; H, 4.79; N, 3.42. IR data (KBr, cm^{-1}): 3 419 (w), 2 929 (w), 1 666 (s), 1 604(s), 1 555(w), 1 509(w), 1 417(s), 1 327 (w), 1 302(m), 1 240(s), 1 176(s), 1 164(m), 1 105(w), 992(s), 871(w), 785(s), 682(w), 609(w).

1.3 Single Crystal X-ray Crystallography

The suitable crystals of compounds **1** and **2** were selected for single-crystal X-ray diffraction. The data collections were carried out on a Bruker Smart APEX II CCD diffractometer at 296 K, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). Data reductions and absorption corrections were performed using the SAINT and SADABS programs^[12], respectively. The structures were solved by direct methods using the SHELXS-97 program and refined with full-matrix least squares on F^2 using the SHELXL-

97 program^[13]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water molecules were not located for compound **1**. In addition, the hydrogen atoms of the water molecules could not be located for compound **2**. Because of the highly disordered solvent molecules in compounds **1** and **2**, the PLATON/SQUEEZE route was employed to calculate the diffraction contribution from the solvent molecules, and thereby to produce a set of solvent-free diffraction intensities^[14]. The final formula were derived from crystallographic data combined with elemental and thermogravimetric analyses data. Details of the crystal parameters, data collection and refinements for complexes **1** and **2** are summarized in Table 1. Selected bond lengths and angles are shown in Table 2.

CCDC: 1011878, **1**; 1011879, **2**.

Table 1 Crystallographic Data for Compounds **1** and **2**

Compound	1	2
Empirical formula	$\text{C}_{32}\text{H}_{36.5}\text{CoN}_2\text{O}_{10.25}\text{Si}$	$\text{C}_{72}\text{H}_{74}\text{Co}_3\text{N}_4\text{O}_{22}\text{Si}_2$
Formula weight	700.16	1 580.34
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pbca$	$Pnna$
a / nm	2.270 2(2)	2.698 2(3)
b / nm	1.456 5(7)	2.188 2(2)
c / nm	2.826 4(7)	1.382 1(9)
V / nm^3	9.346 3(10)	8.161 0(14)
Z	8	4
θ range / ($^\circ$)	1.70~25.00	1.51~25.00
μ / mm^{-1}	0.432	0.681
$F(000)$	2 852	2 508
Reflections collected	44 707	38 885
Independent reflections	8 178	7 124
R_{int}	0.079 7	0.100 2
R_1^a, wR_2^b ($I > 2\sigma(I)$)	0.087 1, 0.223 1	0.079 5, 0.201 6
R_1^a, wR_2^b (all data)	0.145 5, 0.239 2	0.110 8, 0.211 9
Goodness of fit on F^2	1.039	1.018

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

Table 2 Selected bond lengths (nm) and angles ($^\circ$) of compounds **1** and **2**

1					
Co1-O2	0.198 6(3)	Co1-O6 ⁱ	0.192 8(3)	Co1-O8 ⁱⁱⁱ	0.202 5(3)
Co1-O4 ⁱⁱ	0.197 3(3)				

Continued Table 2

O2-Co1-O8 ⁱⁱⁱ	107.3(1)	O2-Co1-O4 ⁱⁱ	110.4(1)	O6i-Co1-O2	132.9(1)
O4 ⁱⁱ -Co1-O8 ⁱⁱⁱ	98.6(1)	O6i-Co1-O8 ⁱⁱⁱ	107.8(1)	O6i-Co1-O4 ⁱⁱ	94.2(1)
2					
Co1-O6	0.221 6(3)	Co1-O7 ⁱⁱ	0.2023(3)	Co1-O10 ⁱⁱⁱ	0.202 5(4)
Co2-O6	0.203 5(4)	Co2-O9 ^{iv}	0.1973(4)	Co2-O12 ^{vi}	0.200 1(6)
Co2-O8 ⁱ	0.198 6(4)				
O6 ^v -Co1-O6	177.4 (3)	O8 ⁱⁱ -Co2-O6	103.8(2)	O10 ⁱⁱⁱ -Co1-O6 ^v	94.6(2)
O7 ⁱⁱ -Co1-O6 ^v	86.6(2)	O8 ⁱⁱ -Co2-O9 ^{iv}	103.5(2)	O10 ^{iv} -Co1-O6 ^v	87.3(2)
O7 ⁱ -Co1-O6 ^v	91.5(1)	O8 ⁱⁱ -Co2-O12 ^{vi}	101.3(3)	O10 ⁱⁱⁱ -Co1-O10 ^{iv}	85.8(3)
O7 ⁱ -Co1-O7 ⁱⁱ	86.2(2)	O9 ^{iv} -Co2-O6	106.2(2)	O12 ^{vi} -Co2-O6	142.2(3)
O7 ⁱ -Co1-O10 ⁱⁱⁱ	173.9(2)	O12 ^{vi} -Co2-O9 ^{iv}	94.8(3)		

Symmetry codes for **1**: ⁱ 1.5-x, 2-y, 0.5+z; ⁱⁱ 0.5+x, 1.5-y, -z; ⁱⁱⁱ 0.5+x, 2.5-y, -z. For **2**: ⁱ 0.5-x, 1-y, z; ⁱⁱ 0.5-x, 0.5+y, 1.5-z; ⁱⁱⁱ -x, 1-y, 1-z; ^{iv} -x, 0.5+y, 0.5+z; ^v x, 1.5-y, 1.5-z; ^{vi} x, y, 1+z

2 Results and discussion

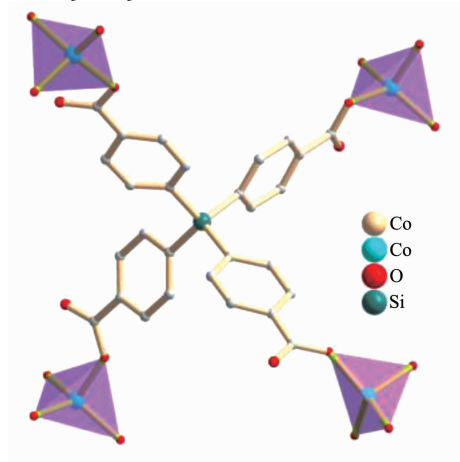
2.1 Structure description

2.1.1 Crystal structure analysis of **1**

The single crystal X-ray diffraction studies reveal that compound **1** crystallizes in the orthorhombic space group *Pbca* with eight asymmetric units in one unit cell. Each asymmetric unit in **1** contains one crystallographically independent Co atom, one crystallographically independent L ligand, two NH₂(CH₃)₂⁺ counter-ions and four water molecules (half-occupied O1w and one quarter-occupied O2w, O3w, O4w). The NH₂(CH₃)₂⁺ cations were likely generated via either hydrolysis of DMA under solvothermal

conditions, which is not without precedent^[15]. As shown in Fig.1, each Co atom coordinates to four carboxylate groups from four different L⁴⁻ ligands in a tetrahedral geometry. The Co-O distances range from 0.198 3(5) to 0.201 4 (5) nm, which are in normal ranges^[16]. The ligand H₄L, with its center Si atom sitting on the S₄-symmetry tetrahedron centre, is fully deprotonated and coordinates via its four carboxylate groups to four Co atoms by monodentate coordination mode.

As shown in Fig.2a, each ligand L in **1** connects four Co centers, while each Co center connects to four L ligands, forming a highly opened 3D framework. The single-layer network contains 1D channels run along the crystallographic *b*- and *c*-axes with pore sizes of *ca.* 1.60 nm × 1.10 nm and 0.90 nm × 0.45 nm (considering the van der Waals radii of H atom), respectively, by measuring the interatomic distances between the nearest protruding H atoms. However, the framework of **1** is 2-fold interpenetrated, with the voids filled with disordered solvent molecules. PLATON^[14] calculations show that the guest accessible void (3.840 9 nm³ per unit cell) comprises 41.1% of the unit cell volume. From a topological viewpoint, compound **1** can be considered as a 4-connected network. Both ligand L and Co center act as a four-connected node. This gives rise to a doubly-interpenetrating 4-connected *sra* net with a point



H atoms are omitted for clarity

Fig. 1 Coordination environments of the tetrahedral L in **1**

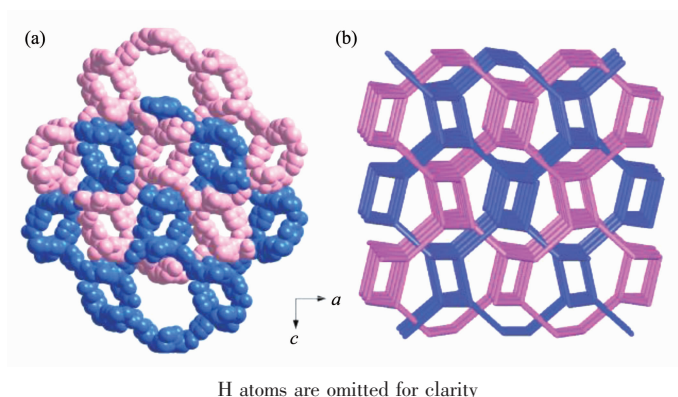


Fig.2 Space-filling (a) and topological (b) views of **1**, showing 2-fold interpenetrated framework

symbol of $\{4^2.6^3.8\}$ (Fig.2b), as calculated with TOPOS program^[17].

2.1.2 Crystal structure analysis of **2**

The single crystal X-ray diffraction studies reveal that compound **2** crystallizes in the orthorhombic space group $Pnna$ with four asymmetric units in one unit cell. Each asymmetric unit in **2** contains two crystallographically independent Co atoms (half-occupied Co1, fully-occupied Co2), one crystallographically independent L ligand, and four H_3O^+ counter-ions (one-quarter-occupied). As shown in Fig.3, Co1 atom is octahedrally coordinated by six oxygen atoms from six different carboxylate groups. Four of these carboxylate groups are in bis-monodentate chelating modes ($\mu-\eta^1:\eta^1$). The other two carboxylate groups are in monodentate bridging modes linking two metal centers via just one of their oxygen atoms, leaving another oxygen uncoordinated. The Co2 atom is tetrahedrally coordinated by two bridging bis-monodentate ($\mu-\eta^1:\eta^1$) carboxylates, one bridging

carboxylate oxygen, and a terminal monodentate carboxylate. Each trinuclear SBU $\{Co_3(OOC)_8\}$ is composed of Co1, Co2 and Co2A, which is symmetry-related to Co2. The Co-O distances range from 0.198 3(7) to 0.221 7(6) nm, which are in normal ranges^[16]. The ligand H_4L is fully deprotonated and coordinates via its four carboxylate groups to four trinuclear $\{Co_3(OOC)_8\}$ units in monodentate, bidentate and bridging coordination modes (Fig.3b), forming a complicated 3D open framework structure.

The structure of **2** shows small 1D channels with a window size of 0.30 nm×0.30 nm along the c axis, in which the disordered solvent molecules locate (Fig. 4a). The solvent accessible volume is estimated by using the PLATON program^[14] to be about 23.8% of the total crystal volume.

A better insight into the nature of **2** can be achieved by the application of topological approach, i.e. reducing a multidimensional structure to a simple node-and-linker net. The trinuclear $\{Co_3(OOC)_8\}$ SBU

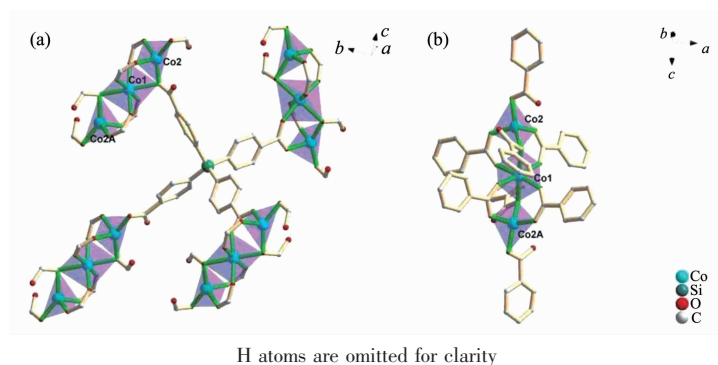
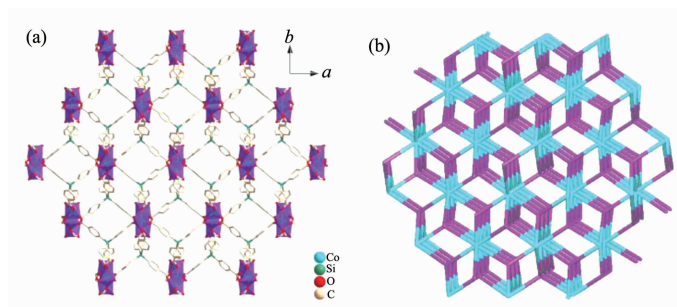


Fig.3 Coordination environments of the tetrahedral L in **2**

is described as a pentagonal dodecahedron and regarded as an eight-connected node. Each L ligand, which bonds to four $\{\text{Co}_3(\text{OOC})_8\}$ inorganic units, is regarded as a four-connected organic SBU. On the basis of this simplification, the structure of **2** is represented as a

binodal (4,8)-connected *alb* net. Its Schflfli symbol is calculated by using the TOPOS program^[17] as $\{4^4 6^2\}_2 \{4^8 6^{17} 8^3\}$ (Fig.4b). It is noted that the structure of **2** has the same connectivity as that of $[\text{Me}_2\text{NH}_2]_2[\text{Zn}_3(\text{L})_2](\text{DMF})_6(\text{IMP-11})^{[8c]}$ and $\text{Zn}_3(\text{HL})_2(\text{PCN-511})^{[9]}$.



H atoms are omitted for clarity

Fig.4 (a) Packing view of **2**, showing small channels along the *c* axis; (b) View of the (4,8)-connected framework of **2** with *alb* topology

2.2 Structure Diversity of H₄L-based MOFs

The tetrahedrally-connected MOFs have been known to constitute the largest subclass of MOFs^[16]. There are quite a few known MOFs based on the rigid tetrahedral carboxylic acid H₄MTB (H₄MTB=4, 4', 4'', 4'''-methanetetrayltetrabenzoic acid)^[3,19], an analogue to H₄L. In these compounds, the organic ligand H₄MTB all adopts a tetrahedral coordination geometry. The resulting structures mainly depend on the coordination geometry of inorganic units, such as square paddle-wheel units $\{\text{Cu}_2\}$ and $\{\text{Zn}_2\}$, tetrahedrally-connected $\{\text{Ni}(\text{cyclam})\}$, 8-connecting cyclotetranuclear clusters $\{\text{Cd}_4\}$, $\{\text{Co}_4\}$, $\{\text{Ni}_4\}$, and $\{\text{Zr}_6\}$, and 12-connecting $\{\text{Zr}_6\}$ units, resulting in *pts*, *dia*, *flu*, and *itb* topologies.

In comparison, the silicon-counterpart 4,4',4'',4'''-silanetetrayltetrabenzoic acid (H₄L) has demonstrated diverse coordination chemistry, due to the increased C-Si-C bond angle, decreased conformational rigidity and longer Si-C bond lengths in H₄L compared with H₄MTB^[7-11]. Davies and co-workers constructed an IMP series of MOFs based on H₄L^[8]. Among those MOFs, the organic ligand H₄L can adopt a regular and distorted tetrahedral coordination geometry, forming MOFs with different topological nets as a result of subtle differences in inorganic SBUs, *e.g.* IMP-5 (*sra*

net with tetrahedral $\{\text{Zn}_2\}$), IMP-8 (rod-like $\{[\text{M}(\text{O}_2\text{C})_2]_n\}$ SBU, M=Cd, Mn), IMP-9 (*pts* net with paddle-wheel $\{\text{Cu}_2\}$), IMP-10 (4,8-net with distorted hexagonal bipyramidal $\{\text{Cd}_3\}$), IMP-11 (*alb* net with bicapped hexagonal $\{\text{Zn}_3\}$), and IMP-12 (*flu* net with cubic $\{\text{Zn}_3\}$). In compounds IMP-13 and IMP-14^[8b], however, ligand H₄L is not fully deprotonated. The topology of the two networks is considered as a puckered (3,6)-connected *kgd*-type layer. Zhou et al. obtained eight MOFs from the solvothermal reactions between the ligand H₄L and different metal salts^[9]. The structures of these MOFs include *pts* (PCN-512 $\{\text{Cu}_2\}$ and PCN-516 $\{\text{Zn}_2\}$), *flu* (PCN-513 $\{\text{Zn}_5\}$, PCN-514 and PCN-517 $\{\text{Cd}_3\}$), *alb* (PCN-511 $\{\text{Zn}_3\}$) and a rare (4,4,4,4,4,

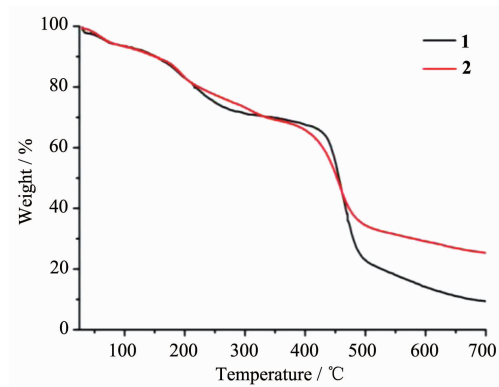


Fig.5 TGA curves of compounds **1** and **1**

5,7)-connected net (PCN-515). Boskovic and co-workers synthesized lanthanide coordination polymers with 4-connecting $\{\varepsilon\text{-PMo}_{12}\text{O}_{37}(\text{OH})_3[\text{La}(\text{H}_2\text{O})_4]_4\}^{4+}$ polyoxocations and 8-connecting di- and trimetallic building blocks $\{\text{Ce}_2\}$ and $\{\text{Eu}_3\}$, resulting in *dia* and *flu* topologies^[10], respectively. We^[7] recently reported the construction of lanthanide metal-organic frameworks with highly-connected topology. The Nd(III) compound is a 3D framework with *flu* net, built from a dinuclear $\{\text{Nd}_2\}$ cuboid building block and a tetrahedral ligand. The Eu(III) and Er(III) compounds are isostructural and possess a noninterpenetrated 3D network with a rare (4, 4, 12) highly-connected topology. In these two compounds, the fully deprotonated ligands act as pseudotetrahedral 4-connecting nodes and S-shaped tetranuclear lanthanide metal-carboxylate building blocks act as 12-connecting nodes. Qiu et al. also reported the synthesis of a series of lanthanide MOFs via hydrothermal methods^[11], including JUC-93 (*flu* net with $\{\text{Pr}_2\}$), JUC-94 (*flu* net with $\{\text{Pr}_3\}$), JUC-95 (rod-like $\{[\text{M}(\text{O}_2\text{C})_2]_n\}$ SBU, $\text{M}=\text{Tb}$, Er , Dy , Tm , Y , Pr) and JUC-99 (4,12-connected net with $\{\text{Er}_4\}$).

In this work, compounds **1** and **2** were solvothermally synthesized by using different cobalt nitrates or chlorides under the otherwise similar conditions, demonstrating that delicate synthetic conditions, *i.e.* counter anions and pH values of the system have influence on the formation of the final products^[20]. X-ray crystal structure analyses revealed that compounds **1** and **2** exhibit different structure topology, showing the diverse coordination modes of the ligand L and inorganic SBUs. In **1**, the ligand H_4L is fully deprotonated and adopts a tetrahedral monodentate coordination geometry, giving rise to a known 4-connected *sra* net. In **2**, the fully deprotonated L ligand is linked via monodentate, bidentate and bridging coordination modes to four linear trinuclear $\{\text{Co}_3\}$ SBUs in a distorted tetrahedral geometry, while each $\{\text{Co}_3\}$ SBU connects to eight L ligands in a pentagonal dodecahedron geometry. This gives rise to a rare (4,8)-connected *alb* net.

The above-mentioned compounds possess diverse structures based on the ligand H_4L , whereas the ligand

H_4L is mainly 4-coordinated and the resulting MOF structure topology is determined by the geometries of the metal clusters. Interestingly, the ligand H_4L exhibits more flexibility and diverse coordination modes compared with its carbon-counterpart H_4MTB . It can readily distort from an ideal tetrahedral geometry to meet different coordination environments, leading to coordination polymers with intriguing topology. These results show that H_4L is a versatile linker for construction of coordination polymers with interesting structures.

2.3 Thermal properties of **1** and **2**

To investigate the thermal stability of compounds **1** and **2**, the TG analyses were carried out (Fig.5). Compound **1** displayed a weight loss of 6.8% at 25 ~ 100 °C, corresponding to a loss of water molecules (Calcd. 5.8%). On further heating, the framework began to decompose with the slow release of the organic L^{4-} ligand. Compound **2** exhibited a similar TGA profile. The first weight loss occurred at 25 ~ 225 °C with weight losses of 20.2% for **2** (Calcd. 22.0%), contributed to the loss of guest molecules. Further heating resulted in the release of the coordinated organic ligand and the collapse of the lattice structure. Attempts to remove the guest solvent molecules in **1** and **2** while keeping the frameworks intact were not successful.

3 Conclusions

In summary, two metal-organic coordination polymers were solvothermally synthesized by using a rigid tetrapodal carboxylic acid 4,4',4'',4'''-silanetetrayltetrabenzoic acid (H_4L). The subtle change in synthetic conditions (*i.e.* counter-anions of metal slats) resulted in the formation of the two compounds with different topological structures. The ligand exhibits different coordination modes and links mononuclear $\{\text{Co}(\text{OOC})_4\}$ and trinuclear $\{\text{Co}_3(\text{OOC})_8\}$ SBUs to give a 3D 4-connected *sra* and (4,8)-connected *alb* net for **1** and **2**, respectively. The results show that H_4L is a more synthetically accessible, versatile connector for construction of coordination polymers with diverse structures.

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