系统研究溶剂和温度对形成三种钴簇基
金属–有机框架化合物的影响：结构和气体吸附性质

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摘要：通过调控 DMSO/DMF/H$_2$O 混合溶剂中溶剂成分的物质的量比和反应温度，合成出 3 种基于 1,3,5-三 (4′-羧甲基苯基)苯 (H$_3$BTB)和氯化钴的钴簇基金属–有机框架化合物(NH$_2$Me$_2$)$_2$[Co$_3$O(BTB)$_2$(H$_2$O)]·2H$_2$O·4.5DMF·7.5DMSO (**1**),(NH$_2$Me$_2$)$_2$[Co$_4$O(BTB)$_{8/3}$]·6H$_2$O·13DMSO (**2**)和(NH$_2$Me$_2$)$_2$[Co$_6$O$_3$(BTB)$_{8/3}$(H$_2$O)$_4$]·5H$_2$O·5DMF·13DMSO (**3**),它们分别含有三核 Co$_3$O 簇、四核 Co$_4$O 簇和六核 Co$_6$O$_3$ 簇。这种六核簇为我们首次发现。研究表明，相对中等的温度 105 ℃和较多 DMF 的使用有利于三核簇的形成；125 ℃高温和溶剂 DMSO 有利于四核簇的构建；与形成 **1** 的条件相比，较低的温度 95 ℃和更多水的存在则有利于六核簇的生成。**2** 和 **3** 虽然由不同的金属簇构成，但具有相同的框架结构，Schlfli 符号为(4^3)$_8$·4^8.6^4.8^{12}.10^4)$_3$。此外，还研究了 **2** 和 **3** 抽出溶剂后产物的气体吸附性质，它们均具有较高的氢气吸附焓。

关键词：金属–有机框架化合物；溶剂和温度效应；钴-氧簇；吸附性质
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Systematic Investigation of the Influences of Solvent and Temperature
on the Formation of Three Co-Cluster-Based Metal-Organic
Frameworks: Structures and Gas Adsorption Properties

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Abstract: By controlling the molar ratio of solvent compositions in DMSO/DMF/H$_2$O solvent and reaction temperature, three Co-cluster-based metal-organic frameworks, (NH$_2$Me$_2$)$_2$[Co$_3$O (BTB)$_2$ (H$_2$O)] ·2H$_2$O ·4.5DMF ·7.5DMSO (**1**), (NH$_2$Me$_2$)$_2$[Co$_4$O(BTB)$_{8/3}$]·6H$_2$O·13DMSO (**2**) and (NH$_2$Me$_2$)$_2$[Co$_6$O$_3$(BTB)$_{8/3}$(H$_2$O)$_4$]·5H$_2$O·5DMF·13DMSO (**3**), (BTB, 4,4′,4″-benzene-1,3,5-triyl-tribenzoate), have been synthesized based on H$_3$BTB and cobalt chloride, containing trinuclear Co$_3$O, tetranuclear Co$_4$O and hexanuclear Co$_6$O$_3$ cluster, respectively. The hexanuclear Co-O cluster is observed unprecedentedly. Systematic researches indicate that relatively moderate temperature, 105 ℃, and more DMF used could facilitate the formation of trinuclear cluster while high temperature, 125 ℃, and DMSO solvent may be in favor of the construction of tetranuclear cluster. However, lower temperature, 95 ℃, and more water may contribute to the generation of hexanuclear cluster. In addition, the transformation of **1** to **3** in mother liquid happened when exposed in atmosphere at room temperature. Interestingly, **2** and **3** exhibit the identical framework with topological type of **the** and the Schlfli symbol of (4^3)$_8$ (4^8.6^4.8^{12}.10^4)$_3$. Furthermore, the adsorption

properties of the evacuated products of **2** and **3** have been investigated and both of them have relatively high H_2 adsorption enthalpy. CCDC: 867443, **1**; 867444, **2**; 867445, **3**.

Key words: metal-organic framework; effects of solvent and temperature; cobalt-oxygen cluster; adsorption properties

0　Introduction

In recent years, metal-organic frameworks (MOFs) or porous coordination polymers have attracted considerable attention due to their fascinating topologies[1] and promising applications in gas adsorption [2], separation[3], molecule/ion recognition and sensing[4], catalysis[5] and drug delivery[6], etc. To some degree, the expected MOFs could be still designed and synthesized, such as, MOF-5 and MOF-177[7], being formed by controlling the *in-situ* generations of metal clusters. However, such coordination assemblies are affected by many factors such as concentration [8], metal-to-ligand ratio[9], temperature[10], solvent[11] and template reagent[12]. Therefore, it is rational to systematically investigate metal/ligands systems on those aspects and finally to construct interesting and potential applicable MOFs.

We are interested in constructing porous coordination polymers with interesting properties by multidentate carboxylic acid ligands[13]. Herein, a system of a rigid ligand, 4,4′,4″-benzene-1,3,5-triyl-tribenzoic acid (H$_3$BTB) and cobalt chloride was selected and systematically investigated in terms of the effects of solvent compositions and reaction temperature on the formation of metal clusters in their MOFs. Three Co-cluster-based MOFs, (NH$_2$Me$_2$)$_2$[Co$_3$O (BTB)$_2$(H$_2$O)]·2H$_2$O·4.5DMF·7.5DMSO (**1**), (NH$_2$Me$_2$)$_2$ [Co$_4$O (BTB)$_{8/3}$]·6H$_2$O·13DMSO (**2**) and (NH$_2$Me$_2$)$_2$ [Co$_6$O$_3$(BTB)$_{8/3}$(H$_2$O)$_4$]·5H$_2$O·5DMF·13DMSO (**3**), were obtained, among which **2** and **3** contain the same topology but the different metal cluster nodes. Interestingly, the hexanuclear Co-O cluster was unprecedentedly observed in **3**. Meanwhile, complex **1** can gradually transform to complex **3** when exposed to air in its mother liquor at room temperature. In addition, the adsorption properties of the evacuated products of **2** and **3** were also reported.

1　Experimental

1.1　Materials and general methods

H$_3$BTB was synthesized according to previously published methods[14]. Other reagents were commercially available and used as purchased without further purification. The FT-IR spectra were recorded from KBr pellets in the range of 4 000~400 cm^{-1} on a VECTOR 22 spectrometer. The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449F3 instrument from room temperature to 600 ℃ with a heating rate of 10 ℃·min^{-1} in N$_2$ atmosphere. X-ray powder diffraction (XRPD) patterns were obtained on a Bruker D8 Advance X-ray diffractometer using Cu $K\alpha$ radiation (0.154 18 nm), in which the X-ray tube was operated at 40 kV and 40 mA. Supercritical CO$_2$ processing was performed with a Tousimis Samdri PVT-30 critical point dryer.

1.2　Synthesis of complex 1, 2 and 3

Synthesis of (NH$_2$Me$_2$)$_2$[Co$_3$O(BTB)$_2$(H$_2$O)]·2H$_2$O· 4.5DMF·7.5DMSO (**1**). A mixture of H$_3$BTB (8.8 mg, 0.02 mmol) and CoCl$_2$·6H$_2$O (7.2 mg, 0.03 mmol) in DMSO (0.5 mL), DMF (0.4 mL) and H$_2$O (0.075 mL) was stirred for 5 min at room temperature. Then the mixture was placed in a 23 mL Parr Teflon-lined stainless steel vessel and heated at 105 ℃ for 48 h. The reaction system was cooled slowly and plate violet crystals of **1** were obtained (16.2 mg, yield 76% based on H$_3$BTB). Elemental analysis (%) calcd. C 48.90, H 6.10, N 4.28, S 11.32; found: C 48.68, H 5.82, N 4.01, S 11.59. Main IR frequencies (KBr pellet): 3 369 (br, m), 3 068 (m), 2 970 (w), 2 929 (w), 1 657 (s), 1 606 (s), 1 585 (s), 1 537 (s), 1 392 (s), 1 254 (w), 1 182 (w), 1 105 (w), 1 016 (w), 856 (w), 806 (w), 781 (s), 706 (w), 667 (w), 482 (w) cm^{-1}.

Synthesis of (NH$_2$Me$_2$)$_2$[Co$_4$O(BTB)$_{8/3}$]·6H$_2$O·

13DMSO (**2**). A mixture of H₃BTB (8.8 mg, 0.02 mmol) and CoCl₂·6H₂O (7.2 mg, 0.03 mmol) in DMSO (0.5 mL), DMF (0.1 mL) and H₂O (0.1 mL) was stirred for 5 min at room temperature. Then the mixture was placed in a 23 mL Parr Teflon-lined stainless steel vessel and heated at 125 ℃ for 48 h. The reaction system was cooled slowly and truncated cubic dark violet crystals of **2** were obtained (12.8 mg, yield 65% based on H₃BTB). Elemental analysis (%) calcd: C 46.60, H 5.60, N 1.07, S 15.86; found: C 46.33, H 5.43, N 0.85, S 15.59. Main IR frequencies (KBr pellet): 3 382 (br, m), 3 064 (m), 3 001 (m), 2 912 (w), 1 606 (s), 1 593 (s), 1 543 (s), 1 398(vs), 1 311 (m), 1 184 (w), 1 016 (s), 951 (m), 858 (m), 806 (w), 783 (s), 706 (m), 669 (w), 486 (w) cm⁻¹.

Synthesis of (NH₂Me₂)₂[Co₆O₃(BTB)₈/₃(H₂O)₄]· 5H₂O·5DMF·13DMSO (**3**). A mixture of H₃BTB (8.8 mg, 0.02 mmol) and CoCl₂·6H₂O (7.2 mg, 0.03 mmol) in DMSO (0.5 mL), DMF (0.4 mL) and H₂O (0.15 mL) was stirred for 5 min at room temperature. Then the mixture was placed in a 23 mL Parr Teflon-lined stainless steel vessel and heated at 95 ℃ for 48 h. The reaction system was cooled slowly and cubic red crystals of **3** were obtained (17.3 mg, yield 72% based on H₃BTB). Elemental analysis (%) calcd: C 43.94, H 5.89, N 3.07, S 13.03; found: C 44.21, H 5.63, N 2.82, S 13.27. Main IR frequencies (KBr pellet): 3 404 (br, m), 3 066 (w), 2 927 (w), 2 870 (w), 1 657 (s), 1 606 (s), 1 587 (s), 1 541 (m), 1 390 (s), 1 254 (w), 1 180 (w), 1 105 (w), 1 016 (w), 856 (w), 806 (w), 781 (s), 706 (w), 667 (w), 480 (w) cm⁻¹.

1.3 X-ray crystallography

Single-crystal X-ray data were collected on a Bruker Smart Apex Ⅱ CCD diffractometer at 291 K using graphite monochromated Mo $K\alpha$ radiation (λ = 0.071 073 nm) and operating at 50 kV and 40 mA. Because of easily losing solvent from their channels when exposed to air, these crystals were sealed in thin-wall capillaries with small amounts of mother liquor. Data reduction was made with the Bruker Saint program. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package. The coordinates of the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were put in calculated positions or located from the Fourier maps and refined isotropically with the isotropic vibration parameters related to the non-hydrogen atom to which they are bonded. Contained within the void spaces of the structure of **1~3** was a combination of highly disordered solvent molecules and charge-compensating counteractions. Thus, the contributions of scattering from the disordered species were removed using the SQUEEZE routine of PLATON[15] and refined further using the data generated. The chemical formulas were determined using a combination of TGA, elemental analysis, single-crystal X-ray diffraction studies, and IR spectra. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1.

CCDC: 867443, **1**; 867444, **2**; 867445, **3**.

Table 1 Crystallographic data and structure refinement details for 1~3

Complex	**1**	**2**	**3**
Empirical formula	C₅₄H₃₂Co₃O₁₄	C₇₂H₄₀Co₄O₁₇	C₇₂H₄₄Co₆O₂₃
Formula weight	1 082.59	1 412.76	1 630.65
Temperature / K	291(2)	291(2)	291(2)
Color	Violet	Dark violet	Red
Shape	Plate	Truncated cubic	Cubic
Crystal system	Orthorhombic	Cubic	Cubic
Space group	*Pnma*	*Im$\bar{3}$m*	*Im$\bar{3}$m*
a / nm	1.741 30(18)	2.563 39(6)	2.738 38(3)
b / nm	2.492 4(2)		
c / nm	2.227 9(2)		

Continued Table 1

Volume / nm³	9.669 1(15)	16.844 0(7)	20.534 4(4)
Z	4	6	6
D_c / (g·cm⁻³)	0.744	0.836	0.791
$F(000)$	2 200	4 296	4 932
θ range / (°)	1.63~26.00	1.95~25.97	1.82~25.99
Abs coeff / mm⁻¹	0.543	0.621	0.75
Reflns collected / unique (R_{int})	51 326 / 9 725 (0.088 2)	46 568 / 1 629 (0.074 9)	56 550 / 3 593 (0.079 2)
Parameter / data (obs)	325 / 6 438	64 / 1 391	125 / 2 851
GOF	1.01	1.118	1.054
R_1, wR_2 ($I>2\sigma(I)$)	0.051 0, 0.114 5	0.043 5, 0.137 2	0.041 6, 0.131 5
R_1, wR_2 (all data)	0.074 4, 0.120 1	0.053 4, 0.140 7	0.053 4, 0.138 3

1.4　Adsorption experiments

N_2 and H_2 adsorption isotherms were measured up to 100 kPa using a Micromeritics ASAP 2020 surface area and pore size analyzer. Before the measurements, the samples of **2** and **3** were soaked in absolute ethanol, which was refreshed every 24 h for 3 d. Then the samples were placed inside the supercritical CO_2 dryer and the ethanol was exchanged with CO_2 (liq.) over a period of 10 h. During this time the liquid CO_2 was vented under positive pressure for five minutes every two hours. Following that, the chamber was sealed and liquid CO_2 was heated up around 40 ℃, and then the CO_2 was slowly vented over the course of 12 h. The collected sample was then tested for gas adsorption immediately. UHP-grade nitrogen (99.999%) gas source was used in the nitrogen sorption measurements. In the hydrogen sorption measurements, high purity hydrogen (99.9995%) was used. The temperature was maintained at 77 and 87 K with liquid nitrogen and liquid argon, respectively.

2　Results and discussion

2.1　Synthesis and thermal stability

Complex **1**, **2** and **3**, containing $Co_3O(H_2O)$, Co_4O and $Co_6O_3(H_2O)_4$ cluster, respectively, were prepared through solvothermal synthesis in DMSO/DMF/H_2O solvent system at different temperatures. To identify the reaction conditions leading to the desired pure products, the molar ratio of solvent components and reaction temperature were altered in the case of the invariant molar ratio of starting materials (H_3BTB/ $CoCl_2$, 1:1.5).

Pure phase **2** with high crystallinity and good yield was observed in the mixed solvent with its component molar ratios of 705:129:555 (DMSO/DMF/ H_2O, volume ratio 5:1:1) at 125 ℃ (Fig.1b). Herein, DMSO is the main component of the solvent and may be the template reagent for forming Co_4O cluster and it is similar to the reaction condition for PCN-9 [16]. However, the solvent molar ratio was adjusted to 705: 517:832 (volume ratio 5:4:1.5) and temperature was
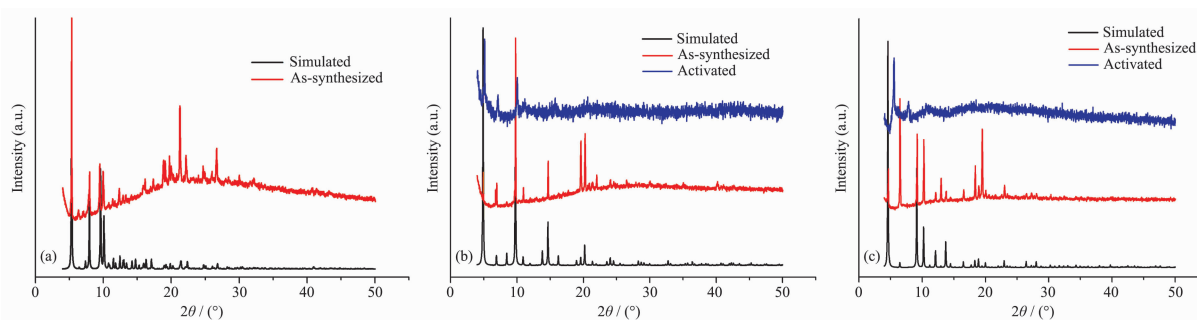

Fig.1　Powder X-ray diffraction patterns for (a) **1**, (b) **2** and (c) **3**

decreased to 95 ℃, pure phase **3** with high yield was obtained (Fig.1c). Comparatively, more water used and lower temperature are of benefit in the formation of $Co_6O_3(H_2O)_4$ cluster. Evidently, the demand for more water is related to the presence of coordinated water molecules in the cluster. If the amount of water used was reduced by half the one for **3**, i.e., the solvent molar ratio being 705:517:416 (volume ratio 5:4:0:75), and temperature rose to 105 ℃, pure phase would be **1** containing trinuclear Co_3O (H_2O) cluster (Fig.1a), which corresponds to half the hexanuclear cluster and only two chelated BTB carboxylate groups substitute one μ_4-O atom and two bridging water molecules in the latter maybe due to the scarcity of water in solvent.

Interestingly, when plate violet crystals of **1** in mother liquor had been exposed to air at room temperature about two weeks, they would be gradually dissolved and transform to cubic red crystals of **3**. However, while the violet crystals in mother liquor had been sealed in a Parr Teflon-lined stainless steel vessel, there would be almost little change in the crystals in two weeks. According to these phenomena, it is speculated that the dissolve of water vapor from atmosphere into the solvent maybe promote this structure transformation. From the structures of the two clusters, the transformation can be viewed as the process of one μ_4-O atom and two bridging water molecules substituting four chelated carboxylate groups of two trinuclear clusters.

Thermogravimetric analyses experiments were conducted to determine the thermal stabilities of complex **1**~**3**. For complex **1**, an almost consecutive weight loss of 45.6% from 59 to 429 ℃ corresponds to the loss of three water molecules (including one coordinated water molecule), four and one half DMF solvent molecules and seven and one half DMSO solvent molecules (calcd. 45.6%). Above 429 ℃ BTB ligands began to depart from Cobalt-Oxygen clusters and decompose. TGA curve of **2** indicates that the almost consecutive weight loss of 42.7% within 51~428 ℃ is consistent with the loss of six water and thirteen DMSO solvent molecules (cacld. 42.8%). The

host framework started to decompose beyond 428 ℃. For complex **3**, there is an almost consecutive weight loss of 48.2% from 60 ℃ to 403 ℃, corresponding to the release of nine water molecules (including four coordinated water molecules), five DMF solvent molecules and thirteen DMSO solvent molecules (cacld. 48.3%). The complex started to decompose at higher temperatures.

2.2 Description of crystal structures

Single crystal X-ray diffraction studies revealed that complex **1** crystallizes in the *Pnma* space group. It has a structure based on $Co_3(\mu_3$-O) clusters in which Co1 center is six-coordinated and bonded with four bridging dimonodentate carboxylates, one water terminal ligand (O1W) and one μ_3-O atom (O7), and each of Co2 center is five-coordinated and bonded with two bridging dimonodentate, two chelate carboxylates and one μ_3-O atom (O7) (Fig.2a). Herein, the difference between **1** and some isostructural ones such as MOF-39[14], MOF-39(Co)[17], and the mixed metal Co/Zn-MOF-39[18] is the chelate carboxylates bonded with Co2 atom instead of monodentate carboxylates. As a further evidence, the absence of a strong band around 1 700 cm^{-1} shows complete deprotonation of the carboxylic acid groups[19]. Thus, in **1** the $Co_3(\mu_3$-O) cluster consists of two CoO_5 distorted pentagonal bipyramids and a CoO_6 octahedron sharing a common corner. Each such cluster is surrounded by six fully deprotonated ligands of BTB while each ligand links to three clusters. The six carboxylate C atoms from one $Co_3O(CO_2)_6$ unit construct a trigonal-prism-like building block (Fig.3a), which link one another by tridentate ligands to form two interpenetrating 3D networks with approximately square channels of 1.56 nm×1.56 nm (atom to atom distance) along *a* axis (Fig.3b). The framework can be simplified to a (6,3)-net which belongs to **sit** topological type with the Schlfli symbol of $(4.6^2)_2$ $(4^2.6^{10}.8^3)$.

Complex **2** crystallizes in the *Im*3*m* space group and is isostructural to PCN-9 (Co/Fe/Mn), only with TATB being substituted by our ligand of BTB[16]. It contains a square-planar $Co_4(\mu_4$-O) clusters with a μ_4-
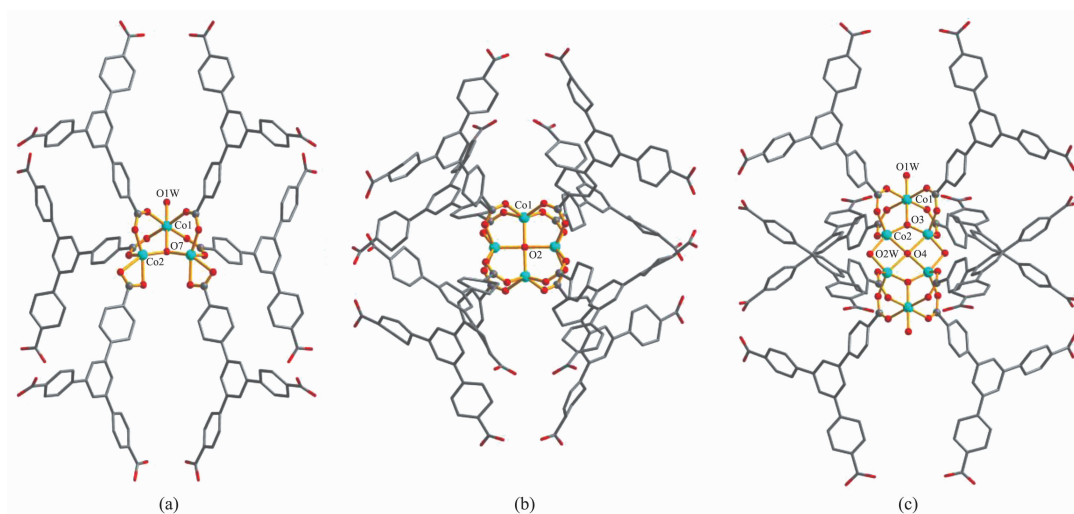
C: gray; Co: turquoise; O: red. Hydrogen atoms have been omitted for clarity

Fig.2　View of (a) trinuclear $Co_3(\mu_3\text{-}O)$ clusters linked to six BTB ligands in **1**; (b) tetranuclear $Co_4(\mu_4\text{-}O)$ clusters linked to eight BTB ligands in **2**; (c) hexanuclear $Co_6(\mu_3\text{-}O)_2(\mu_4\text{-}O)$ clusters linked to eight BTB ligands in **3**
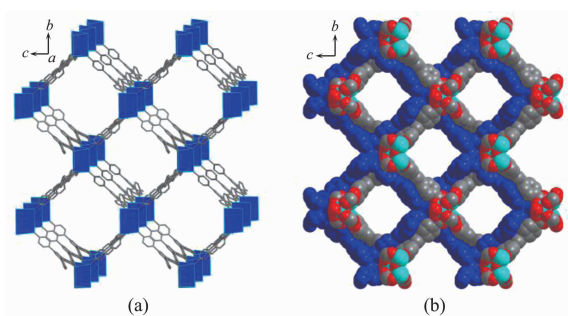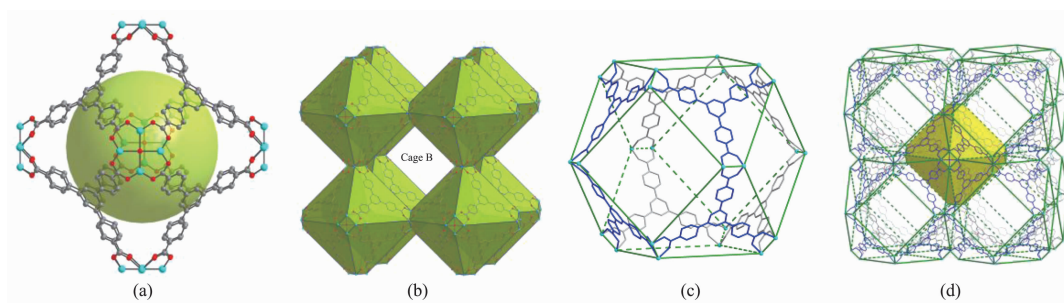

Hydrogen atoms have been omitted for clarity

Fig.3　(a) Trigonal-prism-shaped building blocks (blue) formed by carboxylate carbon atoms (gray) which are connected by BTB ligands in the structure of **1**; (b) Space-filling illustration of **1** along a axis showing 2-fold interpenetrating network with square channels

O atom (O2) locating at the center of a square shaped by four Co atoms (Fig.2b). The Co-μ_4-O bond length of 0.214 2(6) nm is shorter than that of 0.235 1(2) nm in PCN-9. In the cluster, every two adjacent Co atoms are bonded by two bridging dimonodentate carboxylates. Thus, each Co atom is five-coordinated with square-pyramidal geometry constructed by four carboxylate O atoms as base and μ_4-O atom as apex, and each such cluster connects eight BTB ligands. With each ligand connecting three clusters, the structure of **2** can be simplified to a (8,3)-net with topological type of **the** and the Schlfli symbol of $(4^3)_8$ $(4^8.6^4.8^{12}.10^4)_3$.

As an alternative, eight ligands, connected by six clusters, constitute a truncated octahedral cage, named cage A, with the distance of 2.56 nm between the two opposite clusters (Fig.4a). Cage As stack in a primitive cubic fashion via corner-sharing and eight cage As surround a cuboctahedral cage, named cage

Hydrogen atoms have been omitted for clarity

Fig.4　(a) Truncated octahedral cage A; (b) The stack of cage A and the formation of cuboctahedral cage B; (c) cage B; (d) The stack of cage B and their enclosure of cage A in **2**

B, defined by twelve Co_4O clusters and eight BTB ligands (Fig.4b, 4c). Similarly, eight cage Bs also surround a cage A (Fig.4d). Two types of cage stack mutually by sharing triangular BTB faces and Co_4O vertexes to form a set of 3D framework. Two such frameworks are interpenetrated with π-π interactions between the staggered BTB ligand pairs (Fig.5). The cage As of one set of framework are enclosed by the cage Bs of another set, leaving over a *ca.* 0.5 nm× 0.5 nm square pore.
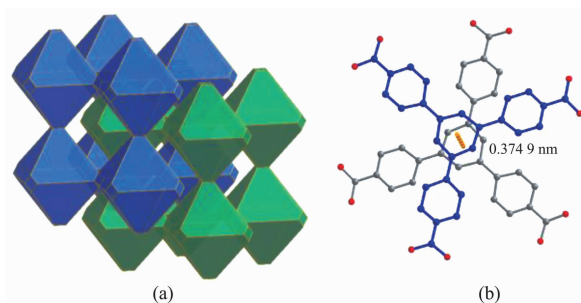
Hydrogen atoms have been omitted for clarity

Fig.5 (a) Doubly interpenetrated network constructed by truncated octahedron and (b) π-π stacking between two staggered BTB from two sets of framework in **2**

Complex **3** crystallizes in the $Im\bar{3}$ space group and has the same topology as **2**. The main difference from **2** is an novel planar $Co_6(\mu_3\text{-O})_2(\mu_4\text{-O})$ cluster instead of the $Co_4(\mu_3\text{-O})$ cluster (Fig.2c). The hexanuclear cluster contains two types of Co atom, Co1 and Co2. Co1 atom is six-coordinated with octahedron geometry constructed by four bridging carboxylate O atoms at equatorial vertexes and one terminal water (O1W) and one μ_3-O atom (O3) at polar vertexes, respectively,

and Co2 atom is five-coordinated with distorted hexahedron geometry which vertexes are composed of two bridging carboxylate O atoms, one bridging water (O2W), one μ_3-O atom and one μ_4-O atom (O4). Each μ_3-O atom links to one Co1 atoms and two Co2 atoms, while each μ_4-O atom bonds with four Co2 atoms. Adjacent Co1 and Co2 atoms are bound by two bridging dimonodentate carboxylates, thus each Co_6O_3 cluster also links to eight BTB ligands.

Similarly, the 3D structure is also composed of two types of polyhedral cages, cage A and B (Fig.6a, 6b). Two sets of interpenetrated frameworks can be viewed as structure constructed by cage A′s stacking with cluster-sharing (Fig.6c). Owing to the bigger cluster, cage A, with the distance of 2.74 nm between the two opposite clusters, is bigger than that in **2**, but which leads to the shorter distance between the staggered BTB ligand pairs from two sets of frameworks (Fig.6d).

2.3 Gas adsorption studies

Owing to the instability of the framework of complex **1** after removing guest molecules, herein, only the porosities of complex **2** and **3** were investigated. N_2 sorption isotherms were measured at 77 K for the samples of **2** and **3** that were activated according to the procedures in the Experimental Section. The latter is named as **3′** due to the variation of the structure of **3** after guest solvent molecules were removed (Fig.1c). As shown in Fig.7a, the two samples exhibit similar N_2 uptake and typical type I sorption behavior. The pore size distributions calculated on the basis of N_2 sorption isotherms for
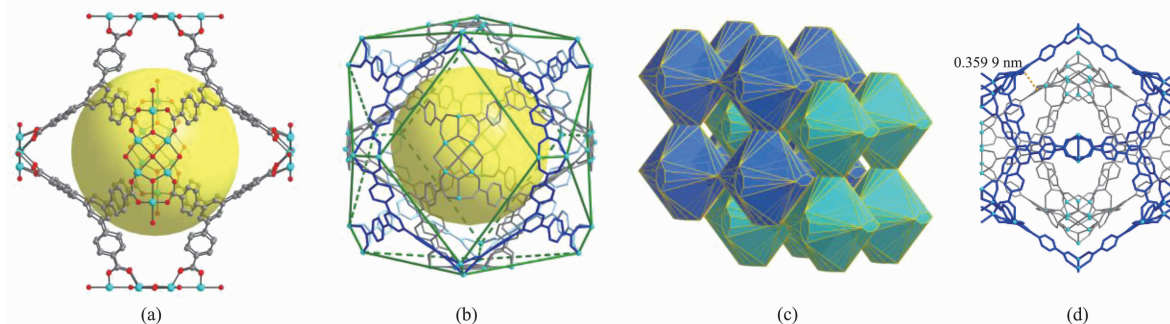
Hydrogen atoms have been omitted for clarity

Fig.6 View of (a) cage A, (b) cage B (enclosing cage A from another set of framework), (c) two sets of interpenetrated frameworks, and (d) π-π stacking between two staggered BTB from two sets of frameworks in **3**
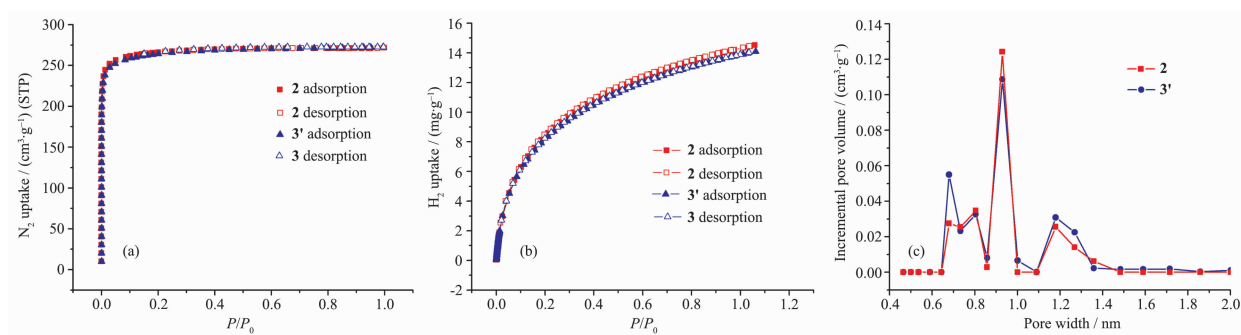
Fig.7　(a) N_2 and (b) H_2 sorption isotherms of **2** and **3′** at 77 K; (c) Pore size distribution of **2** and **3′**

two samples are also similar (Fig.7c). Derived from the N_2 sorption data, the BET surface areas are 1 068 $m^2 \cdot g^{-1}$ (Langmuir surface area, 1 186 $m^2 \cdot g^{-1}$) and 1 059 $m^2 \cdot g^{-1}$ (Langmuir surface area, 1 177 $m^2 \cdot g^{-1}$) for **2** and **3′**, respectively, and the total pore volume is 0.419 $cm^3 \cdot g^{-1}$ for **2** and 0.421 $cm^3 \cdot g^{-1}$ for **3′**.

H_2 sorption measurements at 77 K were also carried out to check their hydrogen storage performances. As indicated in Fig.7b, at 77 K and 101.325 kPa, the hydrogen uptake capacity of **2** is 14.3 $mg \cdot g^{-1}$ (1.41 wt%), and **3′** can adsorb 13.9 $mg \cdot g^{-1}$ (1.37wt%) hydrogen, which are comparable to that of PCN-9[16].

To estimate the H_2 affinities of the two porous MOFs, H_2 adsorption isotherms at 77 and 87 K were used for the calculation of their Q_{st} by the virial method. As indicated in Fig.8, the Q_{st} of hydrogen adsorbed in **2** and **3′** decreases with the increase of hydrogen loadings, which is similar to those observed in other porous MOFs[20]. The adsorption enthalpies of hydrogen at zero coverage for **2** and **3′** are 7.27 and 7.16 $kJ \cdot mol^{-1}$, respectively, which are in upper level amongst those of numerous reported MOFs, maybe
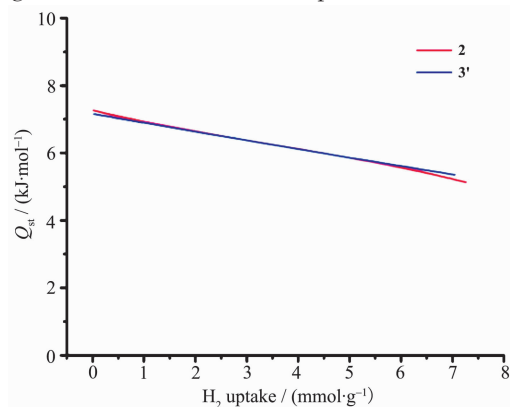
attributed to the coordinative-unsaturated metal centers and framework interpenetration in the two complexes[21].

3　Conclusions

In summary, three Co-cluster-based MOFs, **1**, **2** and **3**, have been obtained by reaction of H_3BTB with $CoCl_2$ in DMSO/DMF/H_2O mixed solvent, which contain trinuclear, tetranuclear and hexanuclear cobalt-oxygen cluster, respectively. By changing the ratio of solvent components and reaction temperature, we noticed that relatively moderate temperature, 105 ℃, and more DMF employed are more suited to forming Co_3O cluster and higher temperature, 125 ℃, and DMSO solvent for the generation of Co_4O cluster whereas lower temperature, 95 ℃, and more water are more propitious to the construction of unprecedented Co_6O_3 cluster. Interestingly, **2** and **3**, based upon different metal clusters, exhibit identical framework structures and the evacuated products of them show the relatively high H_2 adsorption enthalpy.

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Fig.8　Isosteric heats of adsorption of H_2 in **2** and **3′**

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