

基于对叔丁基杯[8]芳烃的 3d-5f 核簇化合物(M_xTh_y , $M=Co, Ni, Zn$)的合成、结构与磁性研究

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摘要: 本文以对叔丁基杯[8]芳烃(H_8C_8A)为配体, 在溶剂热条件下制得了 3 个 3d-5f 化合物, $[Co_2Th_4(HC_8A)_2O_2(OH)_2(DMF)_6]$ (**1**)、 $[Ni_2Th_5(H_2C_8A)(C_8A)O_4(OH)_2(DMF)_5(CH_3OH)_2]$ (**2**)、 $[Zn_2Th_6(HC_8A)(C_8A)O_5(CH_3O)(C_3H_6NO_2)_2(DMF)_5(CH_3OH)]$ (**3**) (其中 H_8C_8A =对叔丁基杯[8]芳烃, $DMF=N,N$ -二甲基甲酰胺)。X-射线单晶测试表明, 这 3 个化合物均为 2 个以尾对尾方式排列的杯[8]芳烃分子中间夹 1 个 3d-5f 核簇的三明治型结构。杯[8]芳烃均表现为双锥式构型, 且每个锥式空腔下缘结合 1 个钍离子, 双锥的连接处及 2 个杯芳烃分子之间由过渡金属离子或钍离子连接。不同过渡金属离子不同的配位环境导致 3 种不同核簇的形成。化合物 **1** 的磁性研究表明, 该化合物在低温下表现出弱铁磁性相互作用。

关键词: 杯芳烃; 钍; 3d-5f 化合物; 晶体结构; 磁性

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Three 3d-5f Compounds (M_xTh_y , $M=Co, Ni, Zn$) Based on *p*-tert-Butylcalix[8]arene: Syntheses, Structures and Magnetic Property

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Abstract: Three compounds, $[Co_2Th_4(HC_8A)_2O_2(OH)_2(DMF)_6]$ (**1**), $[Ni_2Th_5(H_2C_8A)(C_8A)O_4(OH)_2(DMF)_5(CH_3OH)_2]$ (**2**), $[Zn_2Th_6(HC_8A)(C_8A)O_5(CH_3O)(C_3H_6NO_2)_2(DMF)_5(CH_3OH)]$ (**3**) ($H_8C_8A=p$ -tert-butylcalix[8]arene, $DMF=N,N$ -dimethylformide), were obtained by solvothermal method and characterized by single crystal X-ray diffraction, element analysis, and so on. All these three structures are featured by some sandwich-like units which are constructed by two tail-to-tail calix[8]arene molecules and one in-between 3d-5f polynuclear core. All the calix[8]arene molecules adopt a double-cone conformation, each cone of calix[8]arene molecule bonds one thorium cation by its lower rim, and two cones of one calixarene molecule is connected by some thorium or transition metal atoms. Magnetic measurement indicates that compound **1** exhibits weak ferromagnetic interaction between the metals at low temperature. CCDC: 968469, **1**; 968470, **2**; 968471, **3**.

Key words: calixarenes; thorium; 3d-5f cluster compounds; crystal structure; magnetic property

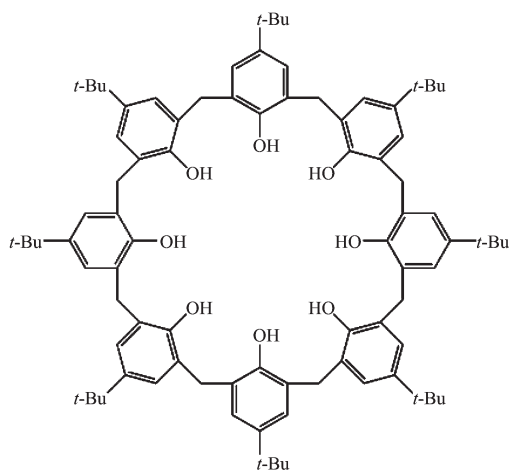
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The chemistry of the actinide elements is of critical importance to the nuclear energy industry^[1]. And the development of nuclear reprocessing and the study on the environmental impact of the radioactive actinides have driven many advances in fundamental actinide chemistry^[2-3]. In the recent years, the heterometallic compounds with transition metals and actinides have drawn increasing attention due to their promising applications in magnetism, luminescence, photochemistry and catalysis^[4-6]. And most of them are studied with transition metals and uranium. The compounds of thorium were studied less^[7].

Calixarenes, one type of macrocyclic ligands comprised of several phenol units, have been documented to be good multidentate ligands in the construction of polynuclear compounds^[8-10]. A series of 3d-4f heterometallic compounds based on *p*-*tert*-butyl (thia)calix[4]-arene and its derivatives have been synthesized^[11-17]. However, the compounds based on calix[8]arene were less reported due to higher charge, more flexible framework and a bigger cavity size of C8A^[18-19]. Actually, more coordination points and larger coordination region of calix[8]arene would benefit the construction of polynuclear compounds including the heterometallic complexes. Recently, we obtained a series of Co-Ln (Ln=Sm, Gd and Dy) compounds based on the *p*-*tert*-butylcalix[8]arene (H₈C8A, scheme 1) under the solvothermal conditions^[20]. As continuation, this work presents three heterometallic compounds of



Scheme 1 Molecular structure of *p*-*tert*-butylcalix[8]arene (H₈C8A)

3d transition metal (Co, Ni and Zn) and thorium, namely, [Co₂Th₄(HC8A)₂O₂(OH)₂(DMF)₆] (**1**), [Ni₂Th₅(H₂C8A)(C8A)O₄(OH)₂(DMF)₅(CH₃OH)₂] (**2**) and [Zn₂Th₆(HC8A)(C8A)O₅(CH₃O)(C₃H₆NO₂)₂(DMF)₅(CH₃OH)] (**3**). These compounds give the first high nuclear clusters based on the related transition metals and thorium.

1 Experimental

1.1 Materials and measurements

p-*tert*-Butylcalix[8]arene was synthesized by literature methods^[21] and other reagents were purchased from commercial sources and used as received. Co/Ni/Zn and Th analyses were performed on a HITACHI S-4800 Scanning Electron Microscope equipped EDS. Elemental analyses for C, H and N were recorded on a VarioEL instrument. TGA measurement was performed on a NETZSCH STA 449F3. FTIR (KBr pellets) spectra were recorded using a Bruker Vertex 70 spectrometer. Magnetic susceptibility measurement for compound **1** was performed on a Quantum Design MPMS XL-5 SQUID system with a 1000 Oe magnetic field in the range of 2 ~300 K. Diamagnetic corrections for the sample and sample holder were applied to the data.

1.2 Synthesis of compounds

Purple single crystals of **1** were obtained by the reaction of a mixture of H₈C8A (0.05 g, 0.039 mmol), ThCl₄·4H₂O (0.05 g, 0.11 mmol), CoSO₄·7H₂O (0.05 g, 0.18 mmol), CH₃OH (3.0 mL), DMF (3.0 mL) and triethylamine (0.65 mL) in a 20 ml Teflon-lined stainless steel autoclave which was kept at 130 °C for 3 d and then slowly cooled to room temperature. The crystals were picked out for X-ray diffraction determination or washed with CH₃OH and DMF for other measurements. The TG result of compound **1** was shown in Fig.1. Based on the TG results and SQUEEZE analysis, a suitable formula containing solvent molecules for **1** would be [Co₂Th₄(HC8A)₂O₂(OH)₂(DMF)₆]·6DMF·7CH₃OH. The EDS analysis reveals that the molar ratio of *n*_{Co}:*n*_{Th}=2.62:5.08, comparable to the expected *n*_{Co}:*n*_{Th} ratio (1:2). Element analysis (%): calculated for Co₂Th₄C₂₁₉H₃₂₄O₃₉N₁₂: C,

54.86, H, 6.81, N, 3.51; Found: C, 53.86, H, 6.65, N, 3.46. FTIR (cm^{-1}): 3 636(w), 3 442(w), 3 046(w), 2 949(s), 2 865(m), 1 682(s), 1 653(s), 1 481(s), 1 391(m), 1 360(m), 1 303(m), 1 254(m), 1 209(m), 1 124(m), 1 094(m), 913(m), 866(m), 821(m), 748(m), 682(m), 530(m), 490(m), 438(m).

Green single crystals of **2** were obtained by the analogous method with $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ replaced by $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (0.05 g, 0.19 mmol) and the amount of DMF reduced to 2.0 mL. The TG analysis of compound **2** was shown in Fig.1. Based on the TG results and SQUEEZE analysis, a suitable formula containing solvent molecules for **2** would be $[\text{Ni}_2\text{Th}_5(\text{H}_2\text{C}_8\text{A})(\text{C}_8\text{A})\text{O}_4(\text{OH})_2(\text{DMF})_5(\text{CH}_3\text{OH})_2] \cdot \text{DMF}$. EDS result reveals that the molar ratio of $n_{\text{Ni}}:n_{\text{Th}}=0.29:0.71$, comparable to the expected $n_{\text{Ni}}:n_{\text{Th}}$ ratio (2:5). Element analysis (%): calculated for $\text{Ni}_2\text{Th}_5\text{C}_{196}\text{H}_{262}\text{O}_{30}\text{N}_6 \cdot \text{C}$, 52.73, H, 5.87, N, 2.02; Found: C, 49.61, H, 5.92, N, 2.22. FTIR (cm^{-1}): 3 548(w), 3 404(w), 2 952(s), 2 867(m), 1 647(s), 1 478(s), 1 392(m), 1 360(m), 1 299(m), 1 260(m), 1 206(m), 1 120(m), 908(m), 866(m), 820(m), 743(m), 681(m), 484(m).

Colorless single crystals of **3** were obtained by replacing $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ with $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (0.05 g, 0.17 mmol) and reducing the amount of DMF to 1.5 mL. TG result of **3** was shown in Fig.1. Based on the TG results and SQUEEZE analysis, a suitable formula containing solvent molecules for **3** would be $[\text{Zn}_2\text{Th}_6(\text{HC}_8\text{A})(\text{C}_8\text{A})\text{O}_5(\text{CH}_3\text{O})(\text{C}_3\text{H}_6\text{NO}_2)_2(\text{DMF})_5(\text{CH}_3\text{OH})] \cdot \text{DMF} \cdot 3\text{CH}_3\text{OH}$. EDS analysis reveals that the molar ratio of $n_{\text{Zn}}:n_{\text{Th}}=0.50:1.45$, comparable to the expected $n_{\text{Zn}}:n_{\text{Th}}$ ratio (2:6). Element analysis (%): calculated for

$\text{Zn}_2\text{Th}_6\text{C}_{205}\text{H}_{282}\text{O}_{36}\text{N}_8 \cdot \text{C}$, 49.61, H, 5.68, N, 2.42; Found: C, 47.57, H, 5.70, N, 2.50. FTIR (cm^{-1}): 3415(w), 3047(m), 2 955(s), 2 861(m), 1 649(s), 1 540(m), 1 478(s), 1 392(s), 1 361(m), 1 300(s), 1 206(s), 1 124(m), 908(m), 864(m), 822(m), 748(m), 679(m), 617(m), 490(s).

1.3 Crystal structure determination

The X-ray intensity data for compounds **1~3** were collected on a Bruker APEX-II CCD diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) operated at 1.5 kW (50 kV, 30 mA). The crystal structures were solved by means of direct methods and refined employing full-matrix least squares on F^2 (SHELXTL-97)^[22]. Details for compound **1**: All non-hydrogen atoms were refined anisotropically except for C83-C88 from butyl groups. Hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors.

The carbon atoms of four butyl groups (C65-C67, C74-C76, C83-C88) were refined with disordered positions and the same displacement parameters. C89, C90 and C91 from one coordinated DMF molecules were also refined with disordered positions and the same displacement parameters. Details of compound **2**: All non-hydrogen atoms were refined anisotropically except for N4, C100-C102, C200-C202. Hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. C71-C73, C101-C103 and N4 were refined with disordered positions and the same equal occupation of 0.25. Details for compound **3**: All non-hydrogen atoms were refined anisotropically except for C196-C199 and N7 from coordinated DMF molecules. Hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Th5, Zn1, C129-C131, C135-C137, C144-C152, C159-C161, C179, C184-C186, C196-C198 and N7 were refined with disordered positions and the same displacement parameters. The disordered C199 site was refined with an equal occupation of 0.5. Solvent molecules in these

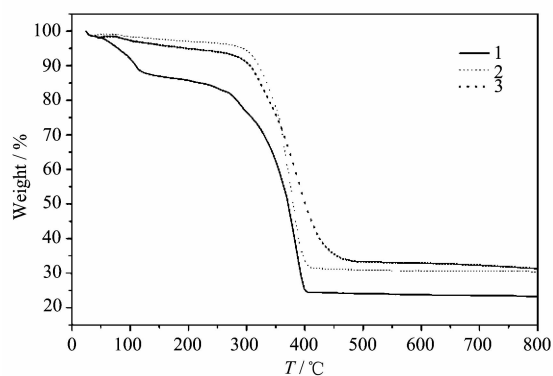


Fig.1 TG curves of compounds **1~3**

structures can not be properly modeled, whose contributions were subtracted by the “SQUEEZE” command as implemented in PLATON^[23]. The high R_1 and wR_2 factors of compounds **1**~**3** would be due to

the weak high-angle diffractions and disorders. The crystallographic data for compounds **1**~**3** are listed in Table 1.

CCDC: 968469, **1**; 968470, **2**; 968471, **3**.

Table 1 Crystal data for compounds **1**~**3**

	1	2	3
Formula	C ₁₉₄ H ₂₅₄ N ₆ O ₂₆ Co ₂ Th ₄	C ₁₉₃ H ₂₅₃ N ₅ O ₂₉ Ni ₂ Th ₅	C ₁₉₉ H ₂₆₃ N ₇ O ₃₂ Zn ₂ Th ₆
Formula weight	4 132.05	4 386.64	4 788.14
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>C2/c</i>	<i>Pnma</i>	<i>Pbca</i>
<i>a</i> / nm	3.731 30(5)	4.648 4(3)	3.294 09(6)
<i>b</i> / nm	2.222 89(3)	2.521 8(2)	2.642 01(5)
<i>c</i> / nm	3.098 95(4)	1.977 5(2)	4.660 28(8)
β / (°)	113.998(1)		
<i>V</i> / nm ³	23.481 7(5)	23.182(3)	40.558(2)
<i>Z</i>	4	4	8
<i>T</i> / K	184(2)	183(2)	120(2)
<i>D_c</i> / (g·cm ⁻³)	1.169	1.257	1.568
μ / mm ⁻¹	2.715	3.409	4.682
<i>F</i> (000)	8 328	8 744	18 896
Tot. data	100 414	217 301	247 125
Uniq. data	20 845	21 020	29 103
<i>R</i> _{int}	0.096 2	0.060 9	0.091 8
GOF	1.083	0.681	1.040
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.061 3	0.067 7	0.082 6
<i>wR</i> ₂ ^b (all data)	0.199 6	0.213 8	0.260 9

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

2 Results and discussion

2.1 Synthesis

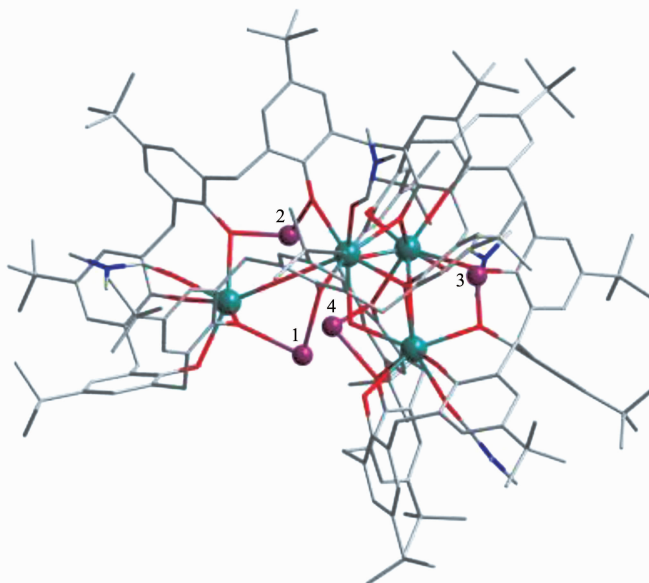
The reaction of *p*-*tert*-butylcalix[8]arene, MSO₄ (M=Co, Ni, Zn), ThCl₄ and triethylamine in a MeOH/DMF mixed solvent at 130 °C results in the formation of compounds **1**~**3**. It should be noted that single crystals of compound **1** could also be obtained when CoSO₄·7H₂O was replaced by CoCl₂·6H₂O while two others could not be obtained if the sulfates were substituted with the chlorides. In addition, another compound was obtained with ZnCl₂·4H₂O, whose structure can not be refined well due to its low crystal quality. It seems that the kind of transition metal salts would influence the final products.

2.2 Description of structures

In these three structures, all the calix [8]arene molecules adopt the double partial-cone conformation, in which each cone subunit bonds one thorium through four phenolic oxygen atoms at the lower rim and one coordinated DMF molecule occupies the cone cavity. Two tail-to-tail C8A molecules are bridged by four thorium cations through the Th-O_{phenolic} bonds into a sandwich-like tetranuclear conglomerate [Th₄(H_xC8A)(DMF)₄O₂] (Fig.2) which is similar to the reported [Th₄(HC8A)(H₂C8A)(dmsO)₄(OH)₃(OH₂)]^[24]. As shown in Fig.2, there are four vacant coordination sites 1~4. Sites 1 and 2 are located on the waist of one calixarene molecule while sites 3 and 4 on the waist of another. All these four sites could be further

bonded by Co, Ni, Zn or Th with the assistance of some auxiliary ligands (such as OH⁻ and solvent molecules). In these three compounds, the bond distances of Co-O, Ni-O, Zn-O and Th-O bonds are comparable with those in the reported literature^[7,16-17,20,24]. The metal oxidation states and the protonation of O²⁻ and OH⁻ groups are

determined by bond valence sum (BVS)^[7,25-26]. In these three compounds, all transition metals are divalent and thorium being tetravalent. The deprotonation of calixarene molecules was decided based on both BVS of the phenolic oxygen atoms and charge balance.



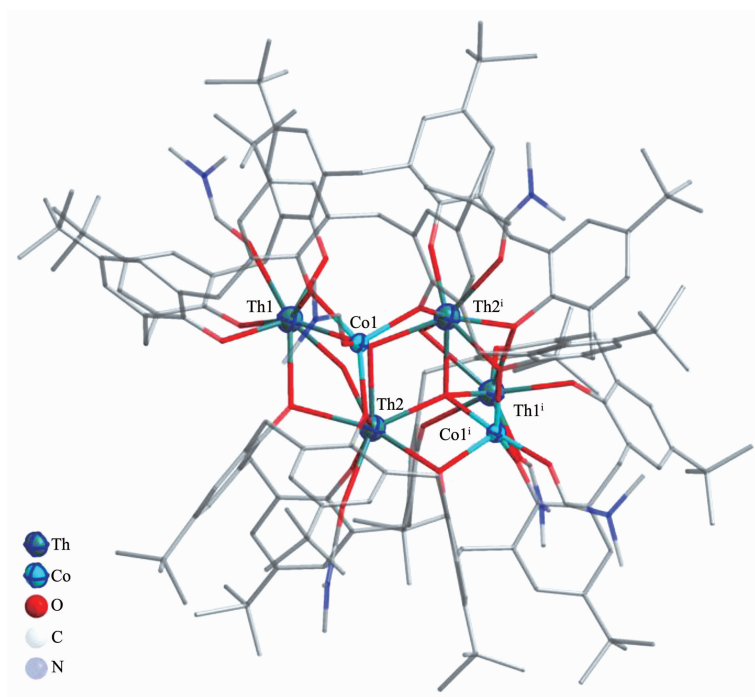
All four thorium atoms bond the partial cones of calix[8]arenes. There are four vacant coordination sites

Fig.2 One tetranuclear conglomerate with two tail-to-tail calix[8]arene molecules

Single-crystal X-ray diffraction reveals that compound **1** crystallizes in a monoclinic system with space group *C2/c*. In an asymmetric unit, there are one whole *p*-tert-butylcalix[8]arene molecule, one cobalt (Co1) and two thorium atoms (Th1 and Th2). As shown in Fig.3, two cobalt atoms occupy sites **1** and **3** of the [Th₄] conglomerate to form a [Co₂Th₄(HC8A)₂O₂(OH)₂(DMF)₆] unit. In this unit, the distances for two adjacent Th atoms is 0.382 nm while the trans Th...Th being of 0.375 or 0.651 nm. The Th...Co distances are in the range of 0.344~0.354 nm. According to the Ugozzoli-Andreotti convention^[27], the actual φ and χ torsion angles values, which define the solid-state conformation of C8A, are -77.0, +81.4; -87.0, +76.1; -72.0, +86.5; +81.4, -75.2; -83.9, +78.1; -88.3, +74.4; -67.3, +91.9; +77.7, -84.4. The deprotonation of calix[8]arene molecule gives a negative heptavalent ligand which bonds three thorium and two cobalt cations.

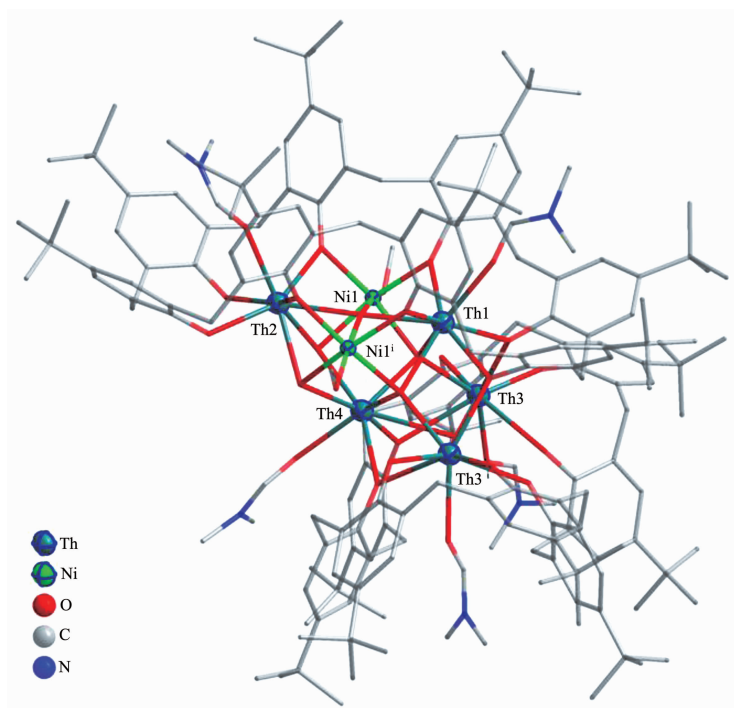
Compound **2** crystallizes in an orthorhombic

system with space group *Pnma*. In an asymmetric unit, there are two halves from different *p*-tert-butylcalix[8]arene molecules, one nickel (Ni1) and four thorium atoms (Th1, Th2, Th3, Th4). As shown in Fig.4, a [Ni₂Th₅(H₂C8A)(C8A)O₄(OH)₂(DMF)₅(CH₃OH)₂] unit was constructed by occupying sites **1** and **2** with two nickel atoms and site 4 with one thorium atom. The distances between two adjacent thorium atoms are in the range of 0.380~0.479 nm. The distances from Ni1 to Th1, Th2 and Th4 are of 0.314, 0.317 and 0.336 nm, respectively. The actual φ and χ torsion angles values for two independent C8A molecules, are -81.0, +72.4; +88.7, -77.1; -79.6, +74.2; -82.8, +82.8; -74.2, +79.6; +77.1, -88.7; -72.4, +81.0; -81.9, +82.0 and -84.2, +73.8; -74.8, +97.4; -89.3, +72.9; +89.4, -89.4; -72.9, +89.3; -97.4, +74.8; -73.8, +84.2; +77.2, -77.2, respectively. Two calix[8]arene molecules deprotonated differently, one giving out eight protons and another giving out six ones. And one calixarene bonds six metal cations and the other



Hydrogen atoms were omitted for clarify, symmetry code $i -x, y, 1/2-z$

Fig.3 Molecular structure of compound **1**



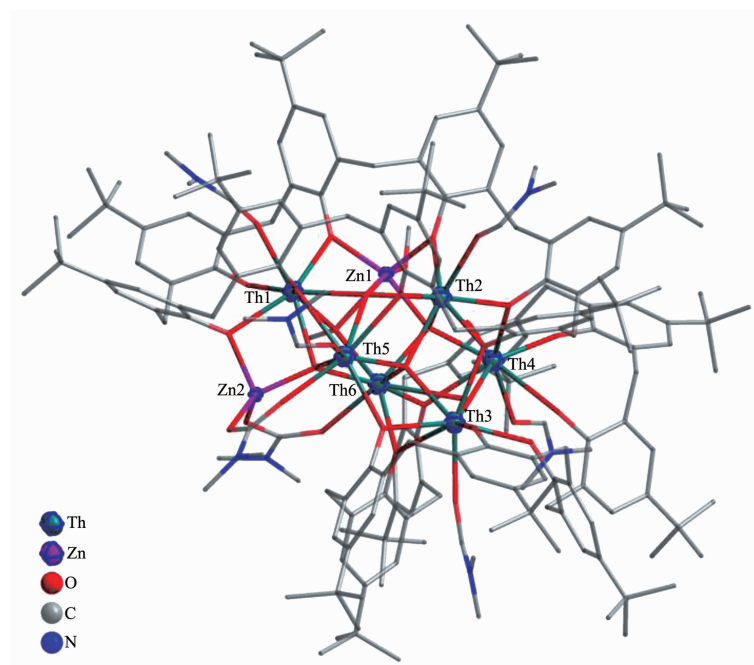
Hydrogen atoms were omitted for clarify, symmetry code $i x, 1/2-y, z$

Fig.4 Molecular structure of compound **2**

bonding three metals.

Compound **3** crystallizes in an orthorhombic system with space group *Pbca*. In an asymmetric unit, there are two whole calix[8]arene molecules, two zinc

and six thorium atoms (as shown in Fig.5). Sites 1 and 3 are occupied by two thorium atoms, and site 2 is occupied by one zinc atom. The left zinc atom (Zn2) is further bonded by one phenolic oxygen atom, two N,



Hydrogen atoms were omitted for clarify.

Fig.5 Structure of compound **3**

N-dimethylformate (DMFA) anions and one μ_3-O^{2-} . And then $[Zn_2Th_6(HC_8A)(C_8A)O_5(CH_3O)(C_3H_6NO_2)_2(DMF)_5(CH_3OH)]$ unit formed. The DMFA anion is generated in situ from the oxadiation of DMF^[28]. The Th...Th distances for the adjacent atoms are in the range from 0.367 to 0.394 nm. The distances from the zinc atoms to the adjacent thorium atoms are in the range of 0.317~0.410 nm. The wide range for the Zn-Th distance would be due to the disorder of thorium and zinc atoms. The actual φ and χ torsion angles values for two independent C8A molecules, are $-74.9, +91.5; -92.9, +76.3; -78.5, +84.0; +80.2, -81.9; -80.9, +82.2; -81.0, +79.4; -76.2, +82.9; +79.5, -86.1$ and $-74.8, +91.9; -98.1, +71.4; -78.3, +83.4; +80.3, -70.3; -85.4, +73.4; -71.9, +94.5; -89.6, +68.7; +92.9, -88.3$. Two calix[8]arene molecules deprotonated differently, this is, one fully deprotonated and the other keeping one proton.

Comparing the polynuclear conglomerates in compounds **1~3**, one can find that the relative calix[8]-arene arrangements differ more. In compound **1**, the angle between two calixarene molecules is of 45.5° (measured with that between two lines through the thorium atoms bonding the partial cones) while that

being of 90.0° and 88.7° for compounds **2** and **3**, respectively. This might be due to, on one hand, the flexibility of calix[8]arene, which allows it to coordinate with different metal centers, and on the other hand, the different radii and the coordination modes of the metal ions. All the extended structures of **1~3** are constructed by stacking these conglomerates via van der Waals interactions and the interstices between the polynuclear units are filled by the solvents.

2.3 Magnetic property of compound **1**

The magnetic property of compound **1** was examined on the polycrystalline samples in 2~300 K (Fig.6). The $\chi_M T$ value at room temperature is $5.47 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ which is larger than two expected spin-only value of $3.75 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ for two non-interacting cobalt (II) ions ($S=3/2, g=2.0$) (thorium (IV) being diamagnetic^[7]). This may be due to the orbital contribution of Co ions. As the temperature decreased from 300 K to 100 K, the $\chi_M T$ values remained nearly unchanged, and then decreased slowly to $4.43 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 20 K. The decrease may due to the single-ion property of Co ions^[29]. As the temperature decreased continued, the $\chi_M T$ value slightly increases to $4.68 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 10 K then declines quickly to

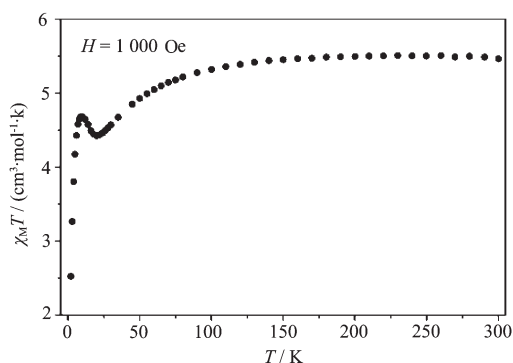


Fig.6 Plot of $\chi_M T$ vs. T for **1** in a 1 kOe applied DC field

$2.52 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K. Due to the orbitally degenerate ground state of cobalt(II) ion, it is difficult to explain the magnetic behavior^[29]. The increase may due to the weak ferromagnetic interactions between the metals.

3 Conclusion

In conclusion, we have synthesized three 3d-5f compounds, M-Th (M=Co, Ni, Zn) with the similar thorium conglomerates skeleton, based on *p*-tert-butylcalix[8]arene under solvothermal conditions. In these three structures, all the cluster cores are capped by two tail-to-tail calix[8]arene molecules to form some sandwich-like units. All the calix[8]arenes adopt a double partial cone conformation. They exhibit different coordination modes to the metals and different relative arrangement in polynuclear motifs. Magnetic study on compound **1** indicates that the metal centers exhibit weak ferromagnetic interactions at 10~20 K.

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