

Mn₄-硫杂杯[4]芳烃单元的 溶剂导向超分子组装

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摘要 以叔丁基硫杂杯[4]芳烃与 Mn(II) 为研究对象, 通过改变体系溶剂分别得到了 2 个四核化合物 Mn₄(T4A)₂ (**1**) 和 Mn₄(T4A)₂(DMF)₂ (**2**) (T4A = thiacalix[4]arene). 当反应溶剂为氯仿和甲醇的混合溶剂时, 形成的是以四核锰为结构单元的二维“笼目”(Kagomé) 状超分子化合物 **1**, 而当反应溶剂为 *N,N*-二甲基甲酰胺 (DMF) 和甲醇的混合溶剂时, 得到的是格子状二维超分子互穿的三维结构化合物 **2**. 化合物 **1** 具有很大的溶剂占有空隙, 是一个潜在的多孔材料, 而化合物 **2** 是一个紧密堆积的拓展结构.

关键词 杯芳烃; 核簇; 诱导作用; 超分子组装

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Solvent-directing Supramolecular Assemblies of Mn₄-thiacalix[4]arene

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Abstract Two tetranuclear compounds, Mn₄(T4A)₂ (**1**) and Mn₄(T4A)₂(DMF)₂ (**2**) (T4A = thiacalix[4]arene), were synthesized *via* the solvothermal reaction of manganese(II) acetate and thiacalix[4]arene with different solvents. Single-crystal analysis reveals that compound **1** with a two-dimensional Kagomé lattice was obtained in the mixed CHCl₃/CH₃OH solvent, while the interpenetrated 2D compound **2** was synthesized in the mixed DMF/CH₃OH solution. Porous compound **1** has some large solvent accessible voids while compound **2** has an impacted extended structure.

Keywords Calixarene; Metal cluster; Inductive effect; Supramolecular assembly

The controlled assembly of molecular building blocks into nanoscale architectures is a fundamental challenge in supramolecular chemistry^[1]. Calixarene is one of the most studied molecular tectonics in supramolecular chemistry because of its intriguing properties and applications in selective metal coordination, catalytic activity, and chemical sensor in solution and in the solid state^[2]. There are many reports on calix[4]arene-based supramolecular assemblies including a few supramolecular nanotubes modulated by organic molecules^[3,4]. Recently, Dalgarno and co-workers^[5] have found that the introduction of metal ions may facilitate the formation of nanostructure arrays *via* forcing the calixarene molecules to pack in a back-to-back fashion

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rather than in the common antiparallel bilayer arrangement. As a counterpart of the most studied *p*-*tert*-butylcalix[4]arene (H₄C4A), *p*-*tert*-butylthiacalix[4]arene (H₄TC4A) was found to exhibit different coordination toward the metal ions compared to C4A due to its bridging sulfur atoms^[6–8]. The hydrophobic interactions of its *t*-butyl moieties also influence the extended structures. *p*-H-thiacalix[4]arene (H₄T4A) that has no *t*-butyl moieties at *p*-positions might lead to some renewed supramolecular assemblies without the steric hindrance and hydrophobic interactions of *t*-butyl moieties^[9,10].

As an extension of our previous work on constructing metal-assisted supramolecular assembly of thiacalixarenes^[8], we present here the preparation and structures of two Mn₄^{II}-thiacalix[4]arene compounds, Mn₄(T4A)₂(**1**) and Mn₄(T4A)₂(DMF)₂.

1 Experimental

1.1 Materials and Methods

p-H-Thiacalix[4]arene (H₄T4A) was synthesized by means of the literature method^[11] and other reagents were purchased from commercial sources and used as received.

The EDS analyses of Mn and S were performed with on a HITACHI S-4800 Scanning Electron Microscope. TGA measurement is performed on a PYRIS DIAMOND instrument. Elemental analysis was carried out on a VarioEL elemental analyzer.

1.2 Synthesis

Colorless single crystal blocks of Mn₄(T4A)₂(**1**) was obtained from the reaction of the mixture of *p*-H-thiacalix[4]arene (0.05 g, 0.1 mmol), Mn(CH₃COO)₂ · 4H₂O (0.1 g, 0.4 mmol), triethylamine (0.40 mL, 4 mmol), CHCl₃ (5 mL) and CH₃OH (5 mL) in a 20 mL Teflon-lined autoclave which was kept at 130 °C for 3 d and then slowly cooled to 20 °C at about 4 °C/h. The crystals were isolated by filtration and then washed with methanol-chloroform (1:1, volume ratio). Yield *ca.* 15% with respect to H₄T4A. The EDS analysis of compound **1** reveals that the molar ratio of Mn to S is 7.64:15.16, comparable to the expected value (4:8 = 1:2). The result of the elemental analysis of C and H deviates much from the calculated values due to the easy loss of the involved solvent molecules in the lattice.

Mn₄(T4A)₂(DMF)₂(**2**) was synthesized *via* the similar procedure to that of compound **1** except that CHCl₃ was replaced by DMF. Yield *ca.* 20% for compound **2** with respect to H₄T4A. The EDS analysis of compound **2** reveals that the molar ratio of Mn to S is 11.43:22.56, comparable to the expected value (4:8 = 1:2). Element anal. (%) calcd. for C₅₄H₃₈Mn₄N₂O₁₀S₈: C 48.00, H 2.83, N 2.07; found: C 47.82, H 2.84, N 2.10.

1.3 X-ray Crystallography

The X-ray intensity data for compounds **1** and **2** were collected on a Bruker APEX-II CCD diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.071073$ nm) operated at 1.5 kW (50 kV, 30 mA). The crystal structure was solved by means of Direct Methods and refined with full-matrix least squares on F^2 *via* the SHELXTL program^[12]. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The diffraction data of compound **1** were treated by the “SQUEEZE” method as implemented in PLATON to remove diffuse electron density associated with the disordered solvent molecules^[13]. The application of squeeze dramatically improved the agreement indices. In addition, the high R_1 and wR_2 factors of compounds **1** and **2** might be due to the weak high-angle diffractions and the disorders. All the crystal data and structure refinement details for these two compounds are given in Table 1. CCDC reference numbers are 822855 (**1**) and 822856 (**2**).

Table 1 Crystallographic data for compounds 1 and 2

Complex	1	2	<i>T</i> /K	185(2)	185(2)
Formula	C ₄₈ H ₂₄ Mn ₄ O ₈ S ₈	C ₅₄ H ₃₈ Mn ₄ N ₂ O ₁₀ S ₈	<i>D_c</i> /(g · cm ⁻³)	1.302	1.720
<i>M_r</i>	1204.91	1351.10	μ/mm ⁻¹	1.117	1.330
Crystal. syst	Monoclinic	Tetragonal	<i>F</i> (000)	7248	2736
Space group	<i>C2/c</i>	<i>P4₂/n</i>	Tot. data	68014	36850
<i>a</i> /nm	1.93649(9)	2.01529(10)	Uniq. data	16580	4647
<i>b</i> /nm	3.34864(15)	2.01529(10)	<i>R</i> _{int}	0.107	0.051
<i>c</i> /nm	2.96918(15)	1.28458(7)	GOF	1.031	1.180
β/(°)	106.657(2)		<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0740	0.1217
<i>V</i> /nm ³	18.4460(15)	5.2172(5)	<i>wR</i> ₂ ^b (all data)	0.2263	0.3124
<i>Z</i>	12	4			

$$a. R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|; b. wR_2 = \{ \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2] \}^{1/2}.$$

2 Results and Discussion

2.1 Description of Crystal Structures

Single-crystal structure analysis reveals that compound **1** crystallized in the monoclinic system with space group *C2/c* and the building unit consisted of four Mn²⁺ and two tail-to-tail calixarene molecules, forming a sandwich-like structure as shown in Fig. 1. Each of the Mn centers is six-coordinated by four μ₂-O_{phenoxo} atoms and two sulfur atoms from two T4A ligands, exhibiting distorted octahedral coordination geometry. Compound **2** crystallized in the tetragonal system with space group *P4₂/n*. The building unit of compound **2** is also a sandwich-like moiety which contains two calixarene molecules, four Mn²⁺ centers and two coordinated DMF molecules. However, there are two crystallographic sites for the metal atoms in compound **2**, the seven-coordinated Mn1 and six-coordinated Mn2, adopting Mn1-Mn2-Mn1A-Mn2A quadrilateral arrangement. The six coordination of Mn atom is similar to that of Mn atom in compound **1**, while the seven-coordination mode was never observed in the thiacalixarene-based Mn compounds^[14,15]. The Mn-Mn distances on the edge (linked by the O_{phenoxo} atoms) and the crosses (free of link) of the Mn₄ quadrangle are of 0.333—0.334 and 0.469—0.474 nm for compound **1** and 0.339 and 0.442—0.514 nm for compound **2**, respectively. That is, the Mn₄ quadrangle in compound **2** shows a slight pinched mode, which can be ascribed to the DMF coordination. The Mn—O_{phenoxo}—Mn angles are in a range of 102.3°—103.7° in compound **1** and in a range of 102.1°—103.5° in compound **2**, respectively, which are similar to those in the other Mn-thiacalixarene compounds^[14,15]. Each T4A ligand in compounds **1** and **2** adopts a cone conformation and captures four Mn²⁺ atoms by four μ₂-O_{phenoxo} atoms and four bridging sulfur atoms.

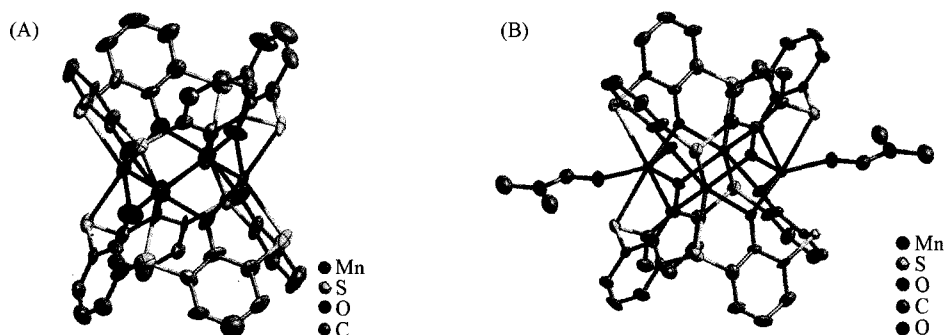


Fig. 1 ORTEP diagrams showing the building units in compounds 1(A) and 2(B)

Six adjacent building units in compound **1** are packed through π - π stacking interactions between aromatic groups of T4A ligands (face-to-face distance 0.365—0.371 nm) into a hexagon-macrocycle (hex-MC) structure with large tubular cavity inside (Fig. 2). The center to center distance between two sandwich-like units is

ca. 0.967 nm and the thickness of a hex-MC is about 1.272 nm (the C16...C28 distance). The peripheral diameter of the hex-MC reaches 3.012 nm (the C53...C53* distance), larger than that of a Co₃₂ nanosphere (2.340 nm) and a Co₂₄ metallamacrocycle (2.994 nm). Three hex-MCs stacked with each other by a corner-sharing mode to form a small trigonal cavity. The structure of compound **1** finally extended to a 2D 4-connectivity node with 3²6² topology (a so-called Kagomé lattice taking the tetranuclear unit as a node, Fig. 3).

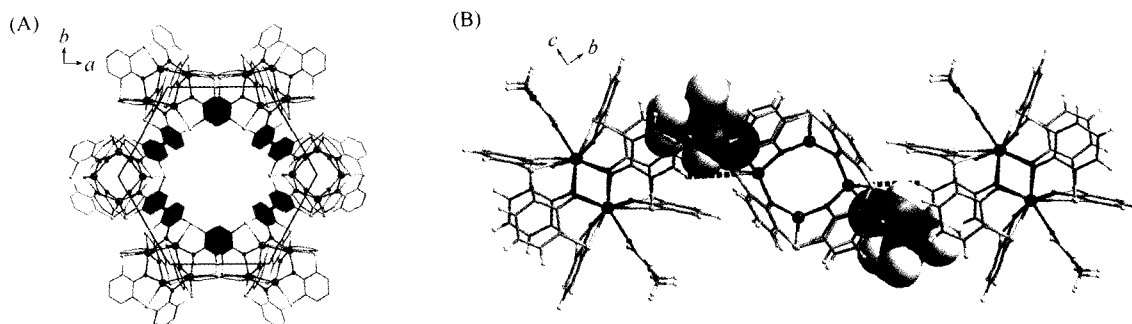


Fig. 2 Supramolecular interactions in compounds **1** (A) and **2** (B)

DMF molecules are highlighted in spacing filling mode for compound **2**.

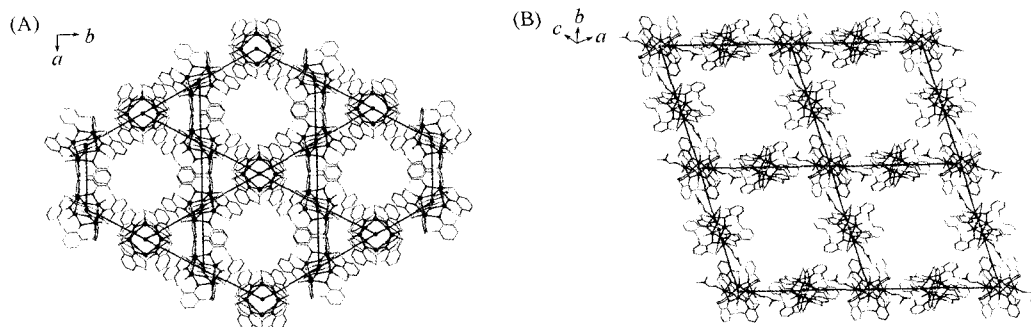


Fig. 3 2D structures of compounds **1** (A) and **2** (B)

However, the 2D layer networks stacked along the *c* axis with some excursion in the *ab* plane, which prevented the formation of infinite tubular channels (Figs. 4 and 5). No other obvious interaction was observed between the 2D layers except van der Waals' forces. The tubular cavity inside the hex-MC, the small trigonal cavity between hex-MCs and the interstices between the layers in compound **1** were occupied by some disordered solvent molecules whose electronic contribution was removed by SQUEEZE. Analysis with the PLATON[†] [6] program reveals that the solvent accessible volume (6.8226 nm³) is approximately 37% of the unit cell volume (18.4460 nm³) which indicates that compound **1** might be a candidate for the porous material.

In the extended structure of compound **2**, two coordinating DMF groups from one sandwich-like unit are

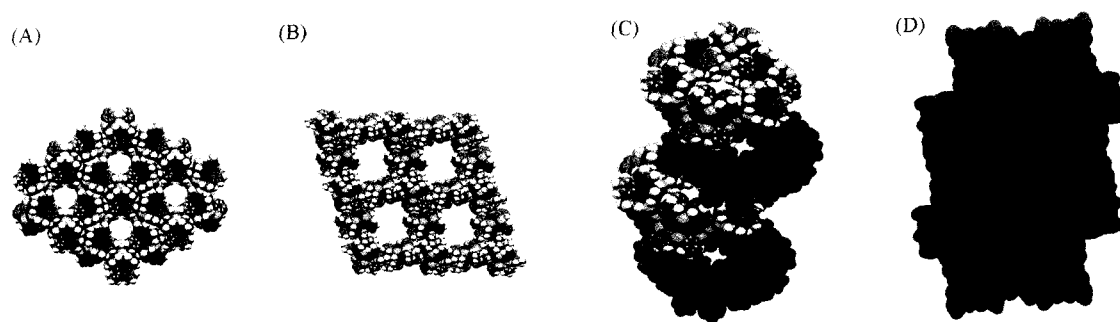


Fig. 4 Space-filling plots of the 2D network of compounds **1** (A) and **2** (B) and the no-channel structure of compound **1** (C) and interlocked structure of compound **2** (D)

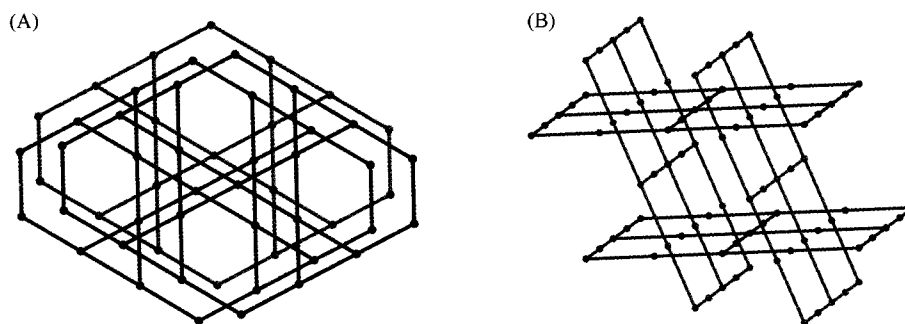


Fig. 5 Topology representations of compounds 1(A) and 2(B)

protruded into the cavity of two neighboring T4A ligands from two different sandwich-like units. Each sandwich-like unit contacts with two others continuously to form a 2D 2-4-connected framework by C—H $\cdots\pi$ interactions (DMF C—H $\cdots\pi$ calixarene ring; 0.344 nm, 137° and 0.349 nm, 114°) as shown in Figs. 2 and 3. C—H \cdots S interactions (C15—H15A \cdots S4, 0.362 nm, 139°) between the two units may play an important role to stabilize the 2D layer network. With close observing the intricate structure of compound 2, one can find that the 2D layers (angles between two layers are of 61.74°) interpenetrate with each other to form an interlocked 3D supramolecular structure (Fig. 5).

2.2 Influence of Solvent on the Structures

Since the only difference in the syntheses of compounds 1 and 2 is the use of different mixed solvent, it is clear that the solvent plays a key role to direct the formation of different extended structures. One can find that the introduction of DMF leads to two seven-coordinated Mn centers beside two six-coordinated ones for a sandwich-like building unit in compound 2. The bonded DMF molecules directed the formation of the interpenetrated extended structure of compound 2 which is distinct from that of compound 1. The introduction of small amounts of other auxiliary ligands, such as N₃⁻, does not influence the products in both cases. It should be noted that the decrease of the amount of triethylamine (less than 0.2 mL) would lead to the single crystals of H₄T4A ligand as reported by Hosseini and co-workers^[11]. It is obviously reasoned that triethylamine acts as a base for the deprotonation of calixarene and plays an important role in the formation of the title compounds.

2.3 Thermal Stability

To investigate the stability of the title compounds, thermal gravimetric (TG) analysis of compounds 1 and 2 were recorded with some fresh samples for which the surface solvents were wiped by filter paper. The result (Fig. 6) indicates that the onset of the solvent loss is at the very beginning of recording and the weight decreases continuously without any plateau up to 300 °C for compound 1, indicating that compound 1 easily lose the solvent molecules involved in the lattice, while compound 2 is relatively stable up to 150 °C. The decomposition is finished up at ca. 780 °C with unidentified decomposition products for compounds 1 and 2. It is difficult to speculate the attribution of the mass loss due to the un conspicuous mass loss stages and the intricate decomposition process.

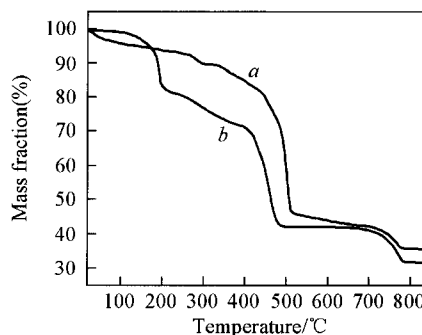


Fig. 6 TG curves of compounds 1(a) and 2(b)

3 Conclusions

In summary, we obtained two thiacalix[4]arene-supported Mn₄ clusters by the solvothermal reactions with different mixed solvent. It is found that the coordination of Mn centers can be affected by the coordination

abilities of the solvent molecules and the bonded DMF molecules directed the assembly of the sandwich-like Mn_4 units to form a distinct structure. After the successful re-arrangements of high nuclearity Co_{32} nanospheres by re-crystallization, we present here another approach to rearrange calixarene-supported metal clusters by changing the solvents.

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