Journal of Molecular Structure 1151 (2018) 29–33

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

A window frame-like square constructed by bridging Co_4-(TC4A-SO_2) SBUs with 1,3-bis(2H-tertazol-5-yl)benzene

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ARTICLE INFO

Article history:
Received 4 April 2017
Received in revised form
8 August 2017
Accepted 9 September 2017
Available online 10 September 2017

Keywords:
Calixarenes
Cobalt
Metal-organic aggregate
Solvothermal synthesis

ABSTRACT

A calixarene-based compound {[$Co_4(H_2O)$ (TC4A-SO_2)]$_4$(DTB)$_8$} (H_4TC4A-SO_2 = *p-tert*-butylsulfonylcalix[4]arene; H_2DTB = 1,3-bis(2H-tetrazol-5-yl)benzene) was obtained under solvothermal condition. The compound was characterized by single crystal X-ray diffraction, elemental analysis, TG analysis and FT-IR spectroscopy. In the structure, the Co_4-(TC4A-SO_2) shuttlecock-like secondary building units (SBUs) are bridged by the DTB ligands into some window frame-like squares, which are further stacked into an extended structure by supramolecular interactions. The results of magnetic measurements indicated an antiferromagnetic interaction between the metal centers. In order to evaluate its porosity, the gas sorption measurement was carried out.

1. Introduction

Coordination compounds have received increasing attention [1] due to their fascinating structures and potential applications in many fields such as gas adsorption and storage [2], encapsulation of unstable species [3,4], transportation of small molecules [5,6], promotion of chemical transformations [7–10], and templated formation of nanoparticles [11]. Calixarenes and their derivatives were proved to be excellent macrocyclic ligands for constructing the polynuclear coordination compounds due to their multiple coordination sites and a variety of conformations [12]. It should be noted that the shuttlecock-like M_4-calix[4]arene entities have been found to be a kind of stable secondary building units (SBUs), which can be bridged by other ligands into high nuclearity assemblies [13]. For instance, a Co_{24} metallamacrocycle and some M_{12} and M_{16} clusters were constructed by bridging the Co_4-TC4A SBUs with 1,2,4-triazole or in situ generated 5-methyltetrazolate [14,15]. A series of calixarene-based octahedral {M_{24}} coordination nanocages were obtained with the M_4-TC4A or M_4-(TC4A-SO_2) SBUs as the vertices and ancillary aromatic acids as the linkers [16]. Recently a calxarene-based trigonal prismatic {Ni_{24}} coordination cage was obtained by linking Ni_4-(TC4A-SO_2) SBUs with 2,5-thiophenedicarboxylic acid [17]. As an extension of our work on constructing novel calixarene-based coordination compounds, we introduced an ancillary linker 1,3-bis(2H-tertazol-5-yl)benzene (H_2DTB) into the cobalt-*p-tert*-butylsulfonylcalix[4]arene system. A window frame-like square {[$Co_4(H_2O)$(TC4A-SO_2)]$_4$(DTB)$_8$} (**CIAC-229**) was successfully obtained, which was constructed by bridging four Co_4-(TC4A-SO_2) SBUs with eight DTB ligands. The magnetic properties and porosity were evaluated.

2. Experimental section

2.1. Materials and instruments

*p-tert-B*utylsulfonylcalix [4]arene (H_4TC4A-SO_2) was synthesized by the literature method [18] and other reagents were purchased from commercial sources and used without further purification. Elemental analysis of C, H, and N was performed using a VarioEL instrument. TGA measurement was performed using a NETZSCH STA 449F3 from room temperature to 800 °C, with a heating rate of 10 °C min^{-1} under atmosphere. FT-IR spectra (KBr pellets) were taken on a Bruker Vertex 70 spectrometer. Magnetic susceptibility measurement for **CIAC-229** was performed with a Quantum Design MPMS XL-5 SQUID system in the temperature range of 2–300 K. N_2 adsorption and H_2 adsorption measurement

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http://dx.doi.org/10.1016/j.molstruc.2017.09.024
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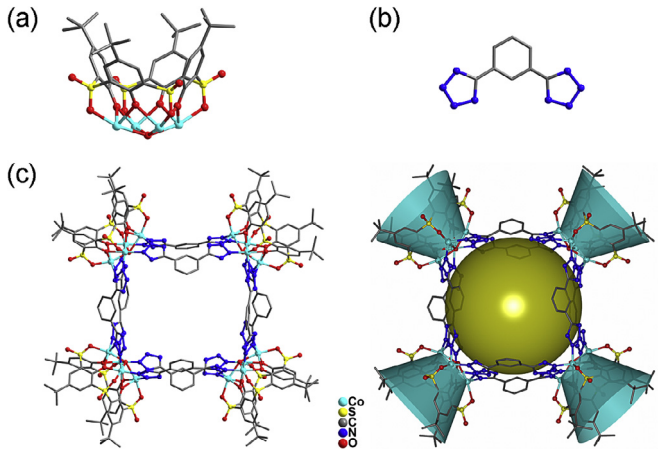

Fig. 1. Co_4-(TC4A-SO_2) SBU (a), 1,3-bis(2H-tetrazol-5-yl)benzene (b) and windows frame-like coordination square (c) in **CIAC-229**. The cyan cones and yellow sphere represent the calixarene molecules and the inner cavity, respectively.

was performed on a Micromeritics ASAP 2020 machine.

2.2. Synthesis of compound *CIAC-229*

Compound **CIAC-229** was obtained from the one-pot reaction of the mixture of H_4TC4A-SO_2 (0.05 g, 0.05 mmol), $CoCl_2 \cdot 6H_2O$ (0.05 g, 0.2 mmol), H_2DTB (0.02 g, 0.09 mmol), $CHCl_3$(5.0 mL), *N*, *N*-dimethylacetamide (DMA) (5.0 mL) and triethylamine (several drops) in a 20 mL Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to room temperature at about 4 °C·h^{-1}. The purple crystals were isolated by filtration. Yield: 36% with respect to calixarene. Elemental analysis: calculated (%) for $C_{224}H_{216}Co_{16}N_{64}O_{52}S_{16}$ (excluding the disordered solvents), C 44.12, H 3.55, N 14.71; found (after drying in vacuum): C 44.22, H 3.45, N 14.73.

FT-IR (cm^{-1}): 3350(m), 2956(s), 2876(m), 1852(w), 1660(s), 1616(s), 1488(s), 1449(s), 1372(m), 1334(m), 1289(s), 1263(s), 1219(m), 1129(s), 1078(s), 1020(w), 905(m), 847(m), 790(s), 745(m), 738(m), 653(w), 623(s), 572(s), 521(m).

2.3. X-ray data collection and structure refinement

The intensity data were recorded on a Bruker D8 QUEST system with Cu-Kα radiation (λ = 1.54178 Å). The crystal structures were solved by means of direct methods (SHELXT) and refined by employing full-matrix least squares on F^2 (SHELXL) [19]. Crystal data for **CIAC-229** (excluding the disordered solvent molecules): $C_{224}H_{216}Co_{16}N_{64}O_{52}S_{16}$, M = 60092.43 g/mol, monoclinic, *Cc*, *a* = 50.8720(11) Å, *b* = 17.5595(4) Å, *c* = 52.0511(11) Å, α = 90°,β = 94.627(1)°, γ = 90°, *V* = 46348.6(18)Å^3, Z = 4, D_{calcd} = 0.873 g/cm^3, *T* = 150(2) K, θ_{max} = 47.454°, F(000) = 12448, crystal dimensions 0.45 × 0.20 × 0.15 mm^3, reflections collected/unique, 290276/41816 (R_{int} = 0.0530), final R_1 = 0.0810, wR_2 = 0.2184 [I>2σ(I)], GooF = 1.090. Due to the weak diffraction at high 2θ angle, the value of sine(theta_max)/wavelength is less than 0.550. The diffraction data were treated by the "SQUEEZE" method as implemented in PLATON to subtract the electronic contribution of the disordered solvent molecules [20]. All the butyl groups and some coordinated solvent molecules were refined isotropically. And because of the disorder of the butyl groups, there are some short intra XH_m...XH_n distances. The hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors.

3. Results and discussion

3.1. Crystal structure of compound *CIAC-229*

Compound **CIAC-229** crystallizes in the monoclinic system with the space group *Cc*, which is non-centrosymmetric, allowing two non-identical inversely related atom arrangements within the unit cell. All the samples represent the inversion twins and contain simultaneously both inversely related atomic configurations instead of a single atomic arrangement. In an asymmetric unit, there is a crystallographically independent coordination square which is constructed by bridging four Co_4-(TC4A-SO_2) SBUs with eight DTB ligands (Fig. 1). Four adjacent cobalt atoms in a square

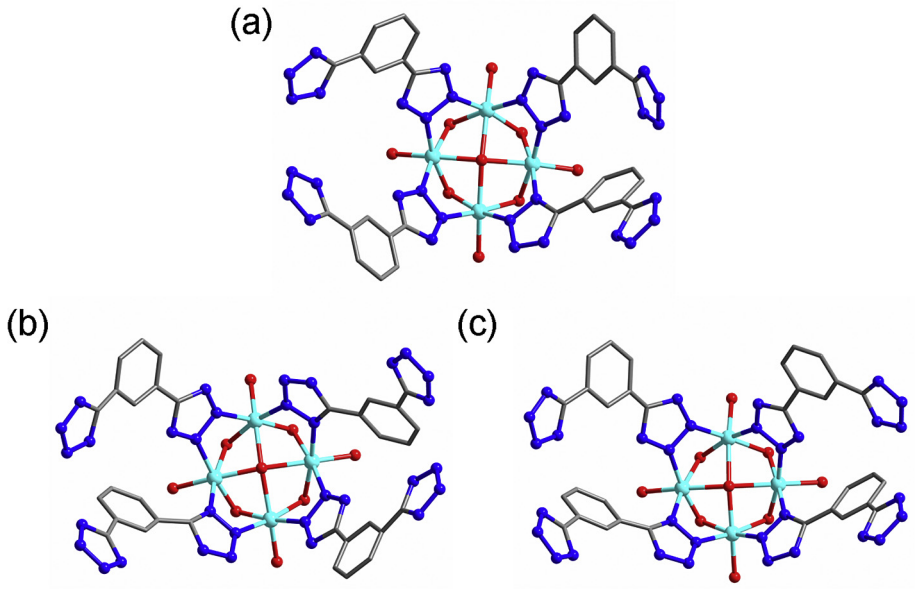

Fig. 2. Different coordination modes of the Co_4-(TC4A-SO_2) SBUs in **CIAC-229**. The calixarene molecules are omitted for clarity.