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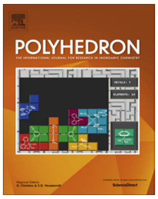

Coordination networks and supramolecular assemblies based on barium cation complexes with cucurbit[6]uril

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ABSTRACT

Three new barium(II)–cucurbit[6]uril complexes were synthesized by heating a mixture of aqueous $BaCl_2\cdot nH_2O$ solution, cucurbit[6]uril (CB[6]) and terephthalic acid (H_2bdc) in the presence of NEt_3. Single-crystal X-ray diffraction revealed the polymeric nature of the complexes with the two-dimensional structure $[Ba_2(bdc)CB[6](H_2O)_6]bdc\cdot 12H_2O$ (**1**), one-dimensional structure $[Ba_2(\mu\text{-}OH)_2(H_2O)_6CB[6]](bdc)\cdot 19H_2O$ (**2**) and the molecular "sandwich" structure of $[Ba_2(\mu\text{-}H_2O)_4(H_2O)_4(dmf)_2(CB[6])_2][Ba(bdc)(H_2O)_5]_2(bdc)_2\cdot 0.5H_2bdc\cdot 25H_2O$ (**3**). All the complexes have been characterized by elemental, XRD, IR, TG and fluorescent analyses.

1. Introduction

Metal–organic frameworks composed of linking metal centers and rigid organic bridging components have received considerable attention in recent years, not only because of the architectural beauty of their structures, but also because of their potential applications as new materials for gas storage, shape- and size-selective separation and catalysis [1]. Considerable progress has been achieved in the design and application of transition metal–organic frameworks. However, the field of coordination polymers containing s-metals has been investigated insufficiently.

Despite the abundance and diversity of the structures of coordination polymers to date, we still need to explore new building blocks and the building principles before we are truly able to design and build specifically engineered solid-state architectures. The family of macrocyclic cavitands cucurbit[*n*]urils (where n = 5=8) are expected to be good examples in this role, since they combine characteristics such as: (1) rigid high-symmetry structures; (2) polarized hydrophilic carbonyl portals capable of forming coordination or hydrogen bonds; (3) high resistance to thermolysis and aggressive media (hot concentrated acids and alkalis). One of the members of the family is cucurbit[6]uril (CB[6], $C_{36}N_{24}O_{12}H_{36}$): a molecule with a shape resembling a barrel and containing oxygen atoms of carbonyl groups (portals) on the top and bottom planes (Scheme 1) [2].

There are a few CB[6]-based polymers or metal–CB[6] frameworks based on the direct coordination of CB[*n*]s to metal ions. The first example of such polymers was reported by Kim and co-workers: the crystal structure showed that rubidium ions and CB[6] formed a one-dimensional polymer by direct coordination through alternate rubidium ions and the portal carbonyl oxygen atoms of CB[6] molecules. In addition, the coordinating polymer chains were arranged to form a honeycomb structure with large linear hexagonal channels parallel to the polymer chains [3]. Later, Kim and co-workers also reported similar coordinated polymer chains based on the direct coordination through alternating potassium ions and the portal carbonyl oxygen atoms of CB[6] molecules [4]. The coordination polymers $(H_3O)_2\{(Na_2(OH)CB[5])_2[HV_4O_{12}]\}Cl\cdot 14H_2O$, $[Na_3(\mu\text{-}H_2O)_4(H_2O)_4(CNPy@CB[6])]Cl_3\cdot 8H_2O$ and $[Rb_2(\mu\text{-}H_2O)_2(CNPy@CB[6])]Cl_2\cdot 8H_2O$ were also obtained [5,6]. In the structures reported in [6], CB[6] not only connects polynuclear complexes but also acts as a container for CNPy. The directly coordinating alternate CB[6] molecules and metal cations give rise to compounds with the common formulas $\{[Ca(H_2O)_3(HSO_4)(CH_3OH)]_2(CB[6])\}(HSO_4)_2\cdot 4H_2O$ [7] and $[Ca(HSO_4)_2]_2CB[6]\cdot 13H_2O$ [8]. As for the structures with barium cations, one can find only chain-like architectures with CB[5] (cucurbit[5]uril) [9], CB[5]* (pentacyclopentanocucurbit[5]uril) [10], OMeCB[6] (octamethylcucurbit[6]uril) [11], TMeCB[6] (tetramethylcucurbit[6]uril) [12], iCB[7] (inverted cucurbit[7]uril) [13] and HMeCB[6] (methyl-substituted cucurbit[6]uril derived from 3α-methyl-glycoluril) [14].

A number of CB[*n*]-based porous supramolecular assemblies have been shown to display unusual properties. For example, Kim and co-workers demonstrated that particular CB[6]- and CB

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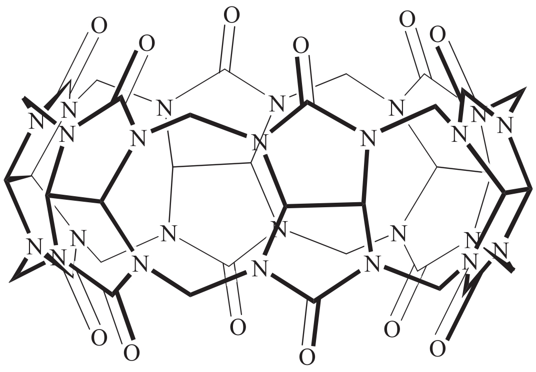

cucurbit[6]uril

Scheme 1. Cucurbit[6]uril.

[8]-based porous supramolecular assemblies, in addition to exhibiting significant porosity and high thermal stability, displayed impressive gas sorption behavior [15] or anisotropic proton conductivity [16]. The outer surface interactions of CB[*n*]s have been postulated to function as the driving force for the formation of such CB[*n*]-based porous supramolecular assemblies [17]. In particular, CB[*n*]-based coordination polymers, as well as other supramolecular assemblies, were shown to be associated with substantial free volumes between their building blocks, resulting in potential applications in selective gas sorption [18], in the extraction coating on solid-phase micro extraction (SPME) fibers [18a,19] and as stationary phases in capillary gas chromatography [20].

Herein, we report the preparation procedure, crystal structures and properties of three new Ba(II)–CB[6] complexes with the unique two-dimensional structure $[Ba_2(bdc)CB[6](H_2O)_6]bdc{\cdot}12H_2O$ (**1**, where bdc = terephthalic anion), the one-dimensional structure $[Ba_2(\mu\text{-}OH)_2(H_2O)_6CB[6]](bdc){\cdot}19H_2O$ (**2**) and the molecular "sandwich" structure of $[Ba_2(\mu\text{-}H_2O)_4(H_2O)_4(dmf)_2(CB[6])_2][Ba(bdc)(H_2O)_5]_2(bdc)_2{\cdot}0.5H_2bdc{\cdot}25H_2O$ (**3**). The crystal structures of compounds **1** and **2** demonstrate a way of constructing metal–organic frameworks using large organic cucurbituril macrocycles.

2. Experimental

2.1. Materials and general methods

All commercially available reagents and starting materials were of reagent-grade quality and used without further purification. Cucurbit[*n*]uril was prepared using the procedure reported in [2b].

Elemental analyses (C, H, N) were performed on a Euro NA 3000 Elemental Analyzer (EuroVector).

The powder X-ray diffraction (PXRD) patterns were collected on a Shimadzu XRD-7000 diffractometer (Cu Kα radiation; a Ni filter; 2θ range of 5–60°; 2θ step, 0.03°; 1 s per step; room temperature). Indexing the diffraction patterns was carried out using the single-crystal data.

The infrared (IR) spectra were recorded on a Scimitar FTS 2000 spectrophotometer with KBr pellets in the range 4000–400 cm^{-1}.

Thermogravimetric analysis (TGA) was performed under a helium atmosphere at a heating rate of 10 °C min^{-1} using a TG 209 F1 NETZSCH thermal analyzer (heating rate of 25/10.0 (K/min) in 70 ml/min helium flow; the sample weight was kept ca. 7–10 mg).

The excitation and emission spectra were recorded with a Horiba Jobin Yvon Fluorolog 3 photoluminescence spectrometer equipped with a 450 W Xe lamp, an integration sphere, Czerny–Turner double grating (1200 grooves per mm) excitation and emission monochromators, and an FL-1073 PMT detector. The excitation spectra were recorded in the wavelength range from 260 to 580 nm and corrected for the spectral distribution of the lamp intensity using a photodiode reference detector. The emission spectra were recorded in the wavelength range from 360 to 800 nm and corrected for the spherical response of the monochromators and the detector using typical correction spectra provided by the manufacturer.

2.2. Synthesis of the complexes

2.2.1. $[Ba_2(bdc)CB[6](H_2O)_6]bdc{\cdot}12H_2O$ (**1**)

A mixture of cucurbit[6]uril, $C_{36}H_{36}N_{24}O_{12}{\cdot}10H_2O$ (0.012 g, 0.01 mmol), $BaCl_2{\cdot}6H_2O$ (0.016 g, 0.05 mmol), H_2bdc (0.010 g, 0.06 mmol) and NEt_3 (50 μL, 3.57×10^{-4} mmol) in 3 ml H_2O were placed in a 7 mL glass vial with a cap. The vial was heated according to the following schedule: (1) heating from room temperature to 95 °C for 5 h; (2) maintenance at 95 °C for 12 h; (3) slow cooling to room temperature over 36 h. Colorless crystals of **1** and **2** shaped as rhombohedrals and sticks, respectively, were isolated after cooling. The yields were 0.018 g for **1** (93%) and 0.001 g for **2** (5%, based on CB[6]). For $C_{52}H_{80}Ba_2N_{24}O_{38}(+3H_2O)$ calculated, %: C, 31.57; H, 4.38; N, 16.99. Found, %: C, 31.3; H, 4.3; N, 17.1. IR (KBr, cm^{-1}): 449 (m), 491 (m), 634 (m), 678 (m), 756 (s), 802 (s), 889 (w), 964 (s), 1145 (s), 1190 (s), 1238 (s), 1328 (s), 1379 (s), 1464 (m), 1485 (s), 1575 (s), 1668 (m), 1724 (s), 174 5 (s), 2059 (vw), 2137 (vw), 2399 (vw), 2480 (vw), 2675 (w), 2854 (m), 2927 (m), 3460 (s), 3535 (s), 3784 (w), 3884 (w), 3975 (w).

2.2.2. $[Ba_2(\mu\text{-}OH)_2(H_2O)_6CB[6]](bdc){\cdot}19H_2O$ (**2**)

A mixture of cucurbit[6]uril, $C_{36}H_{36}N_{24}O_{12}{\cdot}10H_2O$ (0.012 g, 0.01 mmol), $BaCl_2{\cdot}6H_2O$ (0.016 g, 0.05 mmol), H_2bdc (0.010 g, 0.06 mmol) and NEt_3 (100 μL, 7.15×10^{-4} mmol) in 3 ml H_2O were placed in a 7 mL glass vial with a cap. The vial was heated according to the following schedule: (1) heating from room temperature to 95 °C for 5 h; (2) maintenance at 95 °C for 12 h; (3) slow cooling to room temperature over 36 h. Colorless crystals of **1** and **2** shaped as rhombohedrals and sticks, respectively, were isolated after cooling. The yields were 0.002 g for **1** (10%), 0.013 g for **2** (68%, based on CB[6]). For $C_{44}H_{92}Ba_2N_{24}O_{43}(-9H_2O)$ calculated, %: C, 30.06; H, 4.24; N, 19.12. Found, %: C, 30.7; H, 4.2; N, 19.2. IR (KBr, cm^{-1}): 632 (m), 677 (m), 758 (m), 802 (s), 964 (m), 1147 (m), 1190 (s), 1236 (s), 1377 (s), 1462 (m), 1479 (s), 1566 (m), 1730 (s), 2129 (vw), 2391 (vw), 2466 (vw), 2538 (vw), 2852 (m), 2926 (m), 3433 (s).

2.2.3. $[Ba_2(\mu\text{-}H_2O)_4(H_2O)_4(dmf)_2(CB[6])_2][Ba(bdc)(H_2O)_5]_2(bdc)_2{\cdot}0.5H_2bdc{\cdot}25H_2O$ (**3**)

The colorless crystals of compounds **1** and **2** were filtrated off. DMF diffusion into the filtrate solution from synthesis 2.2.2. results in crystals of compound **3**. Compound **3** crystallizes as colorless plates. The product was collected as a minor product with a yield of 0.003 g (7% based on CB[6]). For $C_{55}H_{89}Ba_2N_{25}O_{40}(-13H_2O)$ calculated, %: C, 37.16; H, 3.40; N, 19.69. Found, %: C, 37.3H, 3.8; N, 19.5. IR (KBr, cm^{-1}): 455 (w), 630 (m), 675 (m), 759 (m), 796 (s), 962 (m), 1029 (w), 1147 (m), 1188 (s), 1234 (s), 1327 (s), 1453 (m), 1477 (s), 1593 (s), 1708 (s), 1734 (s), 2237 (w), 2277 (w), 2459 (w), 2540 (w), 2704 (w), 2798 (w), 2877 (m), 2931 (m), 3419 (m).

2.3. X-ray crystal structure analysis

The X-ray single-crystal data of the three compounds were collected on a Bruker-APEX CCD diffractometer using standard