



Research paper

Coordination of lanthanide cations to a symmetrical dicyclohexanocucurbit[6]uril in the presence of tetrachlorozincate facilitates isolation of lighter lanthanides



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ARTICLE INFO

Article history:

Received 1 May 2016

Received in revised form 5 June 2016

Accepted 6 June 2016

Available online 7 June 2016

Keywords:

Symmetrical dicyclohexanocucurbit[6]uril

Lanthanide cation

Coordination

Structure directing agent

Supramolecular assembly

ABSTRACT

Coordination of lanthanide cations (Ln^{3+}) and a symmetrical dicyclohexanocucurbit[6]uril (1,4-DiCyHQ[6]) in the presence of tetrachlorozincate was investigated. X-ray single crystal diffraction analysis revealed that with $[\text{ZnCl}_4]^{2-}$ anions as a structure directing agent, the interaction of lighter lanthanide cations and 1,4-DiCyHQ[6] results in the formation of fast precipitation, whereas the interaction of heavier lanthanide cations and 1,4-DiCyHQ[6] results in solid crystals. This provides a potential strategy for separating lighter and heavier lanthanide cations.

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1. Introduction

The coordination chemistry of cucurbit[*n*]uril-based systems is somewhat less well developed than the host-guest chemistry [1–7], and accounts for only ~15% of all cucurbit[*n*]uril chemistry literature [8–12], even though coordination of cucurbituril (Q[6]) with calcium (Ca^{2+}) was the subject of the first publication in this area [13]. Towards the end of the last century, groups led by Mock and Buschmann began investigating Q[6]-based coordination chemistry [13–15], and since then, group led by Kim has investigated the interaction of Q[6] with alkali metal ions and the resultant supramolecular coordination polymers, and the group of Fedin has systemically investigated the interaction of Q[6] with various metal ions or clusters [8,9], Thuery et al. have extended studies to other Q[*n*]s, such as Q[5], Q[7] and Q[8] [16–25] and our group discovered novel coordination supramolecular assemblies based on partially alkyl substituted Q[5]s [26]. In particular, we found that *p*-hydroxybenzoic acid acts as a template in the presence of KI for the self-assembly of a regular Q[5], which arranges into six-membered ring structures. This solid coordination polymer absorbs volatile organics [27]. More recently we investigated the coordination of various metal ions with a series

of Q[*n*]s in the presence of aromatic molecules as structure directing agents, and a series of unsubstituted and alkyl-substituted Q[*n*]-based supramolecular assemblies were characterised [11,28]. An induction strategy based on polychloride transition metal anions results in the formation of Q[*n*]-based supramolecular coordination polymers in which the anions are arranged into a honeycomb-like assembly that attracts metal ions and leads to their coordination by portal carbonyl oxygens and the consequent formation of 1D coordination polymers [11]. The coordination of Q[*n*]s with metal ions in the presence of a third species (such as aromatic molecules or inorganic anions) that act as structure directing agents, can result in the formation of various macrocycle-based polydimensional supramolecular coordination architectures and polymers [11,28]. Weak noncovalent outer surface interactions of Q[*n*]s are crucial and act as the major driving force for the formation of Q[*n*]-based supramolecular assemblies and functional materials [11,28].

In the present work, a symmetrical dicyclohexanocucurbit[6]uril (1,4-DiCyHQ[6]) was selected as the basic building block (Fig. 1), and coordination with a series of lanthanide cations (Ln^{3+}) was investigated in the presence of tetrachlorozincate anions ($[\text{ZnCl}_4]^{2-}$) as a structure directing agent. X-ray diffraction analysis revealed that 1,4-DiCyHQ[6] preferred to coordinate heavier Ln^{3+} cations, such as Tb, Ho, and Tm in the presence of $[\text{ZnCl}_4]^{2-}$ anions.

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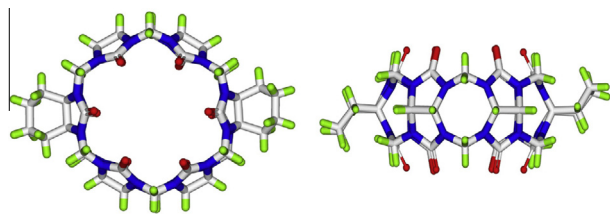


Fig. 1. Structure of the symmetrical dicyclohexanocucurbit[6]uril (1,4-DiCyHQ[6]) viewed from the top (left) and from the side (right).

2. Experimental

2.1. General materials

Chemicals, including $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, ZnCl_2 and HCl were of reagent grade and were used without further purification. 1,4-DiCyHQ[6] was prepared according to as the previously reported procedure [29]. Elemental analyses were carried out on a EURO EA-3000 elemental analyser.

2.2. Preparation of complexes

2.2.1. Synthesis

Many attempts to prepare solid 1,4-DiCyHQ[6]/ Ln^{3+} -based compounds, including in neutral solution or acidic solution without or with the third species, such as small aromatic molecules and inorganic anions as structure directing agents, introducing tetrachlorozincate anions into 1,4-DiCyHQ[6]- Ln^{3+} interaction systems is the most effective due to the outer surface interaction of Q [n]s [28]. A similar process was used to prepare crystals of related compounds: $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (0.031 mmol) and ZnCl_2 (3.18 mg, 0.023 mmol) were dissolved in 1 mL $3 \text{ mol} \cdot \text{L}^{-1}$ HCl (solution A), 1,4-DiCyHQ[6] (10 mg, 0.008 mmol) was dissolved in 1 mL $3 \text{ mol} \cdot \text{L}^{-1}$ HCl (solution B), and solution B was added to solution A and stirred. The systems containing lighter lanthanides, including La, Ce, Pr, Nd, Sm, yielded solid precipitation in a couple of days with yields of 55–65%; the systems containing the rest heavier lanthanides, gave nice X-ray quality crystals at least 3 days, and three crystal structures of them were obtained by X-ray single crystal diffraction analysis. The colour of crystals was dependent on the lanthanide ions. In summary, $\{\text{Tb}_2(\text{H}_2\text{O})_{12}1,4\text{-DiCyHQ[6]}\} \cdot 2[\text{ZnCl}_4] \cdot 2\text{Cl} \cdot 11(\text{H}_2\text{O})$ (**1**) was obtained from $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (28.2 mg), Anal. calcd for $\text{C}_{44}\text{H}_{94}\text{N}_{24}\text{O}_{35}\text{Tb}_2\text{Zn}_2\text{Cl}_{10}$ (%): C, 22.75; H, 4.08; N, 14.47; Found: C, 23.03; H, 3.89; N, 14.57; $\{\text{Ho}_2(\text{H}_2\text{O})_{12}1,4\text{-DiCyHQ[6]}\} \cdot 2[\text{ZnCl}_4] \cdot 2\text{Cl} \cdot 12(\text{H}_2\text{O})$ (**2**) was obtained from $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (27.5 mg), Anal. calcd for $\text{C}_{44}\text{H}_{96}\text{N}_{24}\text{O}_{36}\text{Ho}_2\text{Zn}_2\text{Cl}_{10}$ (%): C, 22.46; H, 4.11; N, 14.29; Found: C, 22.68; H, 3.99; N, 14.57; $\{\text{Tm}_2(\text{H}_2\text{O})_{12}1,4\text{-DiCyHQ[6]}\} \cdot 2[\text{ZnCl}_4] \cdot 2\text{Cl} \cdot 11(\text{H}_2\text{O})$ (**3**) was obtained from $\text{Tm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (27.7 mg), Anal. calcd for $\text{C}_{44}\text{H}_{94}\text{N}_{24}\text{O}_{35}\text{Tm}_2\text{Zn}_2\text{Cl}_{10}$ (%): C, 22.56; H, 4.04; N, 14.35; Found: C, 22.83; H, 3.86; N, 14.51. The reaction yields for (**1**)–(**3**) in terms of 1,4-DiCyHQ[6] were in the range 58–64%. It should be noted that the solid precipitation and crystals are insoluble in the aqueous HCl solution containing ZnCl_2 , whereas, they can be soluble in the neutral water.

2.2.2. X-ray crystallography

A suitable single crystal (ca. $\sim 0.2 \times 0.2 \times 0.1 \text{ mm}^3$) was taken up in paraffin oil and mounted on a Bruker SMART Apex II CCD diffractometer equipped with a graphite-monochromated Mo-K_α ($\lambda = 0.71073 \text{ \AA}$, $\mu = 0.828 \text{ mm}^{-1}$) radiation source operating in the ω -scan mode and fitted with a nitrogen cold stream (-30°C). Data were corrected for Lorentz and polarization effects (SAINT), and semi-empirical absorption corrections based on equivalent reflec-

tions were also applied (SADABS). The structure was elucidated by direct methods and F^2 values were refined by the full-matrix least-squares method using SHELXS-97 and SHELXL-97 program packages, respectively [30,31]. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were introduced at calculated positions, and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Most of the water molecules in the compounds were omitted using the SQUEEZE option of the PLATON program. 9, 10 and 9 water molecules were squeezed for compounds **1**, **2**, and **3**, respectively. Analytical expressions for neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Details of crystal parameters, data collection conditions, and refinement parameters are summarized in Table 1. In addition, crystallographic data for the reported structures have been deposited at the Cambridge Crystallographic Data Centre as Supplementary publication Nos. CCDC 1473243, 1473245, 1473244. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

2.3. Powder X-ray diffraction (PXRD)

PXRD of representative crystals of compounds **1–3** (in black), and comparison with simulations (in red), showed that the samples essentially consisted of pure crystalline phases (Fig. S1 in the SI).

2.4. Isothermal titration calorimetry

Microcalorimetric experiments were performed using an Nano ITC 2G isothermal titration calorimeter (TA, USA). Each experiment consisted of 25 consecutive injections ($10 \mu\text{L}$; $1 \times 10^{-3} \text{ M}$) of 1,4-DiCyHQ[6] of solution into the microcalorimetric reaction cell (1.3 mL) charged with a solution of $\text{Ln}(\text{NO}_3)_3$ ($1 \times 10^{-4} \text{ M}$). The heat of the reaction was corrected for the heat of dilution of the guest solution determined in separate experiments. All solutions were degassed by sonication prior to titration experiments. Computer simulations (curve fitting) were performed using the Nano ITC analyze software.

3. Results and discussion

3.1. Crystal structures of compounds (1–3)

An induction strategy based on polychloride transition metal anions was previously performed in our laboratory to prepare Q [n]-based coordination polymers or supramolecular assemblies [11,28]. In the present work, this strategy produced a similar result, and the honeycomb effect of $[\text{ZnCl}_4]^{2-}$ anions was observed in the resulting 1,4-DiCyHQ[6]/ Ln^{3+} -based supramolecular assemblies. Again, the driving force is derived from the so-called outer surface interactions of Q[n] (1,4-DiCyHQ[6] in the present study), based on ion-dipole interactions between the electropositive outer surface of 1,4-DiCyHQ[6] and $[\text{ZnCl}_4]^{2-}$ anions. Compound **1**, obtained from $\text{Tb}(\text{NO}_3)_3$ -1,4-DiCyHQ[6]- ZnCl_2 system in aqueous HCl solution, has the formula $\{\text{Tb}_2(\text{H}_2\text{O})_{12}1,4\text{-DiCyHQ[6]}\} \cdot 2[\text{ZnCl}_4] \cdot 2\text{Cl} \cdot 11(\text{H}_2\text{O})$ (**1**). Fig. 2a shows the supramolecular assembly constructed from 1,4-DiCyHQ[6]/ Tb^{3+} complexes and $[\text{ZnCl}_4]^{2-}$ anions, and it can be viewed as a $[\text{ZnCl}_4]^{2-}$ -based honeycomb-shaped framework (Fig. 2b) in which the pores are filled with linear supramolecular chain constructed from 1,4-DiCyHQ[6]/ Tb^{3+} complexes through outer surface interactions (dipole-dipole interactions between

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