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A Dodecalanthanide Wheel Supported by *p-tert*-Butylsulfonylcalix[4]arene

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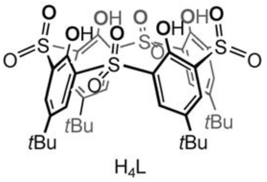
Abstract: A dodecaholmium wheel of $[Ho_{12}(L)_6(mal)_4(AcO)_4(H_2O)_{14}]$ (**1**; mal = malonate) was synthesized by using *p-tert*-butylsulfonylcalix[4]arene (H_4L) as a cluster-forming ligand. The wheel consists of three fragments of mononuclear A^{3-} ($[Ho(L)(mal)(H_2O)]^{3-}$), trinuclear B^{3-} ($[Ho(H_2O)_2(mal)(Ho(L)(AcO))_2]^{3-}$), and C^{3+} ($[Ho(H_2O)_2]^{3+}$), and an alternate arrangement of these fragments (A^{3-}–C^{3+}–B^{3-}–C^{3+}–A^{3-}–C^{3+}–B^{3-}–C^{3+}–) results in a wheel structure. The longest and shortest diameters of the core were estimated to be 17.7562(16) and 13.6810(13) Å, respectively, and the saddle-shaped molecule possesses a pocketlike cavity inside.

Keywords: calixarenes · chelates · lanthanides · macrocycles · wheels

Introduction

Nanosized metal clusters with high nuclearity are synthesized with the aim of obtaining novel functionalities and physical properties[1] on the basis of recent advances in synthetic methodology. The advantages of making nanosized metal complexes are mainly due to a bottom-up construction[2] that enables the fine control of structures and properties. Lanthanide complexes have attracted considerable attention due to their practical properties;[3] however, multinuclear lanthanide complexes are rare[4] because of the lack of rational synthetic methods. In a previous paper, we demonstrated a new synthetic procedure for nanosized lanthanide wheels by step-by-step nucleation.[5] Herein, we employed a *p-tert*-butylsulfonylcalix[4]arene (H_4L)[6a,7] as a cluster-forming ligand that behaves as a multidentate multinucleating ligand through many oxygen sites.[5] The octalanthanide wheels $[Ln_8(L)_4(AcO)_8(ROH)_4(H_2O)_4]$ (Ln = Pr, Nd, Sm, Gd) were formed from a mononuclear precursor $[Ln(L)]^-$ with assistance from acetate groups as coligands. By using a similar precursor, we obtained a larger wheel complex, the dodecalanthanide wheel $[Ho_{12}(L)_6(mal)_4(AcO)_4(H_2O)_{14}]$ (**1**; mal = malonate), with the appropriate adoption of coligands. Herein, we report the synthesis and structure of the giant lanthanide wheel **1**.



H_4L

Results and Discussion

We synthesized **1** by the reaction of $Ho(AcO)_3 \cdot nH_2O$, H_4L, and malonic acid (4:2:1). After several days, **1** crystallized as pale-pink crystals in a tetragonal crystal system. The four quarters of the molecule are crystallographically independent and are defined by a crystallographic fourfold axis parallel to the z axis (Figure 1). The molecule can be considered as an alternating wheel of six $[Ho(L)]^-$ moieties (e.g. Ho2 and Ho4) that bridge six $[Ho(H_2O)_2]^{3+}$ moieties (e.g. Ho1 and Ho3), similar to that observed in the octalanthanide wheels. The presence of mal groups makes the structure more complicated. The compound involves two kinds of mal ligands. One malonate group, which includes O27 and O28, chelates Ho4 via two oxygen atoms, each from one of the two carboxy groups (O27 and O27″), to form

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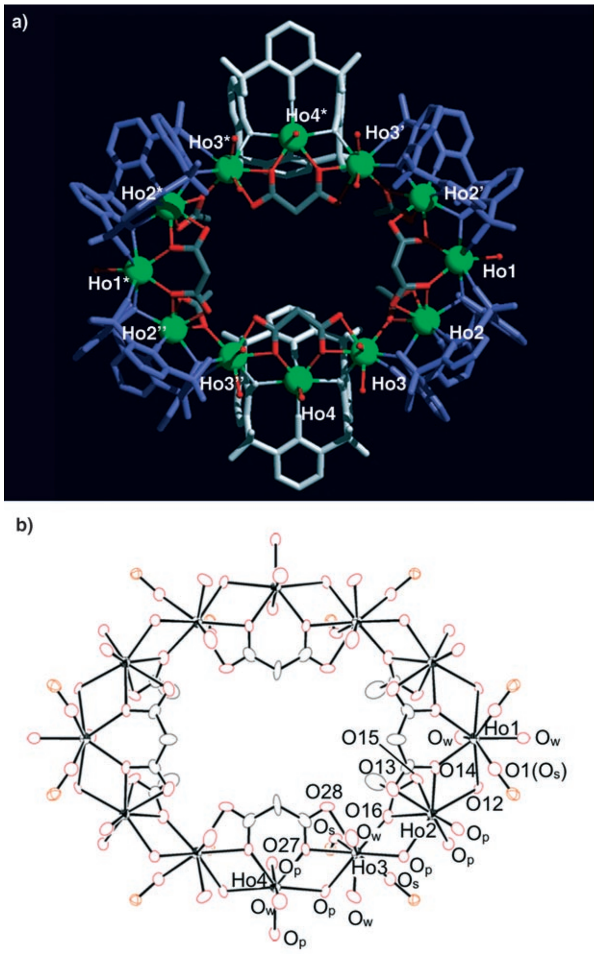

Figure 1. Crystal structure of **1**. a) Top view of the molecule in which two crystallographically independent L^{4-} units are depicted as white and blue frames. Ho = green, O = red, C = gray. b) ORTEP drawing of the Ho_{12} core with thermal ellipsoids at 50 % probability. Oxygen atoms from phenoxo and sulfonyl groups and water molecules are denoted Op, Os, and Ow, respectively. Ho1 and Ho4 are located on the crystallographic mirror planes. Selected atom–atom distances [Å]: Ho1−Op 2.415(3), Ho1−Os 2.348(3), Ho1−Ow 2.329(4) and 2.343(5), Ho1−O14 2.308(3), Ho2−Op 2.147(3)–2.423(3), Ho2−O13 2.478(4), Ho2−O14 2.403(3), Ho3−Op 2.447(3) and 2.495(3), Ho3−Os 2.346(3), Ho3−Ow 2.359(3) and 2.400(4), Ho3−O16 2.300(3), Ho3−O27 2.359(3), Ho3−O28 2.508(3), Ho4−Op 2.180(4)–2.409(3), Ho4−Ow 2.319(5), Ho4−O27 2.327(3), Ho1−Ho2 3.9711(5), Ho2−Ho3 3.9379(4), Ho3−Ho4 4.0132(4), Ho1−Ho1* 17.7563(16), Ho4−Ho4* 13.6810(12). Symmetry transformations: $' = y+{}^{1}\!/_{2}$, $x-{}^{1}\!/_{2}$, z, $'' = -y+{}^{1}\!/_{2}$, $-x+{}^{1}\!/_{2}$, z, $* = -x+2$, $-y+1$, z.

mononuclear $[Ho(L)(mal)(H_2O)]^{3-}$ moieties (fragment A^{3-}; Figure 1 a, L^{4-} frameworks in white). The other malonate dianion bridges two Ho^{III} ions (Ho2 and Ho2′) via two sets of oxygen atoms (O13/O14 and O13′/O14′) from both carboxy groups. The resulting dinuclear $[(Ho(L)(AcO))_2(mal)]^{6-}$ unit (Figure 1 a, depicted with L^{4-} in blue) further acts as a bistridentate ligand for Ho1 through one sulfonyl oxygen (O1), one phenoxo oxygen (O12), and one malonate oxygen (O14) from the one part and through O1′, O12′, and O14′ from the other part of the dinuclear unit. As a result, the trinuclear moiety $[(Ho(H_2O)_2)(mal)(Ho(L)(AcO))_2]^{3-}$ (fragment B^{3-}) is formed. The remaining four Ho^{III} ions (Ho3) form cationic $[Ho(H_2O)_2]^{3+}$ moieties (fragment C^{3+}). The alternate arrangement of these fragments, A^{3-}–C^{3+}–B^{3-}–C^{3+}–A^{3-}–C^{3+}–B^{3-}–C^{3+}–, results in the dodecanuclear wheel of **1**. L^{4-} in pinched-cone conformation acts as a tetradentate ligand via four phenoxo oxygen atoms to Ho2 and Ho4, and also as a bidentate ligand to Ho1 and Ho3 via a phenoxo as well as a sulfonyl oxygen atom. Octacoordination of Ho1, Ho2, and Ho3 and heptacoordination of Ho4 are completed by malonate oxygen atoms and two water molecules for Ho1 and Ho3, malonate and acetate oxygen atoms for Ho2, and malonate oxygen atoms and a water molecule for Ho4. Coordination distances fall into the ranges of 2.147(3)–2.495(3), 2.346(3)–2.457(3), 2.300(3)–2.508(3), and 2.319(5)–2.400(4) Å for $O_{phenoxo}$, $O_{sulfonyl}$, $O_{malonate}$ and $O_{acetate}$, and O_{water}, respectively.

The oval-shaped cluster core (Figure 1 b) is made up of 12 holmium(III) ions separated from each other by distances of 3.9379(4)–4.0131(4) Å, and the longest and shortest diameters of the core were estimated to be 17.7562(16) Å for Ho1⋯Ho1* and 13.6810(13) Å for Ho4⋯Ho4*, respectively. The whole molecule has a saddlelike shape with a pocketlike cavity (Figure 2), inside which four ethanol molecules

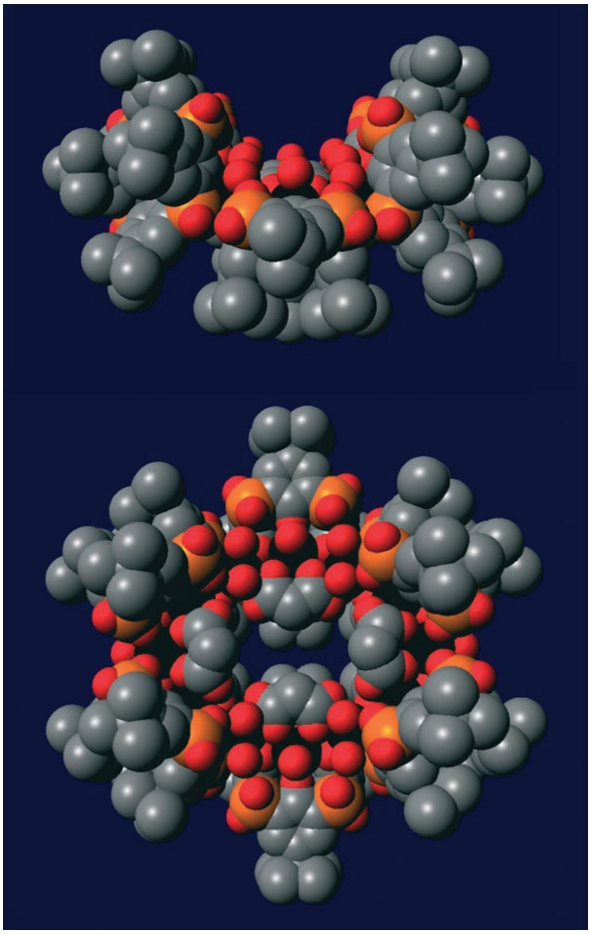

Figure 2. Top and side view of the space-filling diagram of **1**. Ho, S, O, and C are depicted as black, orange, red, and gray spheres, respectively.

were included. In accordance with the van der Waals radii, the size of the whole molecule is up to $3\times3\times2$ nm^3.

We synthesized a dodecaholmium(III) wheel by adoption of a malonate ion as a coligand. In our previous paper, we reported the syntheses of four octalanthanide wheels of Pr, Nd, Sm, and Gd with acetate as a coligand.[5] Although these octalanthanide wheels seemed structurally similar to each other, the detailed structures such as the bridging modes of L^{4-} and the overall symmetry of the molecule were different between Pr/Nd and Sm/Gd. This difference is mainly due to the decrease in ionic radii of these metal ions (1.13, 1.11, 1.08, and 1.05 Å, respectively, each for octacoordination). These nanosized structures were quite sensitive to slight differences in coordination distances, which could be owing to steric repulsion between methyl groups on acetate ligands that were directed toward the center of the core. We first tried to synthesize a similar octaholmium(III) wheel, but failed because of the small ionic radius of the holmium(III) ion (1.02 Å). It was confirmed that the mononuclear precursor $[Ho(L)(AcOH)]^-$ is the major species in the reaction solution,[9] and a rapid association/dissociation equilibrium would occur with additional coligands. To avoid methyl–methyl repulsion, malonate anions were introduced, which led to the formation of a larger wheel with a more complicated sequential structure. In the process of crystallization, the malonate acts as a μ_3-κ^2O,O';κ^2O',O'';κ^2O'',O''' ligand in both A^{3-} and B^{3-}, and especially in the latter case, it seems to act as a linking ligand for two $[Ho(L)]^-$ moieties to stabilize the large B^{3-} fragment in the solid state.

Conclusions

We have synthesized a large lanthanide wheel compound of molecular weight of up to 7900 by using *p-tert*-butylsulfonylcalix[4]arene as a cluster-forming ligand as well as malonate ions as coligands. Nanosized wheel structures are very sensitive to small changes in coordination distances of lanthanide ions, and appropriate adoption of the coligand is essential for the construction and control of the structures of this type of lanthanide wheel cluster.

Experimental Section

1: $Ho(AcO)_3\cdot nH_2O$ (28.8 mg, 0.08 mmol), H_4L (34.0 mg, 0.04 mmol), and malonic acid (2.0 mg, 0.02 mmol) in $EtOH/CHCl_3$ (1:2 (*v*/*v*), 9 mL) were heated at reflux for 15 min, after which the solvent was evaporated to dryness. The resulting pale-pink residue was then recrystallized from $MeOH/CHCl_3$ (1:1 (*v*/*v*), 4 mL), and pale-pink blocks of $\mathbf{1}\cdot4CHCl_3\cdot4EtOH\cdot nH_2O$ ($n\approx26$) were obtained over several days (yield $\approx10\%$). Crystal data for **1** ($C_{260}H_{312}O_{110}S_{24}Ho_{12}$; $M_r=7940.02$): pale-pink prism, tetragonal, space group $P\bar{4}2_1m$, $a=31.738(3)$, $c=23.179(3)$ Å, $V=23348(4)$ Å^3, $Z=2$, $T=200$ K, $\rho=1.289$ g cm^{-3}, $F(000)=8904$, $\mu(\mathrm{Mo_{K\alpha}})=2.253$ mm^{-1}. Complete hemispheres of data were collected by using ω scans. Integrated intensities were obtained with SAINT+,[8] and SADABS[8] was used for absorption correction. The structures were solved by direct methods with SHELXS-97[8] and refined by least squares on F^2 (SHELXL-97)[8] to give $wR_2=0.2070$ (23414 unique reflections) and $R_1=0.0686$ (15153 reflections with $I>2\sigma(I)$) for 1364 parameters. CCDC 600534 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/data request.cif.

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[9] An MS study was carried out for the reaction solution of $Ho(AcO)_3\cdot nH_2O$, H_4L, and malonic acid in a 4:2:1 ratio in $MeOH/CHCl_3$ together with the methanolic solution of **1**. For the former, one signal was observed at $m/z=1070.72$, and for the latter, three intense signals were observed at $m/z=1010.56$, 1042.62, and 1070.67 with relative intensities of 100:40:58, each corresponding to the monoanionic species of $[Ho(L)]^-$ (m/z calcd = 1009.10), $[Ho(L)(MeOH)]^-$ (m/z calcd = 1041.13), and $[Ho(L)(AcOH)]^-$ (m/z calcd = 1069.12), respectively. No significant signals were observed for anionic species larger than $m/z=1200$ and for cationic species larger than $m/z=300$. A small amount of multinuclear species might be present in solution, which fragmented into mononuclear species. The 1:1 adduct of Ho^{III} and L^{4-} is stable enough, the exchange of coligands should be fast, and the most stable neutral wheel complex **1** would be crystallized.

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