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Hydrogen-Bonded Superstructures of a Small Host Molecule and Lanthanide Aquo Ions

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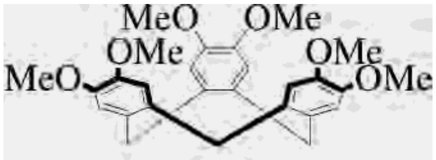
Despite containing only relatively small molecular components, the structure of $[Eu(H_2O)_9]_{1.5}(CTV)_6(CH_3CN)_{5.5}(H_2O)_{7.5}[Co(C_2B_9H_{11})_2]_{4.5}$ ($C_{191}H_{337.5}B_{81}Co_{4.5}Eu_{1.5}N_{5.5}O_{57}$, $a = 54.590(2)$ Å, $b = 37.5788(17)$ Å, $c = 31.8067(14)$ Å, $\beta = 116.573(2)°$, monoclinic, $C2/c$, $Z = 8$) is of an unusually large size and level of complexity, with an intricate hydrogen-bonding network formed between lanthanide aquo ions, water, and the small host molecule cyclotriveratrylene (=CTV). The 3D hydrogen-bonded network structure that results is unique and too complicated to apply the usual topological analysis. Instead a simplified model using structural subunits is described.

The creation of infinite network structures using coordinate and/or hydrogen-bonding interactions is a burgeoning field of chemistry.[2] We are interested in network structures that incorporate known molecular hosts as this creates crystalline materials that may show multiple inclusion behavior. Examples include network structures with calixarenes,[3] cucurbitural,[4] crown ethers,[5] and cyclotriveratrylene (=CTV),[6,7] which is the focus of our work. CTV is emerging as an important host molecule with CTV derivatives having applications in liquid crystal,[8] biological,[9] and anion extraction.[10] CTV can be incorporated into 1D, 2D, or 3D network structures either as a chelating ligand, or as a hydrogen bond acceptor. For instance, an unusual 3,12-connected 3D hydrogen-bonding array is formed between back-to-back CTV tetramers and free and ligated water in $[Sr(H_2O)_8][(CH_3CN)(CTV)]_4(H_2O)_4[Co(C_2B_9H_{11})_2]_2$ and related materials.[7] The use of other metal aquo ions may afford different hydrogen-bonded assemblies with CTV, and lanthanide ions were investigated as their use in network formation is attractive due to their high coordination numbers, which allows for structures with unusual topologies[11] as well as physiochemical properties such as fluorescence.

We report herein a hydrogen-bonding network based on interactions between nonaaquo lanthanide ions, water, and CTV molecules. The structure of crystalline materials obtained is significantly more complicated than previously seen structures involving CTV and establishes a second type of back-to-back CTV tetramer. The size and complexity of this supramolecular assembly is highly unusual, though there are similarities with Atwood's calixarene sphere, where 12 sulfonated calixarenes stack back-to-back to form a large sphere held together by coordinate interactions with lanthanide ions.[12] Hydrogen-bonding interactions between lanthanide aquo ions and host molecules have been previously reported for crown ethers[5] and sulfonated calix[4]arene.[13]



CTV

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Yellow-orange crystals of $[Eu(H_2O)_9]_{1.5}(CTV)_6(CH_3CN)_{5.5}(H_2O)_{7.5}[Co(C_2B_9H_{11})_2]_{4.5}$ **1** grow from a mixture of CTV and $Eu[Co(C_2B_9H_{11})_2]_3$ in aqueous acetonitrile, after the initial formation of a yellow oil. The crystals were weakly diffracting and of monoclinic symmetry with cell volume 58356(4) Å^3. Isostructural crystals are obtained with Sm. The structure was solved in space group *C*2/*c* and is extremely complicated with the formula given above for **1** comprising the asymmetric unit.[14] Notably this is one of the very few structures of small molecular components ($<$50 non-H atoms) with unit cell volume $>$50000 Å^3.[15]

The structure of **1** features a 3D hydrogen-bonded network. 3D network structures are usually analyzed by topological means, breaking down the structure into connections between nodes or centers where the nodes are molecules/ions and the connections individual coordinate or hydrogen bonds.[2] In this case analysis of individual hydrogen-bonding patterns is complicated and somewhat confusing and the network structure may be best understood by considering structural subunits and how they are linked together.

The structure of **1** features two types of $[Eu(H_2O)_9]^{3+}$ cations in 2:1 proportions, with Eu(2) positioned on a center of symmetry. Both $[Eu(H_2O)_9]^{3+}$ cations show distorted capped triangular dodecahedral geometry. Four of the aquo ligands of each $[Eu(H_2O)_9]^{3+}$ cation are at distances consistent with the formation of hydrogen bonds to additional water molecules (Eu(1), O···O separations 2.65, 2.76, 2.87, 3.02 Å; Eu(2), O···O separations 2.63, 2.68 Å). The two $[Eu(H_2O)_9](H_2O)_4$ assemblies show very different arrangements of the hydrogen-bonded water molecules, and both may be regarded as structural subunits, Figure 1. The $[Eu(H_2O)_9](H_2O)_4$ subunits act as hydrogen bond donors to CTV molecules, with each type interacting with eight CTV molecules, at O···O separations ranging from 2.75 to 3.27 Å for Eu(1) and 2.67 to 2.87 Å for Eu(2). Ligated water molecules also hydrogen bond to guest acetonitrile molecules, $Eu(1)-OH_2\cdots NCCH_3$ 2.60, 2.87, 2.93 Å, $Eu(2)-OH_2\cdots NCCH_3$ 2.87 Å. One of the nine aquo ligands of $[Eu(1)(H_2O)_9]$, and four from the same face of the triangular dodecahedron in $[Eu(2)(H_2O)_9]$, are not involved in any hydrogen-bonding interactions.

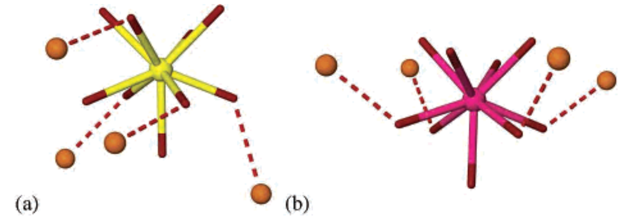

Figure 1. $[Eu(H_2O)_9](H_2O)_4$ subunits for (a) Eu(1) and (b) Eu(2). $Eu(1)-OH_2$ bond lengths range from 2.27(2) to 2.543(15) Å; $Eu(2)-OH_2$ bond lengths from 2.395(11) to 2.607(19) Å.

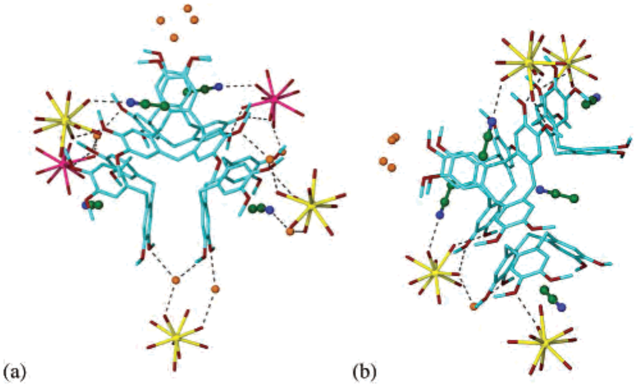

Figure 2. Back-to-back stacking of CTV molecules and hydrogen-bonding interactions: Eu(1) yellow; Eu(2) pink; uncoordinated water molecules shown as orange spheres; guest acetonitrile in green. (a) Regular $[CTV]_4$ assembly, type I. (b) Splayed $[CTV]_4$, type II.

The CTV molecules stack together as back-to-back tetramers with two structurally distinct types. Type I, shown in Figure 2a, has an approximately tetrahedral arrangement of the CTV molecules. Although the arene rings of adjacent CTV molecules are in the slipped coplanar arrangement preferred for π stacking interactions, the distances between them (centroid separations ranging from 3.82 to 4.22 Å) indicate that such interactions are not significant. In type II the $[CTV]_4$ unit is less regular (Figure 2b), having been splayed by the insertion of an acetonitrile molecule. Five of the six pairs of arene ring from adjacent CTV molecules are coplanar at centroid separations ranging from 3.75 to 4.54 Å. Inclusion of the acetonitrile molecule, which is oriented such that the nitrile group points directly toward the center of the $[CTV]_4$ tetramer, pushes the two remaining arene units apart to a centroid separation of 7.34 Å. The type I and II $[CTV]_4$ assemblies exist in 2:1 proportions throughout the structure. Each CTV molecule also hosts an acetonitrile guest.

The dimethoxy groups of the CTV molecules accept hydrogen bonds from either free or coordinated water, Figure 2. The two types of $[CTV]_4$ also hydrogen bond to a water cluster formed by two water molecules disordered over four sites. This water cluster hydrogen bonds to three $[CTV]_4$ clusters (two type I, one type II), acting as a 3-connecting center or node in terms of the topology of the 3D hydrogen bond array found in **1**, Figure 3.

Type I $[CTV]_4$ forms hydrogen-bonding interactions to one water cluster, three $[Eu(1)(H_2O)_9](H_2O)_4$ assemblies, and two $[Eu(2)(H_2O)_9](H_2O)_4$, Figure 2a. Type II $[CTV]_4$ forms hydrogen-bonding interactions to one water cluster and four $[Eu(1)(H_2O)_9](H_2O)_4$ assemblies, Figure 2b. In terms of the

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(14) Crystal data for **2**: $C_{191}H_{337.5}B_{81}Co_{4.5}Eu_{1.5}N_{5.5}O_{57}$, $M_r = 4991.9$, $T = 100(1)$ K, Mo Kα radiation, yellow crystal 0.47 × 0.33 × 0.11 mm, monoclinic, *C*2/*c*, $a = 54.590(2)$ Å, $b = 37.5788(17)$ Å, $c = 31.8067(14)$ Å, $\beta = 116.573(2)°$, $V = 58356(4)$ Å^3, $Z = 8$, $\rho_{calc} = 1.136$ g cm^{-3}, $\mu = 0.631$ mm^{-1} (multipole correction), $\theta_{max} = 20.82°$, 200059 data collected on a Bruker AXS SMART Apex diffractometer, 30548 unique ($R_{int} = 0.049$), 3139 parameters, 157 restraints, R1 = 0.1367 [21586 data $I > 2\sigma(I)$], wR2 = 0.4421 [all data], $S = 1.865$. Structure was solved using SHELXM and refined with block-matrix least squares with SHELXL-97. All non-hydrogen atoms were refined anisotropically aside from two partially occupied CH_3CN molecules and a disordered $[Co(C_2B_9H_{11})_2]^-$. Hydrogen atoms included with a riding refinement, restraints were placed on some Co−B, B−B, and C−B bond lengths, and on some U_{ij} values. Unit cell parameters for Sm analogue: $a = 54.5041(5)$ Å, $b = 37.7273(3)$ Å, $c = 31.6809(3)$ Å, $\beta = 116.596(1)°$.

(15) Other examples: (a) Mascal, M.; Hext, N. M.; Warmuth, R.; Moore, M. H.; Turkenburg, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2204−2206. (b) Coxall, R. A.; Harris, S. G.; Henderson, D. K.; Parsons, S.; Tasker, P. A.; Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2000**, 2349−2356.

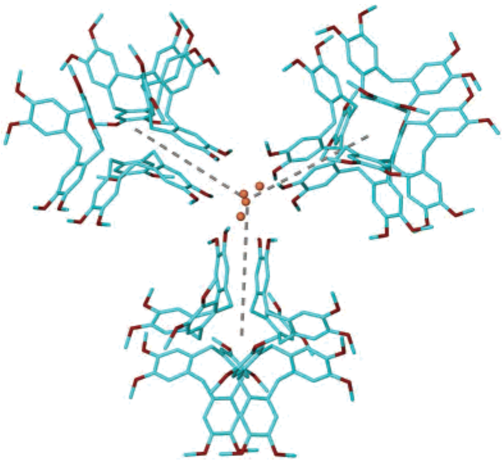

Figure 3. Hydrogen-bonding interactions between the dimethoxy groups of CTV and two water molecules disordered over 4 sites (shown in orange) create a 3-way connection between the water cluster and three $[CTV]_4$ clusters.

simplified topological analysis, type I is a 6-connecting center, and type II a 5-connecting center. Both types of $[Eu(H_2O)_9](H_2O)_4$ subunits hydrogen bond to eight CTV molecules. For Eu(1) these belong to five different $[CTV]_4$ tetramers; hence Eu(I) is a 5-connecting center, whereas Eu(2) connects to only four $[CTV]_4$ subunits and is hence a 4-connecting center. Including the 3-connecting water tetramer, there are five types of subunits that connect together, linking to form a complicated 3D network. The shortest complete circuits between connecting centers are 4-gons or 6-gons. The simplest complete building block of the network is the cage assembly illustrated in Figure 4a. The cage is bound at either end by a 6-gon centered by a 3-connecting water cluster. Other faces are 4-gons or 6-gons from the linking of $[CTV]_4$ and $[Eu(H_2O)_9](H_2O)_4$ subunits. The cages tessellate in 3 dimensions as shown in Figure 4b, to give an unusual network. The large $[Co(C_2B_9H_{12})]^-$ anions occupy spaces within the cages and are in close proximity, Figure 4c.

The structure of **1** shows some similarities with that of $[Sr(H_2O)_8][(CH_3CN)(CTV)]_4(H_2O)_4[Co(C_2B_9H_{11})_2]_2$ and related materials.[7] Using the subunit approach to that structure gives an α-Po related network with regular alternating of $[Sr(H_2O)_8](H_2O)_4$ and $[CTV]_4$ subunits in 3 dimensions. This structure may also be isolated in low yields from solutions containing lanthanide ions.[7b] The identity of the metal center was initially postulated to be a mixed Ln/Na site; however, EDX (energy-dispersive X-ray) analysis indicates it may be Ca^{2+}, presumably from the CaO content of glass.

We have synthesized and characterized a highly complicated hydrogen-bonded assembly with unique 3D topology incorporating the host molecule CTV. The organization of small host molecules into simple lattice structures has produced materials with useful adsorption properties,[16] as have more open framework 3D network structures.[2b] By combining aspects of the two approaches we can reasonably expect to create crystalline materials with similar future applications.

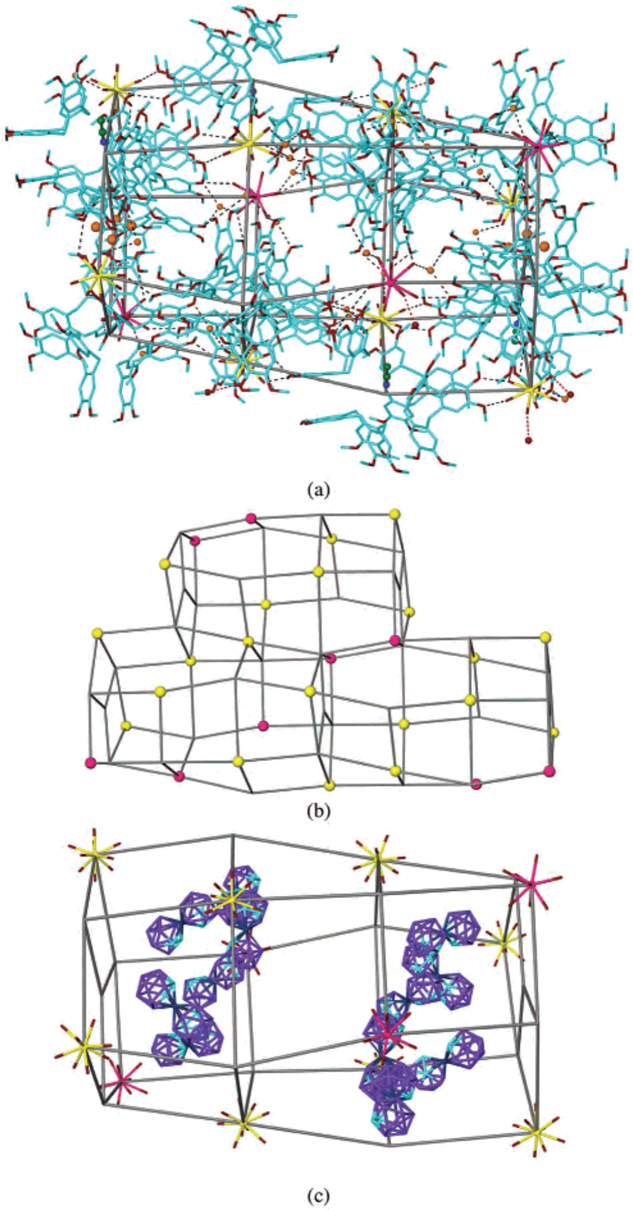

Figure 4. (a) Cage assembly within the 3D hydrogen-bonded network of **2**. Guest CH_3CN and anions omitted for clarity; CH_3CN molecules of type II $[CTV]_4$ are included. Gray lines indicate connectivity between $[CTV]_4$, $[Eu(H_2O)_9]^{3+}$, and $(H_2O)_2$ nodes (see text). (b) Tessellation of cages, with only Eu atomic sites and centers of other connecting nodes shown. (c) Location of $[Co(C_2B_9H_{11})_2]^-$ anions within each cage assembly.

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Supporting Information Available: Crystallographic information for **1** in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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