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Article

Second-Sphere Tethering of Rare-Earth Ions to Cucurbit[6]uril by Iminodiacetic Acid Involving Carboxylic Group Encapsulation

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The reaction of rare-earth nitrates with iminodiacetic acid (H_2IDA) in the presence of cucurbit[6]uril (CB6) in water at room temperature yields a family of isomorphous complexes, $[M(H_2IDA)(NO_3)(H_2O)_6](NO_3)_2 \cdot CB6 \cdot 14H_2O$ with M = Y (**1**), Ce (**2**), Nd (**3**), Eu (**4**), Dy (**5**), Er (**6**), Tm (**7**), and Yb (**8**). In these compounds, the trivalent metal ion is bound to one nitrate ion, six water molecules, and one zwitterionic H_2IDA molecule. The latter is further partly included in the CB6 cavity, with the ammonium group forming two hydrogen bonds with oxygen atoms of one portal. The uncoordinated carboxylic group is thus encapsulated in CB6 and hydrogen-bonded to the other portal via a water molecule. CB6 is a second-sphere ligand in these complexes, but direct bonding of the metal ion to CB6 can be enforced by using a ligand more deeply imbedded in the cavity, such as 2-pyridylacetate (PA) in $[Eu(PA)(CB6)(NO_3)(H_2O)_5](NO_3) \cdot 10H_2O$ (**11**). When the reaction with H_2IDA is performed with Lu(III) or Cu(II), no metal complex is isolated, but the inclusion compounds $[(H_3IDA)_2(CB6)](NO_3)_2 \cdot xH_2O$ with x = 6 (**9**) or 8 (**10**) are obtained instead, in which the two H_3IDA^+ cations are attached to the CB6 portals by ammonium−carbonyl hydrogen bonds and are linked to one another inside the cavity by hydrogen bonding between the carboxylic groups. These complexes are compared to that comprising a dicarboxylic acid devoid of an ammonium functionality, $[(H_2AZ)(CB6)] \cdot 6H_2O$ (**12**), where H_2AZ is azelaic acid. The metal ion complexes **1**−**8** and the organic complexes **9** and **10** display the unprecedented feature of inclusion of carboxylic groups inside the CB6 cavity, with the CB6/acid stoichiometry and the finer details of the host−guest interactions being dependent on the presence of the metal ion.

Introduction

Cucurbit[*n*]urils (n = 5−8),[1] and particularly cucurbit[6]uril (CB6, Scheme 1), the most common member in this family, have been shown to be good complexants for 4f,[2−4] as well as 5f,[2c,5] metal ions, as indicated by the large number of crystal structures reported in both cases. Complexes of CB6 uniting both uranyl and lanthanide ions have even been described.[6] The complexation of lanthanide ions may be accompanied by the encapsulation of a secondary ligand such as isonicotinate[2j,k] or perrhenate[4,6] anions. Encapsulation of cations, and particularly of ammonium cations such as protonated diaminoalkanes, in CBs is however much more widespread than that of anions,[1b−e,7] and binding of ammonium cations by acyclic

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(1) (a) Freeman, W. A.; Mock, W. L.; Shih, N. Y. *J. Am. Chem. Soc.* **1981**, *103*, 7367. (b) Lee, J. W.; Samal, S.; Selvapalam, N.; Kim, H. J.; Kim, K. *Acc. Chem. Res.* **2003**, *36*, 621. (c) Kim, K.; Selvapalam, N.; Oh, D. H. *J. Incl. Phenom. Macrocycl. Chem.* **2004**, *50*, 31. (d) Lagona, J.; Mukhopadhyay, P.; Chakrabarti, S.; Isaacs, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4844. (e) Isaacs, L. *Chem. Commun.* **2009**, 619.

(2) (a) Samsonenko, D. G.; Lipkowski, J.; Gerasko, O. A.; Virovets, A. V.; Sokolov, M. N.; Fedin, V. P.; Platas, J. G.; Hernandez-Molina, R.; Mederos, A. *Eur. J. Inorg. Chem.* **2002**, 2380. (b) Samsonenko, D. G.; Gerasko, O. A.; Lipkowski, J.; Virovets, A. V.; Fedin, V. P. *Russ. Chem. Bull.* **2002**, *51*, 1915. (c) Samsonenko, D. G.; Sokolov, M. N.; Gerasko, O. A.; Virovets, A. V.; Lipkowski, J.; Fenske, D.; Fedin, V. P. *Russ. Chem. Bull.* **2003**, *52*, 2132. (d) Gerasko, O. A.; Sokolov, M. N.; Fedin, V. P. *Pure Appl. Chem.* **2004**, *76*, 1633. (e) Tripolskaya, A. A.; Mainicheva, E. A.; Mitkina, T. V.; Gerasko, O. A.; Naumov, D. Y.; Fedin, V. P. *Russ. J. Coord. Chem.* **2005**, *31*, 768. (f) Mainicheva, E. A.; Tripolskaya, A. A.; Gerasko, O. A.; Naumov, D. Y.; Fedin, V. P. *Russ. Chem. Bull.* **2006**, *55*, 1566. (g) Mainicheva, E. A.; Gerasko, O. A.; Sheludyakova, L. A.; Naumov, D. Y.; Karsanova, I. I.; Amirov, R. R.; Fedin, V. P. *Russ. Chem. Bull.* **2006**, *55*, 1956. (h) Tripolskaya, A. A.; Gerasko, O. A.; Naumov, D. Y.; Fedin, V. P. *J. Struct. Chem.* **2007**, *48*, 949. (i) Tripolskaya, A. A.; Mainicheva, E. A.; Gerasko, O. A.; Naumov, D. Y.; Fedin, V. P. *J. Struct. Chem.* **2007**, *48*, 547. (j) Gerasko, O. A.; Mainicheva, E. A.; Naumova, M. I.; Yurjeva, O. P.; Alberola, A.; Vicent, C.; Llusar, R.; Fedin, V. P. *Eur. J. Inorg. Chem.* **2008**, 416. (k) Gerasko, O. A.; Mainicheva, E. A.; Naumova, M. I.; Neumaier, M.; Kappes, M. M.; Lebedkin, S.; Fenske, D.; Fedin, V. P. *Inorg. Chem.* **2008**, *47*, 8869.

(3) (a) Liu, J. X.; Long, L. S.; Huang, R. B.; Zheng, L. S. *Cryst. Growth Des.* **2006**, *6*, 2611. (b) Liu, J. X.; Long, L. S.; Huang, R. B.; Zheng, L. S. *Inorg. Chem.* **2007**, *46*, 10168. (c) Lin, R. L.; Liu, J. X.; Long, L. S.; Huang, R. B.; Zheng, L. S. *J. Incl. Phenom. Macrocycl. Chem.* **2008**, *62*, 263.

(4) Thuéry, P. *Inorg. Chem.* **2009**, *48*, 4497.

(5) (a) Thuéry, P. *Cryst. Growth Des.* **2008**, *8*, 4132. (b) Thuéry, P. *Cryst. Growth Des.* **2009**, *9*, 1208. (c) Thuéry, P. *CrystEngComm* **2009**, *11*, 1150. (d) Thuéry, P.; Masci, B. *Cryst. Growth Des.* **2010**, *10*, 716.

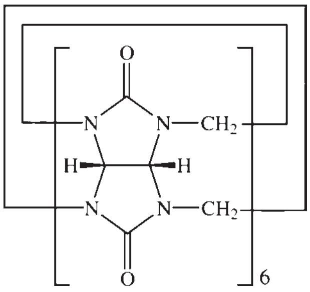
(6) Thuéry, P. *Inorg. Chem.* **2009**, *48*, 825.

(7) (a) Mock, W. L.; Shih, N. Y. *J. Org. Chem.* **1983**, *48*, 3618. (b) Freeman, W. A. *Acta Crystallogr., Sect. B* **1984**, *40*, 382. (c) Mock, W. L.; Shih, N. Y. *J. Org. Chem.* **1986**, *51*, 4440. (d) Jeon, Y. J.; Kim, S. Y.; Ko, Y. H.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Org. Biomol. Chem.* **2005**, *3*, 2122. (e) Heitmann, L. M.; Taylor, A. B.; Hart, P. J.; Urbach, A. R. *J. Am. Chem. Soc.* **2006**, *128*, 12574. (f) Vincil, G. A.; Urbach, A. R. *Supramol. Chem.* **2008**, *20*, 681. (g) Huang, W. H.; Zavalij, P. Y.; Isaacs, L. *Org. Lett.* **2008**, *10*, 2577. (h) Rekharsky, M. V.; Yamamura, H.; Mori, T.; Sato, A.; Shiro, M.; Lindeman, S. V.; Rathore, R.; Shiba, K.; Ko, Y. H.; Selvapalam, N.; Kim, K.; Inoue, Y. *Chem.*—*Eur. J.* **2009**, *15*, 1957. (i) Kim, Y.; Kim, H.; Ko, Y. H.; Selvapalam, N.; Rekharsky, M. V.; Inoue, H.; Kim, K. *Chem.*—*Eur. J.* **2009**, *15*, 6143.

Table 1. Elemental Analyses Results (%)

	1	2	3	4	5	6	7	8	9	11
C calcd	27.22	26.45	26.39	26.28	26.13	26.06	26.03	25.98	35.30	30.76
found	27.16	26.49	27.12	27.13	26.13	25.83	25.73	26.05	35.40	30.43
H calcd	4.74	4.61	4.60	4.58	4.55	4.54	4.53	4.52	4.31	4.32
found	4.46	4.27	4.42	4.29	4.27	4.08	3.93	4.33	4.17	3.96
N calcd	22.22	21.59	21.54	21.45	21.33	21.28	21.25	21.21	26.19	22.52
found	22.19	21.43	21.47	21.54	21.33	21.12	20.51	21.15	25.89	22.95

Scheme 1. Cucurbit[6]uril



glycoluril oligomers has even been observed.[8] A proper choice of the alkyl chain length separating two ammonium groups permits hydrogen bonding of both of them to the CB portals, but hydrophobic and ion−dipole interactions are however likely predominant.[7a,c] This affinity of CBs for alkyldiammonium cations has been exploited in the design of rotaxanes and pseudorotaxanes,[9] while further metal ion coordination by functional groups (pyridyl or carboxylates for example) located at both ends of the included species yields polyrotaxanes or molecular necklaces;[10] in particular, a three-dimensional polyrotaxane includes Tb(III) ions.[11] The "thread" involved in the latter case is 1,4-butanediammonium with terminal carboxylate appendages; a search of the Cambridge Structural Database (CSD, version 5.31)[12] shows that no shorter molecule comprising both carboxylate and ammonium groups has been used as a ligand in association with CBs. One of the simplest examples of such a molecule is iminodiacetic acid (H_2IDA), which is too short to be suitable for the design of CB6-based rotaxanes but could possibly permit complexation of the metal ion to the cucurbituril portal simultaneously with ammonium inclusion. This possibility has been investigated, and a series of eight isomorphous complexes involving rare-earth ions is reported herein, which display carboxylate bonding to the metal cation and second-sphere coordination of CB6 through ammonium bonding, instead of direct coordination. For the sake of comparison, the Eu(III) complex with 2-pyridylacetate, with coordination to both the carboxylate and CB6 moieties, is described. Two original organic inclusion complexes of H_3IDA^+ in CB6, obtained over the course of this study, are also reported, and they are compared with the first pseudorotaxane built from CB6 and a neutral dicarboxylic acid.

Experimental Section

Synthesis. The rare-earth nitrates $M(NO_3)_3 \cdot xH_2O$ (x = 5 or 6) were purchased from either Prolabo, Aldrich, Strem Chemicals, or Alfa Aesar. Iminodiacetic acid, 2-pyridylacetic acid hydrochloride, and cucurbit[6]uril hydrate were purchased from Fluka; the water content in the latter is *ca.* five water molecules per cucurbituril molecule, according to the analysis provided by the seller. Azelaic acid was from Aldrich. Elemental analyses were performed by Service de Microanalyse du CNRS at Gif-sur-Yvette, France.

$[M(H_2IDA)(NO_3)(H_2O)_6](NO_3)_2 \cdot CB6 \cdot 14H_2O$ with M = Y (1), Ce (2), Nd (3), Eu (4), Dy (5), Er (6), Tm (7), and Yb (8). All these compounds were obtained under identical conditions, as exemplified for M = Y. $CB6 \cdot 5H_2O$ (11 mg, 0.01 mmol), a 10-fold excess of $Y(NO_3)_3 \cdot 5H_2O$ (37 mg, 0.10 mmol), and a 20-fold excess of iminodiacetic acid (H_2IDA, 27 mg, 0.20 mmol) were dissolved in demineralized water (1.5 mL) upon heating for ca. 30 min. The solution was then left to evaporate slowly at room temperature. Large, colorless crystals appeared overnight in the case of **1**−**6** and within one week for **7** and **8**. Yields (based on CB6) are in the range 22−65%. Elemental analyses results for compounds **1**−**8** are given in Table 1.

$[(H_3IDA)_2(CB6)](NO_3)_2 \cdot 6H_2O$ (9) and $[(H_3IDA)_2(CB6)](NO_3)_2 \cdot 8H_2O$ (10). When the synthesis described above was performed with M = Lu, no crystals of the corresponding complex appeared, but crystals of compound **9** were reproducibly obtained instead within one week (7 mg, 47% yield based on CB6, elemental analysis results are given in Table 1). The same compound was obtained when $Cu(NO_3)_2 \cdot 3H_2O$ was used as a starting material instead of a rare-earth nitrate, but in this case, it was accompanied by a few crystals of compound **10**, presenting a slightly different morphology. Compound **10** could not be isolated from **9** in sufficient quantity for elemental analysis.

$[Eu(PA)(CB6)(NO_3)(H_2O)_5](NO_3) \cdot 10H_2O$ (11). $CB6 \cdot 5H_2O$ (11 mg, 0.01 mmol), a 10-fold excess of $Eu(NO_3)_3 \cdot 5H_2O$ (43 mg, 0.10 mmol), and a 20-fold excess of 2-pyridylacetic acid (HPA) hydrochloride (34 mg, 0.20 mmol) were dissolved in demineralized water (2 mL) upon heating for ca. 15 min. The solution was then left to evaporate slowly at room temperature. Colorless crystals of compound **11** appeared within 10 days.

$[(H_2AZ)(CB6)] \cdot 6H_2O$ (12). $CB6 \cdot 5H_2O$ (11 mg, 0.01 mmol), a 4-fold excess of $UO_2(NO_3)_2 \cdot 6H_2O$ (20 mg, 0.04 mmol), a 4-fold excess of azelaic acid (H_2AZ, 8 mg, 0.04 mmol), and demineralized water (1.5 mL) were placed in a 10 mL tightly closed glass vessel and heated at 200 °C under autogenous pressure. Crystals of compound **12**, mixed with a powder which was not further characterized, were obtained in very low yield after one week.

Crystallography. The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer[13] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals

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(8) Huang, W. H.; Zavalij, P. Y.; Isaacs, L. *J. Am. Chem. Soc.* **2008**, *130*, 8446.

(9) (a) Jeon, Y. M.; Whang, D.; Kim, J.; Kim, K. *Chem. Lett.* **1996**, 503. (b) Kim, K.; Jeon, W. S.; Kang, J. K.; Lee, J. W.; Jon, S. Y.; Kim, T.; Kim, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2293. (c) Sindelar, V.; Silvi, S.; Parker, S. E.; Sobransingh, D.; Kaifer, A. E. *Adv. Funct. Mater.* **2007**, *17*, 694. (d) Yin, J.; Chi, C.; Wu, J. *Chem.—Eur. J.* **2009**, *15*, 6050.

(10) (a) Whang, D.; Jeon, Y. M.; Heo, J.; Kim, K. *J. Am. Chem. Soc.* **1996**, *118*, 11333. (b) Whang, D.; Kim, K. *J. Am. Chem. Soc.* **1997**, *119*, 451. (c) Whang, D.; Heo, J.; Kim, C. A.; Kim, K. *Chem. Commun.* **1997**, 2361. (d) Roh, S. G.; Park, K. M.; Park, G. J.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 638. (e) Lee, E.; Kim, J.; Heo, J.; Whang, D.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 399. (f) Kim, K. *Chem. Soc. Rev.* **2002**, *31*, 96. (g) Park, K. M.; Whang, D.; Lee, E.; Heo, J.; Kim, K. *Chem.—Eur. J.* **2002**, *8*, 498. (h) Wang, Z. B.; Zhao, M.; Li, Y. Z.; Chen, H. L. *Supramol. Chem.* **2008**, *20*, 689.

(11) Lee, E.; Heo, J.; Kim, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 2699.

(12) Allen, F. H. *Acta Crystallogr., Sect. B* **2002**, *58*, 380.

(13) Hooft, R. W. W. *COLLECT*; Nonius BV: Delft, The Netherlands, 1998.

were introduced into glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames, then refined on all data. The data (combinations of φ- and ω-scans giving complete data sets up to θ = 25.7° and a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[14] Absorption effects in **1**−**8** and **11** were corrected empirically with the program SCALEPACK.[14] The structures of compounds **6** and **9**−**12** were solved by direct methods with SHELXS-97 and expanded by subsequent Fourier-difference synthesis.[15] The structure of **6** served as a starting point for the refinement of the structures of all the other isomorphous complexes. All structures were refined by full-matrix least squares on F^2 with SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. Nine uncoordinated water molecules are well resolved in complexes **1**−**8**, but the others appear to be disordered and the use of restraints was necessary for some atoms which became too strongly anisotropic. Although the overall number of water solvent molecules is 14 in all complexes, the number of occupied positions varies somewhat (hence the differences in the numbers of refined parameters). The hydrogen atoms bound to the oxygen and nitrogen atoms of the H_2IDA and water ligands in **1**−**8** were found on Fourier-difference maps, independently for each compound. Those of the lattice water molecules were only partially found in **6**, and these hydrogen positions were used for the other complexes also. The two nitrate counterions in **9** are disordered. The crystals of compound **11** were of very low quality, and the structure could not be refined to a high precision. Only the hydrogen atoms bound to coordinated water molecules were found, and the use of many restraints on bond lengths and/or displacement parameters was rendered necessary by the low resolution of some parts of the structure (the coordinated nitrate ion in particular) and the disorder affecting the solvent water molecules. In compound **12**, one oxygen and four carbon atoms of the azelaic acid molecule are disordered over two positions, which were given occupancy parameters of 0.5. All of the hydrogen atoms bound to oxygen and nitrogen atoms were found in compounds **9**, **10**, and **12**. In all compounds, the carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom.

Crystal data and structure refinement parameters are given in Table 2, selected bond lengths and angles in Table 3, and selected hydrogen bond parameters in Table 4. The molecular plots were drawn with SHELXTL[15] and ORTEP-3/POV-Ray.[16]

Results and Discussion

The complexes $[M(H_2IDA)(NO_3)(H_2O)_6](NO_3)_2 \cdot CB6 \cdot 14H_2O$ with M = Y (**1**), Ce (**2**), Nd (**3**), Eu (**4**), Dy (**5**), Er (**6**), Tm (**7**), and Yb (**8**) crystallize readily at room temperature, but the Lu(III) complex could never be obtained, the only solid product of the reaction in this case being the organic inclusion complex **9** (see below). Complexes **1**−**8** are isomorphous, and a view of the Er(III) complex **6** is given in Figure 1 as a representative example. The asymmetric unit comprises one metal cation, one H_2IDA ligand in its zwitterionic form, one coordinated and two free nitrate ions, one CB6 molecule, and six coordinated and 14 free water molecules, some of the latter being disordered over several positions varying slightly along the series. The metal ion is bound to the carboxylate group of H_2IDA in a monodentate fashion, with a bond length which decreases regularly from Ce to Er and then remains approximately constant for Tm and Yb (Table 3). These values are close to the average values for similar bonds from the CSD for the lighter lanthanides but larger by about 0.10 Å for Y and the heavier lanthanides (Dy, Er, Tm, and Yb). The cation is also bound to a bidentate nitrate ion and to the six water ligands, with average M−O(NO_3) and M−O(H_2O) bond lengths decreasing from Ce to Tm, and identical for Tm and Yb. The same trend is observed in the mean values for similar groups from the CSD, these values being identical to those in the present complexes for M−O(H_2O) bonds and slightly smaller, although not significantly when the large standard deviations are taken into account, for M−O(NO_3) bonds. The rare-earth ion is thus in a nine-coordinate environment with a quite regular square antiprismatic geometry. The two square faces correspond to atoms O5, O6, O8, and O9 and O10, O11, O12, and O13, respectively, and they define a dihedral angle in the range 7.17(12)−7.63(14)°, while the carboxylate atom O1 is in the capping position. The metal atom is at 1.58−1.65 Å from the first plane and 0.73−0.79 Å from the second. An intramolecular hydrogen bond links one of the water ligands to the uncoordinated oxygen atom of the carboxylate group (Table 4). The metal ion is thus in a very usual environment, and no bond with CB6 is present.

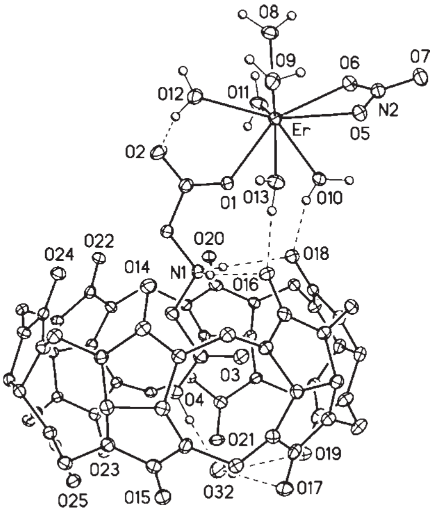

Figure 1. View of complex **6**. Displacement ellipsoids are drawn at the 30% probability level. Counterions, solvent molecules (except for the included water molecule), and carbon-bound hydrogen atoms are omitted. Hydrogen bonds are shown as dashed lines.

The $[M(H_2IDA)(NO_3)(H_2O)_6]^{2+}$ group is located close to a CB6 portal, and two hydrogen bonds are formed between two water ligands and two adjacent carbonyl groups. The zwitterionic H_2IDA molecule has its uncoordinated end included in the CB6 cavity, and, as usual in the case of protonated diaminoalkanes, the ammonium group is involved in hydrogen bonds with two adjacent carbonyl groups (the very same which are bonded to water ligands). This brings the carboxylic group to the center of the cavity, where it forms a hydrogen bond with a water molecule which is itself doubly hydrogen bonded to the portal opposite that bound to the ammonium; a simplified view and a space-filling representation of the assembly are shown in Figure 2. The shortest contacts between the host and guest (ca. 3.1 Å) involve the carboxylic atom O3 of H_2IDA and, in CB6, one nitrogen atom and the carbon atom of the carbonyl group attached to it. Apart from hydrophobic and ion−dipole interactions, H_2IDA is thus held in the cavity by four hydrogen bonds, two of them mediated by a water molecule, while protonated diaminoalkanes are held by

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[14] Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

[15] Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

[16] Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Table 2. Crystal Data and Structure Refinement Details

	1	**2**	**3**	**4**	**5**	**6**
chemical formula	$C_{40}H_{83}N_{28}O_{45}Y$	$C_{40}H_{83}CeN_{28}O_{45}$	$C_{40}H_{83}N_{28}NdO_{45}$	$C_{40}H_{83}EuN_{28}O_{45}$	$C_{40}H_{83}DyN_{28}O_{45}$	$C_{40}H_{83}ErN_{28}O_{45}$
M (g mol^{-1})	1765.25	1816.46	1820.58	1828.30	1838.84	1843.60
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	13.0605(4)	13.0756(2)	13.0621(5)	12.9937(4)	12.9880(4)	13.0235(5)
b (Å)	19.7505(6)	19.7595(7)	19.7614(5)	19.7605(4)	19.7576(6)	19.7226(5)
c (Å)	27.2866(9)	27.2999(9)	27.2760(9)	27.1926(9)	27.1744(8)	27.2450(9)
α (deg)	90	90	90	90	90	90
β (deg)	93.489(2)	93.526(2)	93.512(2)	93.610(2)	93.535(2)	93.423(2)
γ (deg)	90	90	90	90	90	90
V (Å^3)	7025.6(4)	7040.1(4)	7027.4(4)	6968.2(3)	6960.0(4)	6985.6(4)
Z	4	4	4	4	4	4
D_{calcd} (g cm^{-3})	1.669	1.714	1.721	1.743	1.755	1.753
μ (Mo Kα) (mm^{-1})	0.958	0.774	0.866	1.029	1.202	1.330
F(000)	3672	3748	3756	3768	3780	3788
reflns collcd	210125	190130	164501	172037	184214	204723
indep reflns	13272	13310	13276	13179	13170	13206
obsd reflns [$I > 2\sigma(I)$]	9705	10959	10664	10701	10054	9970
R_{int}	0.046	0.053	0.034	0.047	0.044	0.044
params refined	1063	1045	1054	1036	1045	1063
R1	0.053	0.044	0.042	0.041	0.044	0.040
wR2	0.155	0.123	0.117	0.113	0.116	0.105
S	1.029	1.056	1.048	1.057	1.054	1.050
$\Delta\rho_{min}$ (e Å^{-3})	−0.50	−0.79	−0.59	−0.68	−0.85	−0.79
$\Delta\rho_{max}$ (e Å^{-3})	1.32	1.39	1.37	2.06	2.15	1.32

	7	**8**	**9**	**10**	**11**	**12**
chemical formula	$C_{40}H_{83}N_{28}O_{45}Tm$	$C_{40}H_{83}N_{28}O_{45}Yb$	$C_{44}H_{64}N_{28}O_{32}$	$C_{44}H_{68}N_{28}O_{34}$	$C_{43}H_{72}EuN_{27}O_{35}$	$C_{45}H_{64}N_{24}O_{22}$
M (g mol^{-1})	1845.27	1849.38	1497.23	1533.26	1679.24	1293.20
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$Pbca$
a (Å)	13.0420(6)	13.0513(3)	11.8340(6)	11.8996(5)	13.7030(4)	16.4561(6)
b (Å)	19.7104(15)	19.7393(6)	14.2897(6)	21.3947(9)	19.3079(3)	17.7706(7)
c (Å)	27.2183(19)	27.3082(7)	17.4260(7)	12.4175(5)	24.6247(8)	18.0793(7)
α (deg)	90	90	86.938(3)	90	90	90
β (deg)	93.515(4)	93.470(2)	85.903(3)	106.178(3)	101.429(2)	90
γ (deg)	90	90	84.609(2)	90	90	90
V (Å^3)	6983.7(8)	7022.3(3)	2923.0(2)	3036.2(2)	6385.9(3)	5287.0(3)
Z	4	4	2	2	4	4
D_{calcd} (g cm^{-3})	1.755	1.749	1.701	1.677	1.747	1.625
μ (Mo Kα) (mm^{-1})	1.399	1.460	0.146	0.145	1.103	0.132
F(000)	3792	3796	1560	1600	3448	2712
reflns collcd	148063	177021	106620	84620	153510	127769
indep reflns	13191	13264	11102	5739	11974	4996
obsd reflns [$I > 2\sigma(I)$]	9472	11082	8627	4387	10808	3834
R_{int}	0.051	0.043	0.036	0.035	0.071	0.027
params refined	1063	1063	984	478	979	439
R1	0.055	0.039	0.046	0.046	0.106	0.056
wR2	0.153	0.111	0.129	0.114	0.285	0.150
S	1.060	1.042	1.041	1.056	1.150	1.225
$\Delta\rho_{min}$ (e Å^{-3})	−1.42	−0.93	−0.61	−0.31	−1.59	−0.60
$\Delta\rho_{max}$ (e Å^{-3})	1.28	2.04	0.78	0.26	2.20	0.51

Table 3. Environment of the Metal Atoms in Compounds **1**−**8** and **11**: Selected Bond Lengths (Å)

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**		**11**
M−O1	2.422(2)	2.503(2)	2.475(2)	2.444(2)	2.426(3)	2.406(2)	2.408(3)	2.412(3)	Eu−O1	2.484(7)
M−O5	2.535(2)	2.650(3)	2.608(2)	2.569(3)	2.537(3)	2.522(3)	2.516(4)	2.518(3)	Eu−O3	2.444(6)
M−O6	2.523(2)	2.614(2)	2.586(3)	2.557(3)	2.531(3)	2.515(3)	2.505(3)	2.515(3)	Eu−O15	2.627(10)
M−O8	2.434(3)	2.548(3)	2.515(3)	2.475(3)	2.442(3)	2.421(3)	2.403(4)	2.400(3)	Eu−O16	2.529(9)
M−O9	2.386(2)	2.497(2)	2.468(3)	2.424(3)	2.396(3)	2.381(3)	2.362(4)	2.358(3)	Eu−O18	2.400(9)
M−O10	2.374(2)	2.511(2)	2.476(2)	2.429(3)	2.394(3)	2.368(3)	2.338(3)	2.335(3)	Eu−O19	2.384(8)
M−O11	2.359(2)	2.502(3)	2.463(3)	2.409(3)	2.363(3)	2.352(3)	2.323(3)	2.324(3)	Eu−O20	2.360(16)
M−O12	2.342(2)	2.497(3)	2.451(3)	2.414(3)	2.376(3)	2.334(3)	2.308(3)	2.314(3)	Eu−O21	2.446(7)
M−O13	2.375(2)	2.526(3)	2.479(3)	2.433(3)	2.392(3)	2.363(3)	2.335(3)	2.337(3)	Eu−O22	2.442(9)
<M−O(NO_3)>	2.529(6)	2.632(18)	2.597(11)	2.563(6)	2.534(3)	2.519(4)	2.511(6)	2.517(2)		2.58(5)
<M−O(H_2O)>	2.38(3)	2.514(18)	2.48(2)	2.43(2)	2.39(2)	2.37(3)	2.34(3)	2.34(3)		2.41(3)

four bonds involving the two ammonium groups.[9] The average distance between the two nitrogen atoms in protonated 1,4-diaminobutane derivatives included in CB6 is 6.29(2) Å for the structures reported in the CSD, while the distance between N1 and atom O32 of the included water molecule in **1**−**8** is shorter, at ca. 5.87 Å. Both N1 and O32 are located in the mean planes defined by the six oxygen atoms of each portal, with out-of-plane displacements of ca. 0.13 and 0.03 Å, respectively. The

Table 4. Hydrogen Bonding Geometry in Compounds **1** and **9**−**12**: Selected Distances (Å) and Angles (deg)[a]

		D···A	D−H	H···A	D−H···A
1	N1···O16	2.865(4)	0.95	1.96	160
	N1···O18	2.989(4)	0.88	2.15	159
	O4···O32	2.608(4)	0.95	1.67	170
	O10···O18	2.853(3)	0.83	2.06	159
	O12···O2	2.570(4)	0.99	1.61	164
	O13···O16	2.752(3)	0.92	1.84	173
	O32···O17	2.796(4)	0.82	2.00	162
	O32···O19	2.766(4)	0.94	1.94	146
9	N1···O5	2.887(2)	0.91	2.10	145
	N1···O27	2.725(3)	0.89	1.86	164
	O1···O2′	2.627(2)	1.00	1.63	174
	O3···O28	2.572(3)	0.99	1.60	166
	N14···O15	2.852(2)	0.95	1.95	158
	N14···O30	2.669(3)	0.97	1.73	162
	O11···O12″	2.613(2)	0.82	1.80	173
	O13···O31	2.582(2)	0.92	1.68	164
10	N1···O7	2.883(3)	0.93	1.99	160
	N1···O10′	2.855(2)	1.00	2.02	140
	O1···O2′	2.556(2)	0.98	1.58	176
	O3···O11	2.607(3)	0.83	1.79	169
11	O18···O2	2.492(13)	0.92	1.73	139
	O19···O5	2.695(11)	0.90	1.84	158
12	O8A···O4′	2.705(5)	0.93	1.89	144
	O8B···O2′	2.709(5)	0.84	2.06	133

[a] Compound **1** is given as a representative example for compounds **1**−**8**. Symmetry codes: **9**′ = 1 − *x*, 1 − *y*, −*z*; **10**′ = 1 − *x*, −*y*, −*z*; **12**′ = 1 − *x*, −*y*, 1 − *z*.

CB6 molecule is thus a second-sphere ligand for the metal cation, with the first-sphere ligand H_2IDA serving as a link through its free, ammonium-containing chain. The acetate arm bound to the cation appears too long to permit direct coordination of the metal ion to CB6.

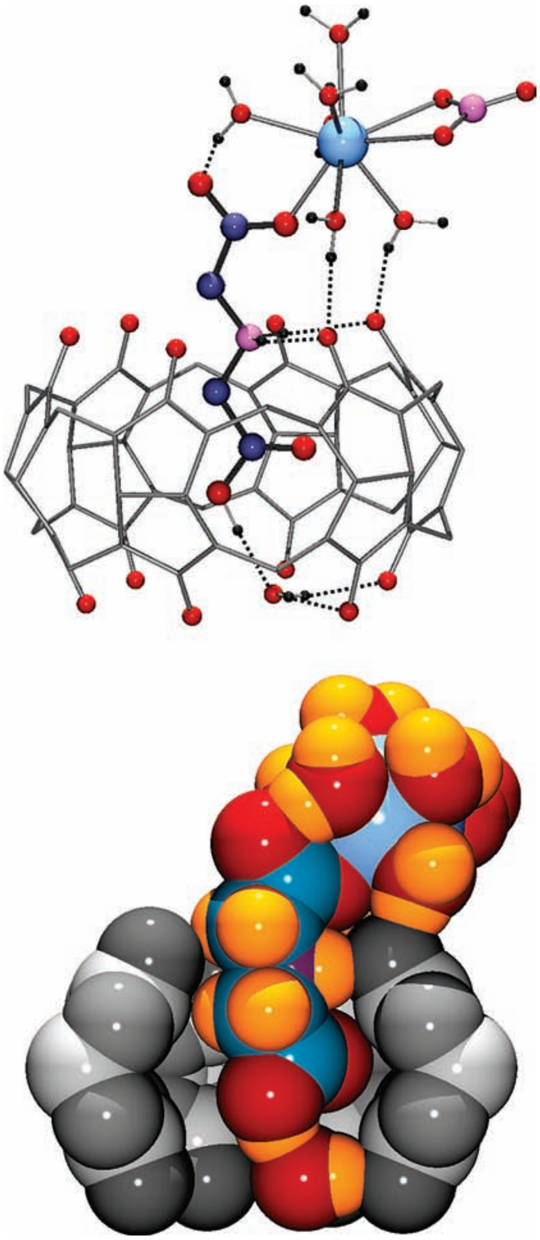

Figure 2. Top: Simplified view of complex **6** with the H_2IDA molecule highlighted. Counterions, solvent molecules (except for the included water molecule), and carbon-bound hydrogen atoms are omitted. Hydrogen bonds are shown as dotted lines. Bottom: Space-filling representation of complex **6**, with the front part of CB6 removed. For contrast, CB6 is represented in shades of gray, and hydrogen atoms are in yellow. The hydrogen atoms of CB6 are omitted for clarity.

It is interesting to compare these structures to that obtained with the anion derived from 2-pyridylacetic acid (HPA), another acetate-bearing ligand with a suitable size for inclusion, but devoid of an ammonium group. The complex $[Eu(PA)(CB6)(NO_3)(H_2O)_5](NO_3)\cdot 10H_2O$ (**11**) crystallizes less readily than complexes **1**−**8**. The crystals being of low quality, the structure of **11** could not be determined with a high degree of precision, but the main features of the complex are unambiguous (Figure 3). The asymmetric unit comprises one Eu(III) ion, one PA^-, one nitrate and five water ligands, one CB6 molecule, one free nitrate ion, and 10 partially disordered lattice water molecules. The Eu−O bond lengths with carboxylate, nitrate, and water ligands are close to those in the europium complex **4**. The pyridine ring of PA^- is included in CB6, but, in the absence of hydrogen bonding interactions with the carbonyl groups, it is more deeply imbedded than H_2IDA, and the carboxylate group is thus closer to the CB6 portal (Figure 4). The out-of-plane displacement of the coordinated carboxylate oxygen atom is 1.423(8) Å, and that of Eu is 2.546(5) Å, whereas the corresponding displacements in **1**−**8** are ca. 2.44 and 4.25 Å. As a consequence and in contrast to the previous cases, the cation is bound to one carbonyl group of CB6 in **11**, with a Eu−O3 bond length of 2.444(6) Å. Examples of monodentate bonding of lanthanide ions to CB6 have been reported,[2f,k,4] although the bi- and tridentate modes are more common. However, it seems that this is the first case of monocoordination in a molecular, nonpolymeric complex. The Eu−O3 bond length is identical to the average value in the bidentate europium complexes with CB6 previously reported, 2.42(4) Å.[2e,j,6] The nine-coordinated europium environment has a capped square antiprismatic geometry with the two square faces defined by atoms O1, O3, O15, and O16 and O18, O19, O20, and O21 [rms deviations of 0.20 and 0.08 Å, respectively; dihedral angle 2.7(4)°], and O22 is in the capping position. Intramolecular hydrogen bonds link two water ligands to the uncoordinated carboxylate oxygen atom and the CB6 moiety. Several tetranuclear lanthanide complexes with CB6 have been reported, in which the isonicotinate (4-pyridinecarboxylate) ligand is encapsulated in the CB6 cavity;[2g,j,k] however, in this case, the isonicotinate anion is bidentate and bridging two cations bound to the same CB6 portal. In the present case, the carboxylate group is tilted to one side of the CB6 portal due to the presence of the acetate methylene group, in spite of the tilting of the aromatic ring in the cavity.

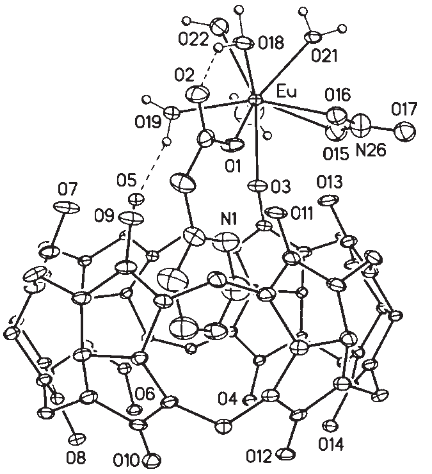

Figure 3. View of complex **11**. Displacement ellipsoids are drawn at the 20% probability level. Counterions, solvent molecules, and carbon-bound hydrogen atoms are omitted. Hydrogen bonds are shown as dashed lines.

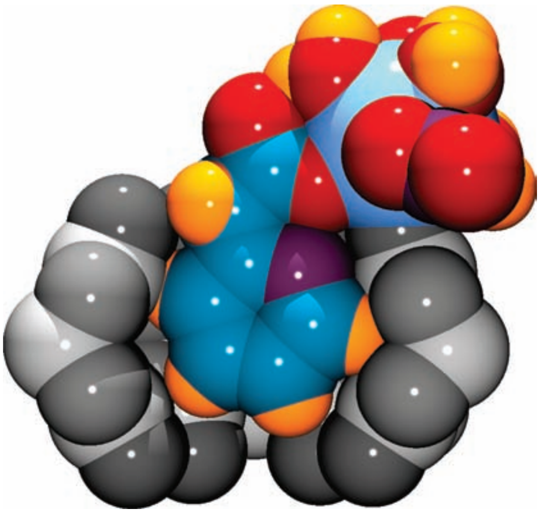

Figure 4. Space-filling representation of complex **11**, with the front part of CB6 removed. For contrast, CB6 is represented in shades of gray, and hydrogen atoms are in yellow. The hydrogen atoms of CB6 are omitted for clarity.

The resulting geometry is maladapted to the bridging of two CB6-coordinated cations, and the situation is similar to that in **1**−**8**, but for the proximity of the cation to the CB6 portal. It thus appears possible to adjust the nature of the included appendage of the carboxylate ligand (both its size and the presence of hydrogen bond donor groups) so that CB6 is either bis-bidentate, monodentate, or noncoordinating.

The CB6 molecule presents in all cases a moderate degree of ellipsoidal distortion,[17] with the distances between diametrically opposed oxygen atoms differing by ca. 0.8−0.9 Å in **1**−**8** and 0.6−0.9 Å in **11**, the smallest distances being in the direction transverse to the plane of the included molecule (this plane contains atoms O3 and O9 in **11**, while it bisects the O16−O18 segment in **1**−**8**). A much larger distortion, with a difference of ca. 2.3 Å, has been observed in the case of CB6 bound to a lanthanide ion in a tridentate fashion, with one perrhenate ion included (differences as low as 0.80 Å are however measured in other perrhenate-containing CB6 complexes).[4] The O···O contacts between adjacent atoms in the CB6 portals are in the range 3.25−3.60 Å in **1**−**8** and **11**.

The two compounds $[(H_3IDA)_2(CB6)](NO_3)_2\cdot6H_2O$ (**9**) and $[(H_3IDA)_2(CB6)](NO_3)_2\cdot8H_2O$ (**10**) have been obtained during experiments similar to those leading to **1**−**8**, but involving either Lu(III) or Cu(II) ions. Although they are not metallic complexes, they will be briefly described since they display an interesting variation of the inclusion phenomenon in **1**−**8**. In both **9** and **10**, a centrosymmetric assembly is formed, comprising one CB6 molecule with two H_3IDA^+ cations half-included in the cavity and held to the portals by hydrogen bonds involving the ammonium groups (two crystallographically independent, but nearly identical, half assemblies are present in **9**). The two H_3IDA^+ cations are facing each other in the cavity, and they are linked to one another by two hydrogen bonds (Figures 5 and 6). H_3IDA^+ in **9** and **10** is less deeply imbedded than H_2IDA in **1**−**8** since the nitrogen atoms are at 1.09 and 1.05 Å from the average portal planes in **9** (two independent molecules) and 0.86 Å in **10**. The carbon atom of the methylene group linked to the included carboxylic group is slightly outside the cavity, with an out-of-plane displacement of ca. 0.3 Å, and it is involved in weak CH···O hydrogen bonds with two carbonyl oxygen atoms [C···O = 2.988(3)−3.337(3) Å, H···O = 2.28−2.47 Å, C−H···O = 129−150°]. Similar CH···O hydrogen bonds are also observed in the pseudorotaxane built from *N*,*N*′-(4-bispyridinecarboxamide)-1,6-hexane and CB6;[18] some may also be present in **1**−**8**, but they involve the methylene group bearing the coordinated carboxylate in these cases. The conformation of the IDA skeleton is also different in **1**−**8** and **9**−**10**: all the O−C−C−N torsion angles are close to *syn* or *anti* in all compounds, but while the C−N−C−C torsion angles are all *anti* in **1**−**8**, they present different combinations of either *gauche*, *anti*, or intermediate values in the two independent molecules of **9** and **10**. As a result of these conformational differences, the ammonium groups in **9** are hydrogen bonded to one carbonyl group and one water molecule and those in **10** to two carbonyl groups.

The question arises as to the origin of the difference between the monoacid (1:1) encapsulation in the metal complexes **1**−**8** and the bis-acid one (2:1) in the metal-free **9** and **10**. It may seem that the inclusion of two acid groups hydrogen bonded to one another and pertaining to two rare-earth complexed H_2IDA molecules could have been possible. However, the trend is very clear: both the 1:1 metal complexes and the 2:1 organic complex **9** were repeatedly synthesized, and no species with a different stoichiometry was ever obtained. The critical parameter is the out-of-plane displacement of the ammonium nitrogen atom with respect to the O_6 portal, which only permits 2:1 inclusion if it is large enough and, as a consequence, the carboxylic group is not too deeply imbedded. It thus appears that the hydrogen bonding of two water ligands to carbonyl oxygen atoms in **1**−**8** may assume an important role in constraining the out-of-plane displacement of the metal cation and thus, indirectly, of the ammonium group. The H_2IDA inclusion mode thus appears to be metal-controlled.

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[17] (a) Samsonenko, D. G.; Virovets, A. V.; Lipkowski, J.; Gerasko, O. A.; Fedin, V. P. *J. Struct. Chem.* **2002**, *43*, 664. (b) Sindelar, V.; Cejas, M. A.; Raymo, F. M.; Kaifer, A. E. *New J. Chem.* **2005**, *29*, 280.

[18] Lu, H.; Mei, L.; Zhang, G.; Zhou, X. *J. Incl. Phenom. Macrocycl. Chem.* **2007**, *59*, 81.

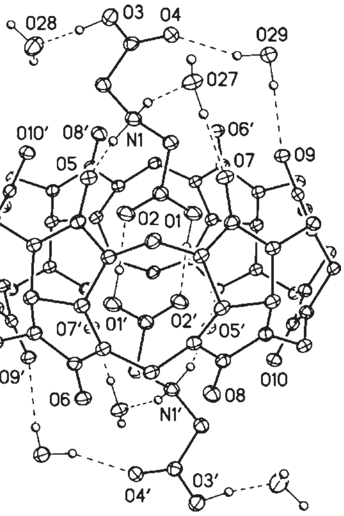

Figure 5. View of one of the two independent assemblies in compound **9**. Displacement ellipsoids are drawn at the 30% probability level. The disordered counterions and the carbon-bound hydrogen atoms are omitted. Hydrogen bonds are shown as dashed lines. Symmetry code: ′ = 1 − *x*, 1 − *y*, −*z*.

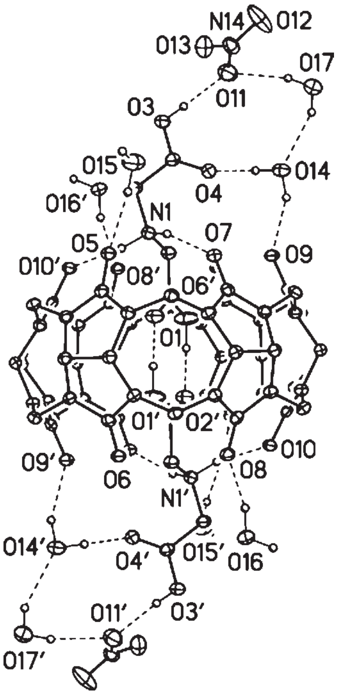

Figure 6. View of compound **10**. Displacement ellipsoids are drawn at the 30% probability level. Carbon-bound hydrogen atoms are omitted. Hydrogen bonds are shown as dashed lines. Symmetry code: ′ = 1 − *x*, −*y*, −*z*.

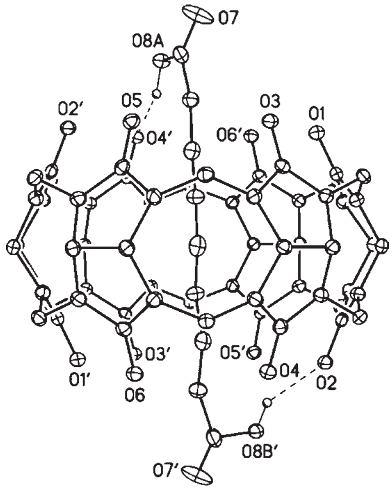

Figure 7. View of compound **12**. Displacement ellipsoids are drawn at the 30% probability level. Only one position of the disordered atoms is represented. Water molecules and carbon-bound hydrogen atoms are omitted. Hydrogen bonds are shown as dashed lines. Symmetry code: ′ = 1 − *x*, −*y*, 1 − *z*.

The inclusion of two, identical or different, aromatic molecular guests in the larger CB8 with π−π stacking interactions,[19] CH−π interactions,[19b] or formation of a charge-transfer complex[20] inside the cavity has been reported. It was also shown that two molecules of *trans*-cinnamic acid derivatives could be included in CB8 and undergo photodimerization; although no crystal structure was reported in this case, it appears that the aromatic ring is likely to be encapsulated while the carboxylic group is located out of the cavity.[21] The structures of compounds **9** and **10** provide the first examples of CB6 molecules with carboxylic groups included (usually, the included group is a hydrophobic part of the guest) and, moreover, of two molecules interacting through OH···O hydrogen bonds inside the cavity. Of course, in contrast to CB8, CB6 is not large enough to enable two molecules to fit in its cavity side-by-side, but inclusion of two species facing each other along the macrocycle main axis appears possible.

One may wonder what would be the behavior of a dicarboxylic acid molecule toward CB6, in the absence of an ammonium group. Compound **12**, $[(H_2AZ)(CB6)]\cdot 6H_2O$, where H_2AZ is azelaic acid, provides some insight on this point. This compound was obtained during attempts to build rotaxane species comprising long-chain dicarboxylic acids bound to uranyl ions, but these resulted in compound **12**, devoid of metal ions, with azelaic acid, or, in the case of the larger sebacic acid, in an assemblage in which dinuclear uranyl−CB6 and uranyl−sebacate complexes coexist, with no acid inclusion[5a] (similar experiments with lanthanide ions yielded no crystalline material). In the case of compound **12**, the unprecedented inclusion of a dicarboxylic acid molecule is observed, but in contrast with compounds **9** and **10**, the absence of the ammonium group leads to the alkyl chain being included in the CB6 cavity, with hydrophobic interactions likely predominant, and the two acid groups being located outside the cavity and hydrogen bonded to carbonyl oxygen atoms (Figure 7). It is notable that the nine-carbon chain length in **12** is much larger than that of the four- or five-carbon chains in the most usual alkyldiammonium guests, and the hydrogen bonded carboxylic oxygen atoms are quite distant from the O_6 portals, at ca. 1.96 Å. This result suggests

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[19] (a) Kim, J.; Jung, I. S.; Kim, S. Y.; Lee, E.; Kang, J. K.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *J. Am. Chem. Soc.* **2000**, *122*, 540. (b) Xiao, X.; Liu, J. X.; Chen, K.; Zhu, Q. J.; Xue, S. F.; Tao, Z. *Eur. J. Inorg. Chem.* **2010**, 2956.

[20] (a) Kim, H. J.; Heo, J.; Jeon, W. S.; Lee, E.; Kim, J.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 1526. (b) Sindelar, V.; Cejas, M. A.; Raymo, F. M.; Chen, W.; Parker, S. E.; Kaifer, A. E. *Chem.—Eur. J.* **2005**, *11*, 7054. (c) Bush, M. E.; Bouley, N. D.; Urbach, A. R. *J. Am. Chem. Soc.* **2005**, *127*, 14511. (d) Ko, Y. H.; Kim, E.; Hwang, I.; Kim, K. *Chem. Commun.* **2007**, 1305.

[21] Pattabiraman, M.; Natarajan, A.; Kaanumalle, L. S.; Ramamurthy, V. *Org. Lett.* **2005**, *7*, 529.

that the inclusion of a carboxylic group is unfavorable with respect to inclusion of an alkyl chain and is probably enforced in compounds **1**−**8** and **11** by the strong affinity of ammonium groups for carbonyl oxygen atoms. It also shows that alkyl chains with functional groups other than ammonium at both ends can be included in CB6 to form pseudorotaxane species.

Conclusion

A family of isomorphous rare-earth element ion complexes has been synthesized and structurally characterized. In these compounds, the metal ion is complexed in a monodentate fashion by the zwitterionic H_2IDA ligand, the latter being further partly included in the cavity of a CB6 molecule, in which it is held by ammonium−carbonyl hydrogen bonds. The affinity of ammonium cations for CBs is well-known and is ascribed to the presence of cation−dipole interactions and, to a lesser extent, of hydrogen bonds. However, ammonium binding to CBs is generally accompanied by the inclusion of a hydrophobic residue in the cavity, notably in the case of protonated diaminoalkanes, whereas the uncomplexed carboxylic group of H_2IDA is included in the present cases. There is no direct metal cation bonding to CB6 in these complexes, but coordination to one carbonyl group can be attained with a more deeply imbedded carboxylate ligand, 2-pyridylacetate. The complexes with H_2IDA crystallized readily for Y(III) and for seven lanthanide elements spanning the whole series, but not for Lu(III). In this last case, the organic complex comprising two H_3IDA^+ cations hydrogen bonded to either portal of CB6 was repeatedly obtained instead; the two included carboxylic groups are doubly hydrogen bonded to one another inside the host, which is an unprecedented feature with CB6. The presence of one or the other mode of inclusion of H_2IDA/H_3IDA^+ appears to be metal-directed and may be a consequence of the hydrogen bonds linking the water ligands to the carbonyl groups in the complexes indirectly constraining the location of the included fragment in the cavity. These results show that cucurbituril complexes with original and versatile arrangements of metal ions and organic ligands/guests can be obtained with included molecules different both in size and functionalization from the usual alkyldiammonium cations.

Supporting Information Available: Tables of crystal data, atomic positions and displacement parameters, anisotropic displacement parameters, and bond lengths and bond angles in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.