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Lanthanide Complexes with Cucurbit[*n*]urils ($n = 5, 6, 7$) and Perrhenate Ligands: New Examples of Encapsulation of Perrhenate Anions

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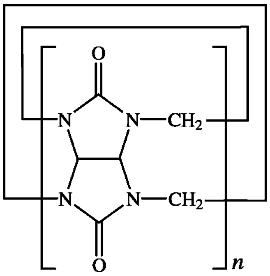
The reaction of lanthanide nitrates with cucurbit[*n*]urils (CB*n*, $n = 5, 6, 7$) under hydrothermal conditions in the presence of perrhenic acid and, for some of them, other reactants such as KNO_3 yielded 14 new complexes which were crystallographically characterized and present some original features. Four of the five complexes with CB5 are capsules closed by a lanthanide ion (Ce, Sm, Gd) on one side and potassium on the other and have an encapsulated bridging nitrate ion, but the fifth is a monodimensional polymer with both bidentate portals of CB5 complexed to ytterbium. All eight CB6 complexes (Ce, Pr, Sm, Gd, Yb, Lu) and the single ytterbium complex of CB7 (the first lanthanide complex of CB7 to be characterized) involve perrhenate encapsulation, in a form which is either bridging the lanthanide ions coordinated at each tridentate portal, or terminal when the CB is bidentate and the cation is further from the portal, or even noncoordinating in one case. The orientation of the cation in the cavity varies depending upon its coordination mode, as well as the nature of the shortest contacts in the cavity. Some original architectures are described, in particular a sinuous chain, ribbonlike assembly in a cerium complex of CB6 and a novel samarium−CB6 sandwich complex. The ubiquitous encapsulation of ReO_4^- in CB6 and CB7 may open new perspectives for the investigation of anion complexation by these macrocycles.

Introduction

Much attention has recently been paid to cucurbit[*n*]urils (CB*n*, Scheme 1), the pumpkin-shaped organic macrocycles resulting from the condensation of glycoluril and formaldehyde, which display outstanding host behavior toward neutral or charged guests as well as metal cation complexing properties.[1] Concerning the latter, the complexes formed by CB6 with lanthanide ions have been extensively investigated by Fedin et al., who have synthesized compounds with several different structures, from molecular species to one-dimensional coordination polymers and various metal/CB6 stoichiometries.[2] The macrocycle is usually bidentate toward each metal ion, but examples of mono- and tridentate coordination exist as well.[2f] CB6 was also shown to act as a supporting ligand for tetranuclear lanthanide complexes with a cubane structure.[2g,j,k] In this case, the additional ligand isonicotinate can be encapsulated in the CB6 cavity, and its nitrogen atom, which points toward the free portal, can be used to complex silver ions to generate heterometallic coordination polymers of remarkable architecture.[2k] Recently, some examples of lanthanide ion coordination to CB5 have also been reported, in which the metal ion is bound to either the five or only two of the carbonyl groups, giving rise to closed or half-open molecular capsules.[3] No example of lanthanide coordination to the larger CB7 and CB8 molecules has yet been reported. In the course of previous work on uranyl complexes of CB*n* ($n = 5-8$),[4] it appeared possible to isolate heterobimetallic uranyl−lanthanide molecular complexes of CB6 when using perrhenate ions as additional ligands.[5] Apart from the scarcity of such 4f−5f complexes[6] and also of the structurally characterized examples of perrhenate bonding to uranyl[7] as well as to lanthanide ions,[8]

Scheme 1. Cucurbit[*n*]urils



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the inclusion of one perrhenate ligand in the CB6 cavity is an extremely interesting feature of these compounds. CBs are well-known hosts for cationic species, with in particular the inclusion of protonated diaminoalkanes in CB6 being a first step toward the synthesis of rotaxanes and polyrotaxanes,[9] but anion encapsulation is much less documented, although chlorine inclusion in CB5 has been reported,[3,10] as well as the inclusion of various anionic ligands such as nitrate in CB5,[3b] CB6, and CB8[11] or isonicotinate in CB6.[2j,k] Anion complexation is notoriously an important and challenging problem.[12] Perrhenate is a particularly relevant anion in this context since it is analogous to the highly soluble pertechnetate ion TcO_4^-, which contains the long-lived β-emitter ^{99}Tc (half-life 2.13×10^5 years). This latter anion is present in large quantities in nuclear wastes, and a better knowledge of its chemical behavior, particularly relating to its extraction, is of importance from an environmental viewpoint.[13] The double aim of the present work is to investigate the influence of perrhenate ions on the structure of lanthanide complexes with CB*n* ($n = 5-7$) and to further probe the perrhenate encapsulation properties of CBs. A total of 14 structures of lanthanide complexes of CBs are reported, among which is the first involving CB7, as well as novel examples of perrhenate inclusion in CB6 and CB7.

Experimental Section

Synthesis. The hydrated lanthanide nitrates were purchased from Prolabo or Aldrich, and potassium nitrate was from Prolabo. Perrhenic acid (76.5% solution in water) was purchased from Acros. Cucurbit[5]uril hydrate and cucurbit[7]uril hydrate were provided by Aldrich, and cucurbit[6]uril hydrate was provided by Fluka. The water content in CB*n* was estimated at *ca.* 12, 5, and 10 water molecules per CB*n* molecule for $n = 5$, 6, and 7, respectively, according to the analyses provided by the sellers. Elemental analyses were performed by Analytische Laboratorien GmbH in Lindlar, Germany. The reaction conditions used often result in the formation of insoluble powders, and only in some out of many attempts with varying concentrations and stoichiometries was it possible to get single crystals suitable for structure determination, albeit of rather low quality in some cases. The presence of insoluble material and/or the low yield in crystals prevented performance of elemental analyses in most cases. Some of the compounds were obtained during the course of attempts at the synthesis of heterometallic uranyl−lanthanide complexes.[5] In some cases, it was possible to obtain the same compounds in the absence of uranyl ions, but in other cases (Ce and Yb with CB6), different compounds resulted from the different experimental conditions, and both are reported herein.

$[CeK(CB5)(NO_3)_2(H_2O)_2](ReO_4)_2 \cdot 3H_2O$ (1). $CB5 \cdot 12H_2O$ (10 mg, 0.010 mmol), a 10-fold excess of $Ce(NO_3)_3 \cdot 6H_2O$ (44 mg, 0.101 mmol) and KNO_3 (10 mg, 0.099 mmol), a 20-fold excess of $HReO_4$ (50 mg, 0.199 mmol), and demineralized water (1.6 mL) were placed in a 10 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of compound **1**, mixed with a white powder which was not further characterized, appeared within one month.

$[SmK(CB5)(NO_3)(H_2O)_4](ReO_4)_3 \cdot 3H_2O$ (2) and $[SmK(CB5)(NO_3)(ReO_4)(H_2O)_4]_2(ReO_4)_4 \cdot CB8 \cdot 4H_2O$ (3). $CB5 \cdot 12H_2O$ (10 mg, 0.010 mmol), a 2-fold excess of $Sm(NO_3)_3 \cdot 6H_2O$ (9 mg,

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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.* **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) Zhang, Y. Q.; Zhu, Q. J.; Xue, S. F.; Tao, Z. *Molecules* **2007**, *12*, 1325.

(4) (a) Thuéry, P. *Cryst. Growth Des.* **2008**, *8*, 4132. (b) Thuéry, P. *Cryst. Growth Des.* **2009**, *9*, 1208. (c) Thuéry, P. *CrystEngComm*, in press.

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

(6) Thuéry, P. *CrystEngComm* **2008**, *10*, 1126.

(7) (a) John, G. H.; May, I.; Sarsfield, M. J.; Steele, H. M.; Collison, D.; Helliwell, M.; McKinney, J. D. *Dalton Trans.* **2004**, 734. (b) Sutton, A. D.; John, G. H.; Sarsfield, M. J.; Renshaw, J. C.; May, I.; Martin, L. R.; Selvage, A. J.; Collison, D.; Helliwell, M. *Inorg. Chem.* **2004**, *43*, 5480. (c) John, G. H.; May, I.; Sarsfield, M. J.; Collison, D.; Helliwell, M. *Dalton Trans.* **2007**, 1603. (d) Karimova, O. V.; Burns, P. C. *Inorg. Chem.* **2007**, *46*, 10108.

(8) (a) Oliveira, M. A.; Miranda, J. M.; Castellano, E. E.; Scoralick, E.; Zinner, L. B.; Vicentini, G. *Lanth. Actin. Res.* **1986**, *1*, 205. (b) Miranda, J. M.; Oliveira, M. A.; Castellano, E. E.; Scoralick, E.; Zinner, L. B.; Vicentini, G. *Inorg. Chim. Acta* **1987**, *139*, 131. (c) Fedosseev, A. M.; Grigoriev, M. S.; Charushnikova, I. A.; Budantseva, N. A.; Starikova, Z. A.; Moisy, P. *Polyhedron* **2008**, *27*, 2007.

(9) Kim, K. *Chem. Soc. Rev.* **2002**, *31*, 96.

(10) (a) Day, A. I.; Blanch, R. J.; Arnold, A. P.; Lorenzo, S.; Lewis, G. R.; Dance, I. *Angew. Chem., Int. Ed.* **2002**, *41*, 275. (b) Samsonenko, D. G.; Gerasko, O. A.; Virovets, A. V.; Fedin, V. P. *Russ. Chem. Bull.* **2005**, *54*, 1557.

(11) Gerasko, O. A.; Virovets, A. V.; Samsonenko, D. G.; Tripolskaya, A. A.; Fedin, V. P.; Fenske, D. *Russ. Chem. Bull.* **2003**, *52*, 585.

(12) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486.

(13) See, for example: (a) Korpusov, G. V.; Krylov, Y. S *Radiokhimiya* **1984**, *26*, 408. (b) Jalhoom, M. G. *Radiochim. Acta* **1986**, *39*, 195. (c) Jalhoom, M. G. *J. Radioanal. Nucl. Chem.* **1986**, *104*, 131. (d) Kubota, M. *Radiochim. Acta* **1993**, *63*, 91. (e) Omori, T.; Tadokoro, M.; Suzuki, Y.; Suganuma, H.; Yoshihara, K. *J. Radioanal. Nucl. Chem.* **1994**, *181*, 71. (f) Rohal, K. M.; Van Seggen, D. M.; Clark, J. F.; McClure, M. K.; Chambliss, C. K.; Strauss, S. H.; Schroeder, N. C. *Solv. Extr. Ion Exch.* **1996**, *14*, 401. (g) Holman, K. T.; Halihan, M. M.; Jurisson, S. S.; Atwood, J. L.; Burkhalter, R. S.; Mitchell, A. R.; Steed, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 9567. (h) Leonard, R. A.; Conner, C.; Liberatore, M. W.; Bonnesen, P. V.; Presley, D. J.; Moyer, B. A.; Lumetta, G. J. *Sep. Sci. Technol.* **1999**, *34*, 1043. (i) Beer, P. D.; Hopkins, P. K.; McKinney, J. D. *Chem. Commun.* **1999**, 1253. (j) Thuéry, P.; Nierlich, M.; Asfari, Z.; Vicens, J.; Dozol, J. F. *Polyhedron* **2000**, *19*, 1749. (k) Farrell, D.; Gloe, K.; Gloe, K.; Goretzki, G.; McKee, V.; Nelson, J.; Nieuwenhuyzen, M.; Pál, I.; Stephan, H.; Town, R. M.; Wichmann, K. *Dalton Trans.* **2003**, 1961. (l) Watson, J. H. P.; Ellwood, D. C. *Nucl. Eng. Des.* **2003**, *226*, 375. (m) Darab, J. G.; Amonette, A. B.; Burke, D. S. D.; Orr, R. D.; Ponder, S. M.; Schrick, B.; Mallouk, T. E.; Lukens, W. W.; Caulder, D. L.; Shuh, D. K. *Chem. Mater.* **2007**, *19*, 5703. (n) Lamb, J. D.; Morris, C. A.; West, J. N.; Morris, K. T.; Harrison, R. G. *J. Membr. Sci.* **2008**, *321*, 15.

0.020 mmol), a 4-fold excess of KNO_3 (4 mg, 0.040 mmol), a 20-fold excess of $HReO_4$ (50 mg, 0.199 mmol), and demineralized water (1.3 mL) were placed in a 10 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. A mixture of colorless crystals of compounds **2** (predominant) and **3** (the latter in the form of thin platelets) appeared within three weeks. The presence of CB8 in an experiment using CB6 was previously observed.[4a] This could be due either to the presence of CB8 as an impurity in the samples of CB5 and CB6 or to the transformation of the latter molecules into CB8 under the rather severe conditions used (acidity, temperature).

$[GdK(CB5)(NO_3)(H_2O)_4](ReO_4)_3\cdot 4H_2O$ (4). $CB5\cdot 12H_2O$ (10 mg, 0.010 mmol), a 10-fold excess of $Gd(NO_3)_3\cdot 5H_2O$ (43 mg, 0.099 mmol) and KNO_3 (10 mg, 0.099 mmol), a 20-fold excess of $HReO_4$ (50 mg, 0.199 mmol), and demineralized water (1.3 mL) were placed in a 10 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of compound **4**, mixed with an off-white powder which was not further characterized, were obtained in low yield within one month.

$[Yb(CB5)(H_2O)_4](ReO_4)_3\cdot H_2O$ (5). $CB5\cdot 12H_2O$ (10 mg, 0.010 mmol), a 2-fold excess of $Yb(NO_3)_3\cdot 5H_2O$ (9 mg, 0.020 mmol), a 10-fold excess of KNO_3 (10 mg, 0.099 mmol), a 20-fold excess of $HReO_4$ (50 mg, 0.199 mmol), and demineralized water (1.3 mL) were placed in a 10 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of compound **5**, mixed with a white powder which was not further characterized, appeared within three days.

$[Ce_2(CB6)(ReO_4)(NO_3)_3(H_2O)_5](ReO_4)_2\cdot 2H_2O$ (6). $CB6\cdot 5H_2O$ (15 mg, 0.014 mmol), a 20-fold excess of $Ce(NO_3)_3\cdot 6H_2O$ (122 mg, 0.281 mmol), a 10-fold excess of $UO_2(NO_3)_2\cdot 6H_2O$ (70 mg, 0.139 mmol), a 20-fold excess of $HReO_4$ (70 mg, 0.279 mmol), and demineralized water (2.0 mL) were placed in a 15 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of compound **6** appeared within three days and were recovered after filtration and washed with water (15 mg, 46% yield on the basis of CB6). Anal. calcd for $C_{36}H_{50}Ce_2N_{27}O_{40}Re_3$: C, 18.48; H, 2.15; N, 16.16. Found: C, 17.18; H, 2.37; N, 15.26%. Up to five extra water molecules are seemingly present in the analyzed sample.

$[Pr_2(CB6)(ReO_4)(NO_3)_3(H_2O)_5](ReO_4)_2\cdot 2H_2O$ (7). $CB6\cdot 5H_2O$ (15 mg, 0.014 mmol), a 10-fold excess of $Pr(NO_3)_3\cdot 4H_2O$ (56 mg, 0.140 mmol) and $UO_2(NO_3)_2\cdot 6H_2O$ (70 mg, 0.139 mmol), a 20-fold excess of $HReO_4$ (70 mg, 0.279 mmol), and demineralized water (1.5 mL) were placed in a 15 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of compound **7** appeared within five days and were recovered after filtration and washed with water (11 mg, 34% yield on the basis of CB6). Anal. calcd for $C_{36}H_{50}N_{27}O_{40}Pr_2Re_3$: C, 18.47; H, 2.15; N, 16.15. Found: C, 19.63; H, 2.32; N, 16.49%.

$[Ce_3(CB6)_2(ReO_4)_2(H_2O)_{12}](ReO_4)_7\cdot 8H_2O$ (8). $CB6\cdot 5H_2O$ (30 mg, 0.028 mmol), a 2-fold excess of $Ce(NO_3)_3\cdot 6H_2O$ (25 mg, 0.058 mmol), a 10-fold excess of $HReO_4$ (70 mg, 0.279 mmol), and demineralized water (1.5 mL) were placed in a 15 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Few colorless crystals of compound **8**, mixed with a white powder which was not further characterized, appeared within 10 days.

$[Sm_4(CB6)_2(ReO_4)_4(NO_3)_4(H_2O)_{14}](ReO_4)_4\cdot 6H_2O$ (9). $CB6\cdot 5H_2O$ (20 mg, 0.018 mmol), a 4-fold excess of $Sm(NO_3)_3\cdot 6H_2O$ (32 mg, 0.072 mmol), a 10-fold excess of $HReO_4$ (45 mg, 0.179 mmol), and demineralized water (2.3 mL) were placed in a 15 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of compound **9** appeared in low yield within 10 days.

$[Gd_2(CB6)(ReO_4)_4(H_2O)_6](ReO_4)_2\cdot H_2O$ (10). $CB6\cdot 5H_2O$ (20 mg, 0.018 mmol), a 2-fold excess of $Gd(NO_3)_3\cdot 5H_2O$ (16 mg, 0.037 mmol), a 10-fold excess of $HReO_4$ (45 mg, 0.179 mmol), and demineralized water (1.8 mL) were placed in a 15 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of compound **10** appeared within four days and were recovered after filtration and washed with water (21 mg, 40% yield on the basis of CB6). Anal. calcd for $C_{36}H_{50}Gd_2N_{24}O_{43}Re_6$: C, 14.71; H, 1.72; N, 11.44. Found: C, 14.66; H, 1.80; N, 11.28%.

$[Yb(H_2O)_8](ReO_4)_3\cdot CB6\cdot 6H_2O$ (11). $CB6\cdot 5H_2O$ (30 mg, 0.028 mmol), a 4-fold excess of $Yb(NO_3)_3\cdot 5H_2O$ (50 mg, 0.111 mmol), a 2-fold excess of $UO_2(NO_3)_2\cdot 6H_2O$ (28 mg, 0.056 mmol), a 10-fold excess of $HReO_4$ (70 mg, 0.279 mmol), and demineralized water (1.8 mL) were placed in a 15 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of compound **11** appeared within two weeks and were recovered after filtration and washed with water (20 mg, 33% yield on the basis of CB6). Anal. calcd for $C_{36}H_{64}N_{24}O_{38}Re_3Yb$: C, 19.90; H, 2.97; N, 15.47. Found: C, 20.07; H, 2.95; N, 15.90%.

$[Yb(CB6)(ReO_4)(H_2O)_4]_2[Yb(H_2O)_8](ReO_4)_4(NO_3)_3\cdot 2H_2O$ (12). $CB6\cdot 5H_2O$ (30 mg, 0.028 mmol), a 10-fold excess of $Yb(NO_3)_3\cdot 5H_2O$ (126 mg, 0.281 mmol) and $HReO_4$ (70 mg, 0.279 mmol), and demineralized water (1.5 mL) were placed in a 15 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of compound **12**, mixed with a white powder which was not further characterized, appeared within four days.

$[Lu(CB6)(ReO_4)(H_2O)_4]_2[Lu(H_2O)_8](ReO_4)_4(NO_3)_3\cdot 2H_2O$ (13). $CB6\cdot 5H_2O$ (30 mg, 0.028 mmol), a 10-fold excess of $Lu(NO_3)_3\cdot 6H_2O$ (131 mg, 0.279 mmol) and $HReO_4$ (70 mg, 0.279 mmol), and demineralized water (1.5 mL) were placed in a 15 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. Colorless crystals of compound **13**, mixed with a white powder which was not further characterized, appeared within 10 days.

$\{[Yb(CB7)_2(H_2O)_4][Yb(ReO_4)(NO_3)(H_2O)_5]_2\}[Yb(CB7)(ReO_4)(H_2O)_3][Yb(H_2O)_8](ReO_4)_{10}\cdot CB7\cdot 21H_2O$ (14). $CB7\cdot 10H_2O$ (10 mg, 0.007 mmol), a 4-fold excess of $Yb(NO_3)_3\cdot 5H_2O$ (13 mg, 0.029 mmol), a 10-fold excess of $HReO_4$ (18 mg, 0.072 mmol), and demineralized water (1.1 mL) were placed in a 10 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure. A few colorless crystals of compound **14** appeared within 10 days.

Crystallography. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[14] using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystals 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 $\theta = 25.7°$ and a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[15] The structures were solved by direct methods with SHELXS-97, expanded by subsequent Fourier-difference synthesis, and refined by full-matrix (**1**−**7**, **9**−**11**) or blocked-matrix (**8**, **12**−**14**) least-squares on F^2 with SHELXL-97.[16] Absorption effects were corrected empirically with the program SCALEPACK.[15] All non-hydrogen atoms were refined with anisotropic displacement parameters. The carbon-bound hydrogen atoms

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

(15) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.

(16) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

were introduced at calculated positions, and they were treated (as well as the oxygen-bound hydrogen atoms when found) as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. In all compounds but **1** and **3**, the highest residual electron density peaks are located near rhenium atoms, which indicates the presence of disorder affecting some of the perrhenate groups, with one of the positions largely predominant; however, the resolution of the different oxygen positions was possible in none of the cases. Restraints on bond lengths and/or displacement parameters had to be applied for some badly behaving atoms, particularly in the perrhenate and nitrate ions and the solvent molecules, in all compounds; the problems of disorder are particularly important in compounds **8** and **14**. All hydrogen atoms bound to oxygen atoms were found on a Fourier-difference map in compounds **1**, **2**, and **11** and were only partially found in **3**, **4**, **6**, and **7**. They could not be found in compounds **5**, **8**−**10**, and **12**−**14**. Large voids in the lattice of compounds **3**, **5**, and **14** indicate the presence of other, unresolved solvent water molecules. Special details follow.

Compound 1. Although ADDSYM (PLATON[17]) detects an additional mirror plane of pseudosymmetry, no acceptable model could be found in the space group *Pnma*.

Compound 5. The perrhenate ions containing Re5A and Re5B have been given 0.5 occupancy factors in order to retain acceptable displacement parameters and to account for their positions too close to one another; they have also been refined with restraints on bond lengths and angles. The oxygen atoms of the perrhenate ion containing Re6 could not be found, nor even approximate starting positions for subsequent restrained refinement, which indicates important rotational disorder.

Compound 8. Some short O···O and O···C contacts involving the oxygen atoms of the badly resolved perrhenate counterions are likely due to the imperfect description of these moieties.

Compound 14. The atom Yb3 is disordered over two positions related by the mirror plane, and it is likely that some of its aqua ligands are missing due to the low resolution of this part of the structure. Six of the water molecules around Yb4 are also disordered over two positions around the mirror plane and have been given 0.5 occupancy factors. Four solvent water molecules (O91−O94) were given 0.5 occupancy parameters in order to account for their too-short contacts with either their image by symmetry or with one another.

Crystal data and structure refinement parameters are given in Table 1 and selected bond lengths and angles in Table 2. The molecular plots were drawn with SHELXTL,[16] Balls & Sticks,[18] and ORTEP-3/POV-Ray.[19]

Results and Discussion

A drawback frequently encountered during the synthesis of lanthanide, as well as uranyl,[4] complexes of CBs under hydrothermal conditions is the formation of insoluble powders and the small quantity of crystals obtained, which often prevents further characterization of the complexes. Some of the crystals used in the present study were also of rather poor quality, and in most cases, the perrhenate ions were seemingly affected by unresolved disorder evidenced by the presence of large residual electron density peaks near the rhenium atoms (see Experimental Section). However,

Table 1. Crystal Data and Structure Refinement Details

	1	**2**	**3**	**4**	**5**	**6**	**7**
chemical formula	$C_{30}H_{40}CeKN_{22}O_{29}Re_2$	$C_{30}H_{44}KN_{21}O_{32}Re_3Sm$	$C_{108}H_{132}K_2N_{74}O_{78}Re_6Sm_2$	$C_{30}H_{46}GdKN_{21}O_{33}Re_3$	$C_{30}H_{40}N_{20}O_{27}Re_3Yb$	$C_{36}H_{50}Ce_2N_{27}O_{40}Re_3$	$C_{36}H_{50}N_{27}O_{40}Pr_2Re_3$
M (g mol^{-1})	1724.46	1958.91	5210.98	1983.83	1844.46	2339.87	2341.45
cryst syst	orthorhombic	orthorhombic	orthorhombic	orthorhombic	triclinic	orthorhombic	orthorhombic
space group	$Pna2_1$	$Pna2_1$	*Pccn*	$Pna2_1$	$P\bar{1}$	$Pna2_1$	$Pna2_1$
a (Å)	20.0520(4)	20.0767(8)	22.1502(9)	20.0457(3)	13.6207(13)	12.0805(3)	12.0575(3)
b (Å)	19.9954(6)	14.1783(3)	36.173(2)	14.1521(4)	19.3081(14)	21.5528(7)	21.5172(8)
c (Å)	11.5863(3)	17.7384(7)	20.0440(12)	17.7711(5)	20.788(2)	23.6878(8)	23.7178(9)
α (deg)	90	90	90	90	107.076(6)	90	90
β (deg)	90	90	90	90	93.389(5)	90	90
γ (deg)	90	90	90	90	90.370(6)	90	90
V (Å^3)	4645.5(2)	5049.3(3)	16060.0(15)	5041.5(2)	5215.3(8)	6167.6(3)	6153.4(4)
Z	4	4	4	4	4	4	4
D_{calcd} (g cm^{-3})	2.466	2.577	2.155	2.614	2.349	2.520	2.527
μ (Mo Kα) (mm^{-1})	6.380	8.522	5.400	8.689	8.823	7.444	7.565
F(000)	3332	3732	10136	3780	3484	4464	4472
reflns collected	83782	96219	209326	83837	148272	104509	154703
ind reflns	8522	9228	15021	9042	19721	11215	11204
obsd reflns [$I > 2\sigma(I)$]	8019	8667	8338	8615	11750	10371	10522
R_{int}	0.034	0.048	0.079	0.023	0.093	0.042	0.052
params refined	767	794	1216	803	1477	974	974
R1	0.030	0.041	0.059	0.037	0.094	0.039	0.034
wR2	0.074	0.101	0.147	0.093	0.286	0.095	0.090
S	1.058	1.037	1.006	1.024	1.049	1.048	1.010
$\Delta\rho_{min}$ (e Å^{-3})	−1.30	−3.20	−2.71	−3.16	−3.60	−5.13	−4.92
$\Delta\rho_{max}$ (e Å^{-3})	1.34	3.37	1.63	3.16	3.50	3.46	2.62

	8	**9**	**10**	**11**	**12**	**13**	**14**
chemical formula	$C_{72}H_{112}Ce_3N_{48}O_{80}Re_9$	$C_{72}H_{112}N_{52}O_{88}Re_8Sm_4$	$C_{36}H_{50}Gd_2N_{24}O_{43}Re_6$	$C_{36}H_{64}N_{24}O_{38}Re_3Yb$	$C_{72}H_{108}N_{51}O_{75}Re_6Yb_3$	$C_{72}H_{108}Lu_3N_{51}O_{75}Re_6$	$C_{168}H_{260}N_{114}O_{160}Re_{13}Yb_5$
M (g mol^{-1})	5026.26	5205.14	2938.70	2172.75	4524.41	4530.20	9722.70
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*Cc*	$P2_1/c$	$P\bar{1}$	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_1/m$
a (Å)	14.1241(4)	14.3634(8)	12.3295(9)	21.4401(8)	22.6501(8)	22.6169(10)	22.6367(8)
b (Å)	44.1171(18)	23.9396(13)	15.6924(10)	11.8371(3)	17.2183(5)	17.2210(5)	30.5839(11)
c (Å)	21.0763(7)	19.8421(6)	20.2732(12)	24.8039(10)	30.2918(10)	30.3087(12)	22.9937(4)
α (deg)	90	90	67.504(4)	90	90	90	90
β (deg)	104.696(2)	108.873(3)	87.614(4)	102.587(2)	92.457(2)	92.445(2)	90.921(2)
γ (deg)	90	90	67.055(3)	90	90	90	90
V (Å^3)	12703.3(8)	6456.0(6)	3310.5(4)	6143.7(4)	11802.8(7)	11794.1(8)	15916.9(8)
Z	4	2	2	4	4	4	2
D_{calcd} (g cm^{-3})	2.628	2.678	2.948	2.349	2.546	2.551	2.029
μ (Mo Kα) (mm^{-1})	9.718	9.392	13.020	7.524	8.616	8.755	6.488
F(000)	9476	4920	2712	4188	8628	8640	9342
reflns collected	132719	134858	131901	94165	474369	288994	367110
ind reflns	23663	12225	12462	5816	22310	22278	30629
obsd reflns [$I > 2\sigma(I)$]	19033	10054	10584	5103	15211	14337	19204
R_{int}	0.051	0.044	0.090	0.031	0.040	0.045	0.056
params refined	1910	1009	1000	461	1864	1864	2167
R1	0.059	0.067	0.113	0.029	0.067	0.067	0.067
wR2	0.160	0.158	0.288	0.077	0.219	0.217	0.214
S	1.009	1.137	1.063	1.065	1.022	1.091	1.023
$\Delta\rho_{min}$ (e Å^{-3})	−3.58	−3.20	−3.76	−2.32	−6.67	−5.26	−3.48
$\Delta\rho_{max}$ (e Å^{-3})	4.14	5.53	6.30	2.20	6.18	5.30	4.03

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(17) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.
(18) Ozawa, T. C.; Kang, S. J. *J. Appl. Crystallogr.* **2004**, *37*, 679.
(19) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

Table 2. Environment of the Metal Atoms in Compounds **1**−**14**: Selected Bond Lengths (Å)[a]

1		**2**		**3**		**4**		**5**	
Ce−O1	2.547(4)	Sm−O1	2.569(7)	Sm−O1	2.619(8)	Gd−O1	2.592(6)	Yb1−O1	2.278(12)
Ce−O3	2.536(4)	Sm−O3	2.434(7)	Sm−O3	2.567(7)	Gd−O3	2.428(6)	Yb1−O3	2.318(12)
Ce−O5	2.539(4)	Sm−O5	2.541(7)	Sm−O5	2.465(8)	Gd−O5	2.527(6)	Yb1−O11	2.325(12)
Ce−O7	2.548(4)	Sm−O7	2.440(7)	Sm−O7	2.441(8)	Gd−O7	2.413(7)	Yb1−O13	2.311(11)
Ce−O9	2.627(5)	Sm−O9	2.588(7)	Sm−O9	2.527(7)	Gd−O9	2.559(6)	Yb1−O21	2.335(12)
Ce−O11	2.413(14)	Sm−O11	2.411(9)	Sm−O11	2.462(12)	Gd−O11	2.397(7)	Yb1−O22	2.318(11)
Ce−O14	2.625(5)	Sm−O14	2.421(7)	Sm−O14	2.459(7)	Gd−O14	2.411(6)	Yb1−O23	2.310(12)
Ce−O17	2.517(4)	Sm−O15	2.471(7)	Sm−O18	2.404(7)	Gd−O15	2.385(7)	Yb1−O24	2.343(13)
Ce−O18	2.475(4)	Sm−O16	2.415(7)	Sm−O19	2.434(7)	Gd−O16	2.442(7)	Yb2−O6′	2.305(14)
K−O2	2.758(5)	K−O2	2.773(8)	K−O2	2.798(8)	K−O2	2.805(7)	Yb2−O8′	2.327(11)
K−O4	2.679(5)	K−O4	2.886(8)	K−O4	2.678(8)	K−O4	2.714(7)	Yb2−O16	2.325(11)
K−O6	2.997(5)	K−O6	2.683(8)	K−O6	2.782(8)	K−O6	2.701(7)	Yb2−O18	2.251(15)
K−O8	2.713(5)	K−O8	2.737(7)	K−O8	2.791(8)	K−O8	2.894(7)	Yb2−O25	2.327(16)
K−O10	2.882(5)	K−O10	2.830(8)	K−O10	2.745(8)	K−O10	2.776(7)	Yb2−O26	2.284(14)
K−O12	2.811(12)	K−O12	2.716(10)	K−O12	2.851(19)	K−O12	2.703(8)	Yb2−O27	2.334(15)
K−O14″	3.159(5)	K−O1″	2.944(7)	K−O20	2.714(13)	K−O9″	2.937(7)	Yb2−O28	2.302(14)
K−O17″	2.929(5)	K−O14″	2.834(7)	K−O21	2.480(17)	K−O14″	2.837(7)		
K−O18″	2.831(5)	K−O17	3.134(8)			K−O17	3.140(7)		

6		**7**		**8**		**9**		**10**	
Ce1−O1	2.596(7)	Pr1−O1	2.579(7)	Ce1−O1	2.587(15)	Sm1−O1	2.415(10)	Gd1−O1	2.40(2)
Ce1−O3	2.518(7)	Pr1−O3	2.490(7)	Ce1−O3	2.401(15)	Sm1−O3	2.386(10)	Gd1−O3	2.34(2)
Ce1−O5	2.599(8)	Pr1−O5	2.575(7)	Ce1−O5	2.667(16)	Sm1−O9′	2.402(11)	Gd1−O9′	2.323(19)
Ce1−O13	2.635(8)	Pr1−O13	2.613(7)	Ce1−O13	2.491(15)	Sm1−O13	2.609(16)	Gd1−O13	2.46(2)
Ce1−O14	2.609(8)	Pr1−O14	2.601(7)	Ce1−O15	2.551(16)	Sm1−O14	2.611(15)	Gd1−O17	2.38(2)
Ce1−O16	2.519(8)	Pr1−O16	2.509(7)	Ce1−O25	2.571(16)	Sm1−O16	2.422(12)	Gd1−O21	2.36(2)
Ce1−O17	2.739(8)	Pr1−O17	2.728(7)	Ce1−O33	2.496(15)	Sm1−O17	2.427(11)	Gd1−O22	2.37(2)
Ce1−O22	2.551(8)	Pr1−O22	2.522(7)	Ce1−O34	2.548(17)	Sm1−O18	2.449(12)	Gd1−O23	2.40(2)
Ce1−O23	2.469(8)	Pr1−O23	2.437(7)	Ce1−O35	2.536(16)	Sm1−O19	2.522(11)	Gd2−O2	2.29(2)
Ce1−O27	2.631(7)	Pr1−O27	2.613(6)	Ce2−O2	2.430(15)	Sm2−O6	2.479(12)	Gd2−O4	2.43(2)
Ce2−O2	2.565(7)	Pr2−O2	2.538(7)	Ce2−O4	2.619(15)	Sm2−O8	2.359(12)	Gd2−O8”	2.38(3)
Ce2−O10	2.607(7)	Pr2−O10	2.592(6)	Ce2−O12	2.659(16)	Sm2−O20	2.445(17)	Gd2−O24	2.38(2)
Ce2−O12	2.446(8)	Pr2−O12	2.426(7)	Ce2−O26	2.629(16)	Sm2−O24	2.481(12)	Gd2−O28	2.37(2)
Ce2−O19	2.605(8)	Pr2−O19	2.576(7)	Ce2−O36	2.507(16)	Sm2−O28	2.593(12)	Gd2−O32	2.36(2)
Ce2−O20	2.587(8)	Pr2−O20	2.567(7)	Ce2−O37	2.552(17)	Sm2−O29	2.491(12)	Gd2−O33	2.42(2)
Ce2−O24	2.469(7)	Pr2−O24	2.461(7)	Ce2−O38	2.491(16)	Sm2−O31	2.433(12)	Gd2−O34	2.37(2)
Ce2−O25	2.516(7)	Pr2−O25	2.496(7)	Ce2−O39	2.504(16)	Sm2−O32	2.424(13)		
Ce2−O26	2.479(8)	Pr2−O26	2.452(7)	Ce2−O40	2.547(15)	Sm2−O33	2.436(13)		
Ce2−O28	2.589(7)	Pr2−O28	2.568(7)	Ce3−O9	2.455(14)				
				Ce3−O14′	2.748(19)				
				Ce3−O22′	2.599(16)				
				Ce3−O24′	2.445(17)				
				Ce3−O29	2.453(15)				
				Ce3−O41	2.46(2)				
				Ce3−O42	2.59(2)				
				Ce3−O43	2.514(18)				
				Ce3−O44	2.58(3)				

11		**12**		**13**		**14**[b]	
Yb−O7	2.267(4)	Yb1−O1	2.483(9)	Lu1−O1	2.480(8)	Yb1−O1	2.280(7)
Yb−O8	2.336(4)	Yb1−O3	2.200(8)	Lu1−O3	2.217(9)	Yb1−O3	2.318(7)
Yb−O9	2.309(4)	Yb1−O5	2.376(8)	Lu1−O5	2.364(8)	Yb1−O15	2.351(9)
Yb−O10	2.328(4)	Yb1−O25	2.331(9)	Lu1−O25	2.315(10)	Yb1−O16	2.353(8)
		Yb1−O33	2.359(9)	Lu1−O33	2.373(9)	Yb2−O17	2.317(10)
		Yb1−O34	2.316(9)	Lu1−O34	2.303(9)	Yb2−O18	2.277(11)
		Yb1−O35	2.343(9)	Lu1−O35	2.337(9)	Yb2−O22	2.423(8)
		Yb1−O36	2.284(8)	Lu1−O36	2.264(9)	Yb2−O23	2.359(9)
		Yb2−O13	2.404(8)	Lu2−O13	2.409(8)	Yb2−O25	2.331(9)
		Yb2−O15	2.213(9)	Lu2−O15	2.198(9)	Yb2−O26	2.324(9)
		Yb2−O17	2.438(9)	Lu2−O17	2.432(9)	Yb2−O27	2.351(9)
		Yb2−O29	2.318(9)	Lu2−O29	2.288(10)	Yb2−O28	2.278(8)
		Yb2−O37	2.374(10)	Lu2−O37	2.405(11)	Yb2−O29	2.298(8)
		Yb2−O38	2.315(9)	Lu2−O38	2.317(9)		
		Yb2−O39	2.371(11)	Lu2−O39	2.323(12)		
		Yb2−O40	2.330(8)	Lu2−O40	2.325(9)		
		Yb3−O41	2.304(12)	Lu3−O41	2.291(11)		
		Yb3−O42	2.345(10)	Lu3−O42	2.358(10)		
		Yb3−O43	2.323(10)	Lu3−O43	2.331(10)		
		Yb3−O44	2.286(12)	Lu3−O44	2.277(12)		
		Yb3−O45	2.302(12)	Lu3−O45	2.278(11)		
		Yb3−O46	2.344(10)	Lu3−O46	2.328(10)		
		Yb3−O47	2.352(11)	Lu3−O47	2.352(11)		
		Yb3−O48	2.284(11)	Lu3−O48	2.302(11)		

[a] Perrhenate anions excluded. [b] The values in the trinuclear ytterbium complex only are given. Symmetry codes: **1**: (″) = *x*, *y*, *z* −1. **2**: (″) = *x* + 1/2, 3/2 − *y*, *z*. **4**: (″) = *x* + 1/2, 1/2 − *y*, *z*. **5**: (′) = *x*, *y* + 1, *z*. **8**: (′) = *x* + 1/2, 1/2 − *y*, *z* + 1/2. **9**: (′) = 1 − *x*, 2 − *y*, −*z*. **10**: (′) = 2 − *x*, 2 − *y*, 1 − *z*. (″) = 2 − *x*, 1 − *y*, 2 − *z*.

notwithstanding these qualifications, the crystal structures of the complexes could be unambiguously determined.

CB5 Complexes. Five complexes involving CB5 could be characterized, with lanthanide ions spanning the whole 4f series (Ce, Sm, Gd, and Yb). However, all but the last include potassium ions as well, resulting in the formation of mixed capsules, as previously observed with the uranyl ion;[4b] no suitable crystal could be obtained in the absence of the KNO_3 reactant in this series, even when potassium is absent from the final product. Further, complexes **2** and **3** were obtained from the same batch, the second complex including an extra CB8 molecule (see Experimental Section). The presence of CB8 has previously been observed in an experiment with CB6,[4a] but its origin remains obscure. The quantity of crystals formed being small in both cases, the presence of CB8 impurities in the commercial samples of CB5 and CB6 cannot be excluded. However, it is also possible that the latter transform partly into CB8 under the conditions used (presence of metal ions, acid medium, and prolonged heating at 180 °C), although CB8 is known to be less thermally stable than the smaller homologs under the conditions used for the CB acid-catalyzed synthesis and to be liable to undergoing contraction to these lower members of the series.[20]

The same motif comprising one CB5 molecule capped by one Ln^{3+} ion at one portal and a K^+ ion at the other is present in complexes **1**−**4** (Figures 1−3). Complexes **2** and **4** are isomorphous, although one more solvent water molecule has been located in **4**. Both cations are bound to the five carbonyl groups, with average bond lengths of 2.56(3) Å for Ce^{3+}, 2.52(7) Å for Sm^{3+} (two compounds), and 2.50(7) Å for Gd^{3+} and an overall average of 2.78(8) Å for K^+. For comparison, the average distance for La^{3+} in the same environment is 2.58(3) Å,[3a,b] and that for Pr^{3+} is 2.54(3) Å.[3c] Although the dispersion around the mean value is always quite large, these values fit nicely with lanthanide contraction. Average values of 2.80(6) and 2.78(7) Å for the K−O(CB) bond lengths were found in similar complexes with the uranyl ion replacing the lanthanide,[4b] whereas values of 2.71(4) and 2.73(3) Å were reported for potassium/CB5 bicapped and monocapped capsules, respectively.[3a,21] There is some distortion of CB5 in compounds **1**−**4**, and the two portals are not equivalent in size, with average O···O separations between adjacent atoms of 2.93(5) and 3.21(11) Å for the portals bound to Ce and K, respectively, in **1**, for example. In compounds **1**−**4**, a bidentate nitrate ion bridging the two cations is included in the CB5 cavity. Such an encapsulation of nitrate ions in CB5 has previously been investigated.[3b] The Ln−O(nitrate) bond lengths are 2.413(14) Å for Ce, 2.411(9) and 2.462(12) Å for Sm, and 2.397(7) Å for Gd, and the average K−O(nitrate) bond length is 2.77(6) Å. The former values are in agreement with the average ones for monodentate nitrate ions reported in the Cambridge Structural Database (CSD, version 5.30):[22] 2.47(9), 2.44(8), and 2.44(4) Å for Ce, Sm, and Gd, respectively. In compound **1**, the cerium and potassium atoms from adjacent capsules are also bridged by two water molecules and one nitrate ion, which results in the formation of linear columns directed along the *c* axis (Figure 1), whereas in the isomorphous compounds **2** and **4**, zigzag columns arise from bridging by one carbonyl group and one water molecule (the Ln and K ions also being bound to two and one terminal water molecule, respectively).

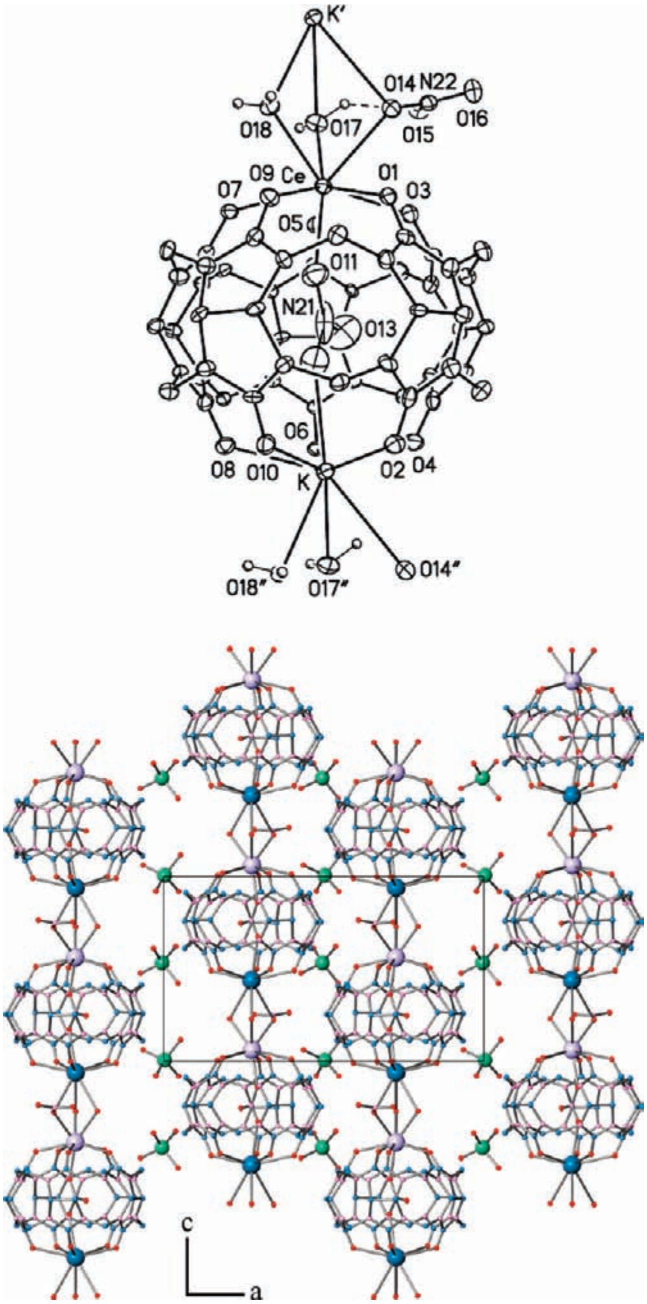

Figure 1. (Top) View of complex **1** with counterions, solvent molecules, and carbon-bound hydrogen atoms omitted. The hydrogen bond (O17···O15) is shown as a dashed line. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (′) = *x*, *y*, *z* + 1; (″) = *x*, *y*, *z* −1. (Bottom) View of the arrangement of the columns in the *ac* plane. Solvent molecules and hydrogen atoms are omitted. Cerium is in violet, potassium in blue, and rhenium in green.

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(20) Day, A.; Arnold, A. P.; Blanch, R. J.; Snushall, B. *J. Org. Chem.* **2001**, *66*, 8094.

(21) Liu, J. X.; Long, L. S.; Huang, R. B.; Zheng, L. S.; Ng, S. W. *Acta Crystallogr., Sect. E* **2005**, *61*, m1021.

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

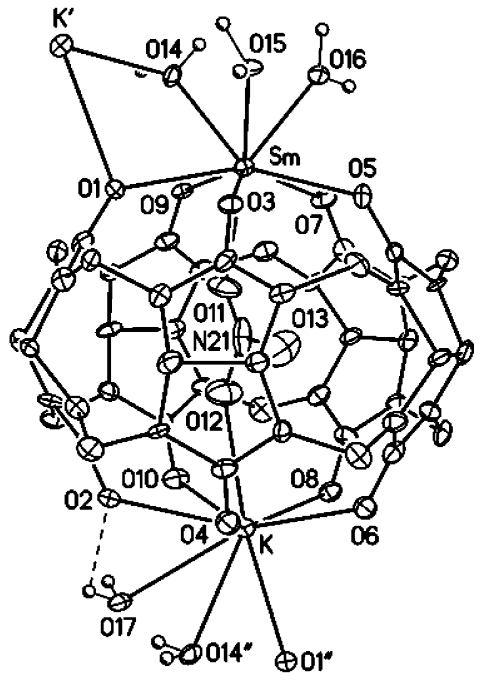

Figure 2. View of complex **2** with counterions, solvent molecules, and carbon-bound hydrogen atoms omitted. The hydrogen bond is shown as a dashed line. Displacement ellipsoids are drawn at the 40% probability level. Symmetry codes: (′) = $x - 1/2$, $3/2 - y$, z. (″) = $x + 1/2$, $3/2 - y$, z. Compound **4** is isomorphous to **2**.

The lanthanide ion is in a nine-coordinate environment in all compounds **1**−**4**, with a capped square antiprismatic geometry. Among the five carbonyl donor groups, two are in each square face, and the last is in a capping position. In these compounds, the perrhenate ions are simple counterions located between the columns, the latter being arranged parallel to one another, with a shift bringing the bulky CB5 moieties and the small bridging ligands side-by-side, giving compact assemblies with Kitaigorodski packing indexes of 0.80, 0.78, and 0.78 for **1**, **2**, and **4**, respectively.[17] Numerous hydrogen bonds link the aqua ligands and water molecules as donors to the CB5 molecules and the counterions as acceptors in all compounds **1**−**4**.

Complex **3** is a molecular species in which the coordination sphere of samarium is completed by one monodentate perrhenate ion and two water molecules. The Sm−O(ReO_3) bond length of 2.459(7) Å is slightly smaller than that of 2.520(7) Å in the uranyl−samarium complex of CB6 previously reported.[5] Few other examples of perrhenate coordination to lanthanide ions are reported in the CSD,[8] and the examples of coordination to actinide ions are also scarce[7,23] (for obvious reasons, the crystal structures of pertechnetate complexes of f element ions are even rarer,[23d,24] and none has been reported with a lanthanide ion). The average Nd−O(ReO_3) bond length from the CSD is 2.48(6) Å, and a value of 2.457 Å has been measured for Ho.[8b] All of these values are in very good agreement with that measured in **3**. The uncomplexed CB8 unit in **3** is involved in four hydrogen bonds with the two aqua ligands of Sm; some CH···O hydrogen bonds[25] between three CH groups of CB5 and three carbonyl groups of CB8 (shortest H···O distance 2.09 Å) are also present, as often is the case in such compounds.[2a,j,26] The CB5−CB8 units thus formed are the most conspicuous features of the quite compact packing (packing index 0.71).

Complex **5**, with the ytterbium ion, is the most interesting in this series with CB5. In contrast to the previous cases and probably owing to the smaller size of the cation, each of the two crystallographically independent Yb^{3+} ions is bound to only two carbonyl groups from each of two CB5 units, with an average bond length of 2.31(3) Å, much smaller than those in the previous complexes. The eight-coordinate environment geometry is square antiprismatic with each square face defined by the two carbonyl groups of one CB5 and two water molecules. No potassium ion is present in the structure, the CB5 molecules being bound to one Yb at each portal, and as a consequence of the cations being farther apart than in the previous complexes, no bridging nitrate is included in the CB5 cavity. Zigzag columns, with a dihedral angle of about 29° between adjacent CB5 molecules, are thus formed (Figure 4), which pack themselves in a manner similar to that observed in compounds **2** and **4**, with a packing index of 0.66, indicative of the presence of voids in the lattice (see Experimental Section). A bimetallic complex of La^{3+} with CB5 has previously been reported, in which one cation is bound to the five donors of one portal while the second is bound to two donors of the second portal only, giving an open molecular capsule containing one coordinated chlorine atom,[3a] so that an incomplete use of the five donors is also encountered with a larger-sized lanthanide ion. Complex **5** is the first lanthanide-based coordination polymer of CB5, but very similar arrangements have been found with, for example, potassium ions.[3a]

CB6 Complexes. Eight lanthanide complexes of CB6 have been obtained, with the common trend of perrhenate coordination in all but one case, in contrast to the CB5 series. CB6 is too large for all six donors of one portal to be bound to one lanthanide ion. Examples of mono-, bi-, and tridentate coordination exist, the latter with praseodymium.[2f] Tridentate coordination to three adjacent carbonyl groups is also found for the cerium and praseodymium ions, close in size to one another, in the isomorphous discrete complexes **6** (Figure 5) and **7**. Two independent cations are present in the asymmetric unit, each of them bound to one portal of the CB6 molecule,

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[23] (a) Budantseva, N. A.; Andreev, G. B.; Fedoseev, A. M.; Antipin, M. Y. *Russ. J. Coord. Chem* **2003**, *29*, 322. (b) John, G. H.; May, I.; Sharrad, C. A.; Sutton, A. D.; Collison, D.; Helliwell, M.; Sarsfield, M. J. *Inorg. Chem.* **2005**, *44*, 7606. (c) Sutton, A. D.; May, I.; Sharrad, C. A.; Sarsfield, M. J.; Helliwell, M. *Dalton Trans.* **2006**, 5734. (d) Helliwell, M.; Collison, D.; John, G. H.; May, I.; Sarsfield, M. J.; Sharrad, C. A.; Sutton, A. D. *Acta Crystallogr., Sect. B* **2006**, *62*, 68.

[24] Sarsfield, M. J.; Sutton, A. D.; May, I.; John, G. H.; Sharrad, C.; Helliwell, M. *Chem. Commun.* **2004**, 2320.

[25] (a) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063. (b) Desiraju, G. *Acc. Chem. Res.* **1991**, *24*, 290. (c) Steiner, T. *Chem. Commun.* **1997**, 727. (d) Gu, Y.; Kar, T.; Scheiner, S. *J. Am. Chem. Soc.* **1999**, *121*, 9411. (e) Steiner, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 49.

[26] Hwang, I.; Jeon, W. S.; Kim, H. J.; Kim, D.; Kim, H.; Selvapalam, N.; Fujita, N.; Shinkai, S.; Kim, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 210.

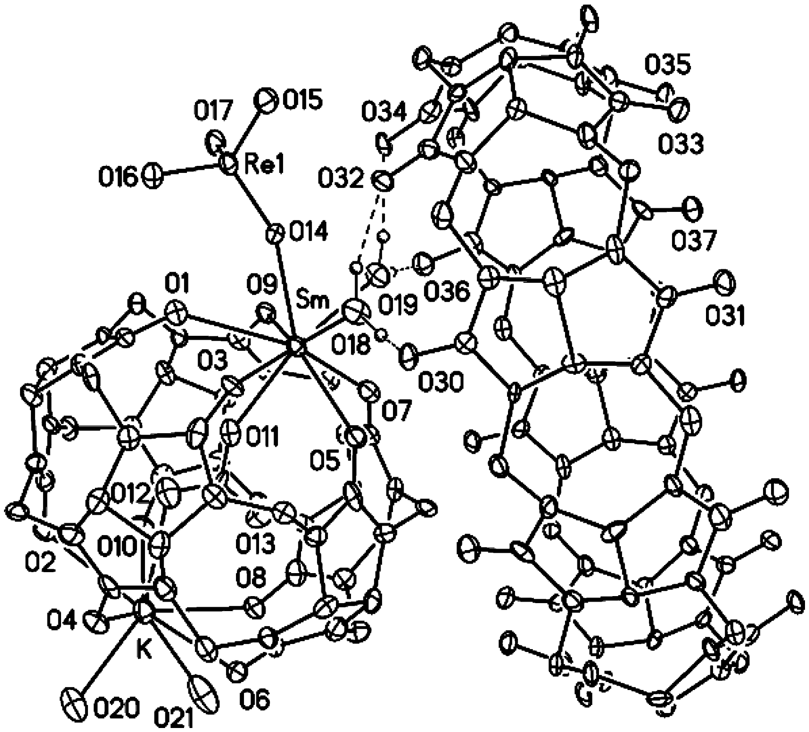

Figure 3. View of complex **3** with counterions, solvent molecules, and carbon-bound hydrogen atoms omitted. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level.

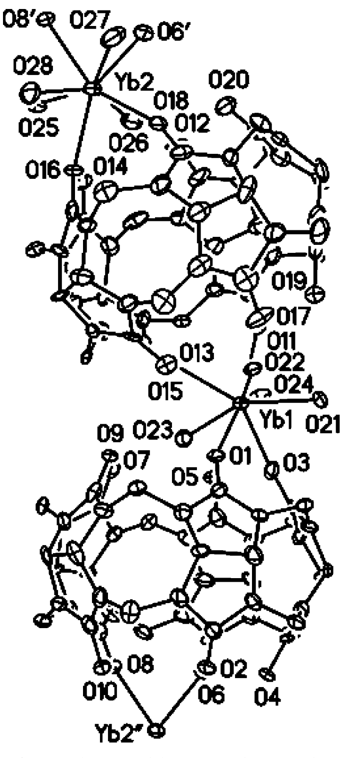

Figure 4. View of complex **5** with counterions, solvent molecules, and hydrogen atoms omitted. Displacement ellipsoids are drawn at the 30% probability level. Symmetry codes: (′) = *x*, *y* + 1, *z*; (″) = *x*, *y* −1, *z*.

with an average bond length of 2.56(6) Å for Ce and 2.53(6) Å for Pr. The former is equal to that found in compound **1**, which suggests that the size match between Ce and CB5 is quite perfect in the latter compound. The two cations share a glycoluril unit (containing O1 and O2), the other two coordinated units for each cation being on either side of it. The coordination sphere of Ce1 (Pr1) is completed by two bidentate nitrate ions and two aqua ligands outside the CB6 cavity and one ReO_4 ion inside, the latter bridging between the two cations. The coordination sphere of Ce2 (Pr2) is completed by one bidentate nitrate ion and three water molecules. The two cations are thus in 10- and 9-coordination environments, respectively, the first of very irregular shape and the second a capped square antiprism with the carbonyl donors O2, O10, and O12 and the aqua ligand O24 defining one face, the nitrate atoms O19 and O20 and the aqua ligands O25 and O26 defining the other face (dihedral angle of 7.4° between the fwo faces), and the perrhenate atom O28 in a capping position. The cations are displaced from the average O_6 plane of the associated portal by 1.048(3) and 0.872(3) Å for Ce1 and Ce2 in **6** and 1.036(3) and 0.856(3) Å for Pr1 and Pr2 in **7**, which gives Ce1···Ce2 and Pr1···Pr2 separations of 8.0301(8) and 8.0039(7) Å, respectively. The average Ln−O(ReO_3) bond lengths are 2.61(2) and 2.59(2) Å for Ce and Pr, respectively. These values are much larger than those previously measured, in particular the average value of 2.48(6) Å for the Nd^{3+} ion obtained from the CSD, which is likely due to both the bridging nature of the perrhenate ion in **6** and **7** and its encapsulation preventing the most convenient geometry from being attained. The Re−O−Ln(1,2) angles are nearly equal [143.4(4) and 141.7(4)° in **6**, 143.5(3) and 141.4(3)° in **7**]. These are the first instances of encapsulated bridging perrhenates, and the differences in positioning inside the cavity with respect to encapsulated terminal perrhenates will be discussed later. Numerous OH···O hydrogen bonds, both intra- and intermolecular, are formed between

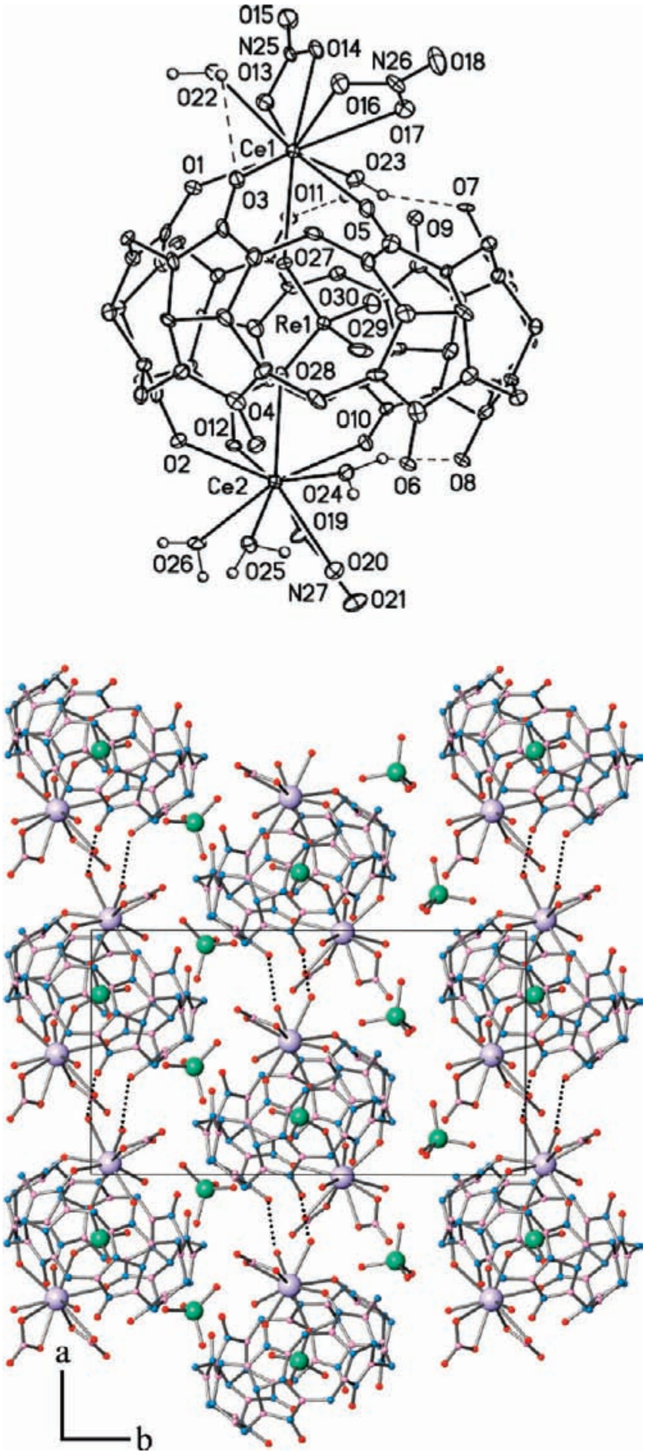

Figure 5. (Top) View of complex **6** with counterions, solvent molecules, and carbon-bound hydrogen atoms omitted. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level. (Bottom) View of the packing in the *ab* plane. Solvent molecules and hydrogen atoms are omitted. Intermolecular hydrogen bonds only are represented as dotted lines. Compound **7** is isomorphous to **6**.

the aqua ligands and carbonyl groups. They are associated with the formation of columns parallel to the *a* axis, these columns being arranged with respect to one another so that the CB units match the intermolecular spaces of the neighboring chains (Figure 5). The resulting packing index is 0.76 for both structures.

Compounds **6** and **7** were obtained in good yield during attempts at the synthesis of heterometallic uranyl−lanthanide complexes, but a similar experiment to that giving **6** in the absence of uranyl nitrate did not provide this compound but gave instead the cerium complex **8** in low yield. The asymmetric unit in this complex comprises three cerium atoms, two CB6 molecules, nine perrhenate ions, two of which are coordinated; 12 aqua ligands; and eight uncoordinated water molecules (Figure 6). The arrangement of Ce1 and Ce2 around the first CB6 unit is comparable to that in complex **6**, with each cation bound to three carbonyl groups, but two glycoluril units are shared in this case (those containing O1 and O2 or O3 and O4). The average Ce−O bond length with the encapsulated bridging perrhenate, 2.60(3) Å, is similar to that in **6**. However, whereas the coordination sphere of Ce2 is completed by five terminal aqua ligands, Ce1 is bound to two carbonyl groups of the second CB6 molecule and to three aqua ligands, and it is thus bridging as ytterbium in complex **5**. The nine-coordinate environment of both cations is capped square antiprismatic with carbonyl groups pertaining to the same CB6 unit in the same square face and the perrhenate oxygen atom in a capping position. Atom Ce3 is bound to three carbonyl groups of the second CB6, with one glycoluril unit (containing O13 and O14) in common with Ce1, to one carbonyl donor from the first CB6 (O9), one terminal perrhenate, and four aqua ligands. The Ce3−O(ReO_3) bond length of 2.453(15) Å is much shorter than those with bridging perrhenates and slightly shorter than those found in the uranyl−lanthanide complexes [2.520(7) Å for Sm].[5] The nine-coordinate environment of Ce3 is of very distorted capped square antiprismatic geometry, with one of the three carbonyl oxygen atoms from the same CB6 molecule in each square face and the third in a capping position. The perrhenate-bridged atoms Ce1 and Ce2 are located at 1.020(5) and 0.983(5) Å, respectively, from the mean O_6 planes of the associated portals, and Ce3 is only slightly closer to the portal of the other tridentate CB6, at 0.878(5) Å. In contrast, Ce1 is much farther from the bidentate portal, with a separation of 2.035(6) Å. The Ce1···Ce2, Ce1···Ce3′ (symmetry code (′) = $x - 1/2$, $1/2 - y$, $z - 1/2$), and Ce2···Ce3 distances are 7.9829(12), 9.4084(13), and 10.9037(13) Å, respectively. The former is close to that measured for perrhenate-bridged cations in complexes **6** and **7**, while the other two are much larger and do not permit such bridging. The Ce−O(CB6) bond lengths are in the range 2.401(15)−2.748(19) Å, with an average value of 2.55(11) Å, similar to that found in **1** and **6**. Although the hydrogen atoms of the aqua ligands have not been found, the presence of hydrogen bonds between these ligands and the carbonyl groups is likely. Both Ce1 and Ce3 are bridging two CB6 units, in a very asymmetric manner, while Ce2 is terminal. Considering the ligands, one CB6 unit is bound to three cations, Ce2 at one portal and Ce1 and Ce3 at the other portal, and the other to the two cations Ce1 and Ce3 on its two sides. This bonding scheme results in the formation of a strongly sinuous chain directed along the [101] direction, in which the terminal Ce2 ions mark the turning points

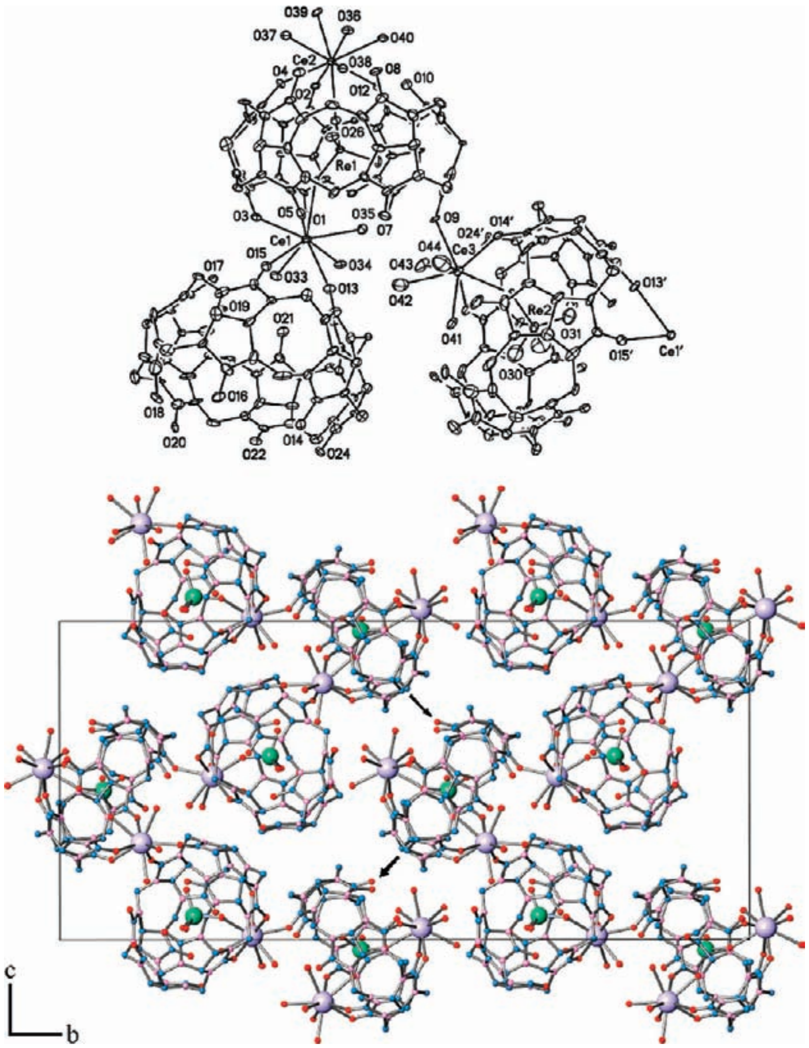

Figure 6. (Top) View of complex **8** with counterions, solvent molecules, and hydrogen atoms omitted. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: (′) = $x + 1/2$, $1/2 - y$, $z + 1/2$. (Bottom) View of the arrangement of the ribbons projected on the *bc* plane. Counterions, solvent molecules, and hydrogen atoms are omitted. The CH···O interactions between adjacent ribbons are indicated by arrows.

(Figure 6). Due to their large width along the *b* axis, equal to about 29 Å, these chains can also be viewed as undulating ribbons, which are packed edge-to-edge along the *b* axis with some interdigitation, allowing for the presence of interchain CH···O interactions (shortest H···O contact 2.23 Å), giving a packing index of 0.74. The formation of such sinuous chains is quite original in this family of compounds, the most common arrangements being columnar or of the herringbone type, the latter associated to CH···O bonding between the perpendicular or at least strongly tilted CB molecules.

The samarium complex **9** displays a very different, discrete structure in which two CB6 molecules are held by two cations, while their two portals directed outward are bound to two more cations, thus giving a centrosymmetric tetranuclear assembly (Figure 7). The bridging Sm1 atoms are bound to two carbonyl groups from one CB6 and only one from the other, this particular bonding scheme having been encountered previously in a neodymium complex, which is however polymeric.[2f] The coordination sphere of Sm1 is completed by one bidentate nitrate ion and four aqua ligands to give a capped square antiprismatic nine-coordinate environment with the aqua atom O19 in the capping position and the faces defined by atoms O1, O3, O16, and O17 and O9′, O13, O14, and O18 (dihedral angle 11.3°). Sm2 is bound to two carbonyl groups; one bidentate nitrate and two monodentate perrhenate ions, one of the latter being included in the macrocycle cavity; and three aqua ligands, with the included perrhenate atom O20 capping the square antiprism defined by the faces O6, O8, O32, and O33 and O24, O28, O29, and O31 (dihedral angle 0.4°). The Sm−O(CB) bond length averaged over the two cations is 2.41(4) Å, in perfect agreement with the value in the uranyl−samarium complex, 2.393(2) Å, and the average value in comparable structures, 2.43(4) Å.[2b,c] The Sm2−O(ReO_3) bond lengths are 2.445(17) and 2.481(12) Å for the anions located in and out of the cavity, respectively. These values are not significantly smaller than that in the uranyl−samarium complex, 2.520(7) Å. The Sm1 and Sm2 cations are separated by 1.771(6) and 1.177(6) Å, respectively, from the mean O_6 planes of the associated bidentate portals, which results in a Sm1···Sm2 distance of 9.5858(13) Å, preventing bridging by the included perrhenate anion. Triple-decker sandwich complexes displaying three CB6 molecules held by two bridging metal ions have been described;[2a,4a] complex **9** can be viewed as illustrating the

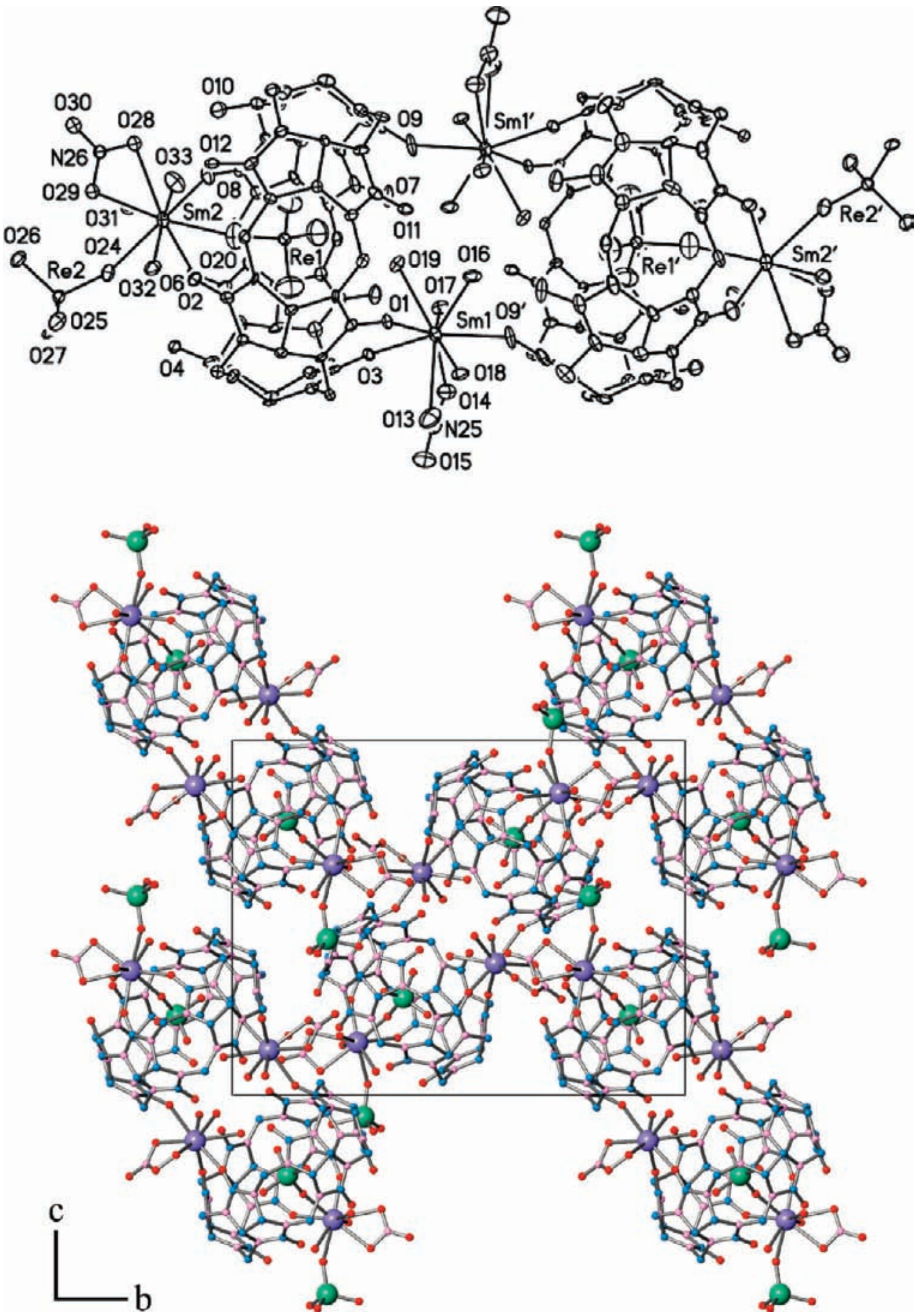

Figure 7. (Top) View of complex **9** with counterions, solvent molecules, and carbon-bound hydrogen atoms omitted. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: (′) = 1 − *x*, 2 − *y*, −*z*. (Bottom) View of the packing down the *a* axis. Counterions, solvent molecules, and hydrogen atoms are omitted. Samarium is in blue−violet and rhenium in green.

reverse situation, in which four metal atoms (two of them associated) are bridged by two CB6 units. Intramolecular hydrogen bonds between the aqua ligands and the CB6 oxygen atoms are likely present, but neither OH···O nor CH···O interactions are to be found between complexes. The molecules are arranged in rows along the [101] direction, with a tilt between the complex main axis and this direction. When viewed down the *a* axis, the rows are widely separated along *b*, being located at $y = 0$ and 1, whereas the neighboring row along *a*, at $y = 1/2$, is located so that the complexes match the space thus left (packing index 0.76), the barycenters of the complex molecules being arranged in a body-centered frame (Figure 7). This packing is analogous to that found in the triple-decker sandwich complex previously described.[2a]

An analogous monodentate−bidentate bridging of two CB6 molecules by two cations is found in the gadolinium complex **10** (Figure 8). However, in this case, a one-dimensional assembly is formed, which is similar to that found in the neodymium complex previously described.[2f] The average Gd−O(CB) bond length is 2.36(5) Å, to be compared to 2.373(1) Å in the uranyl−gadolinium complex[5]

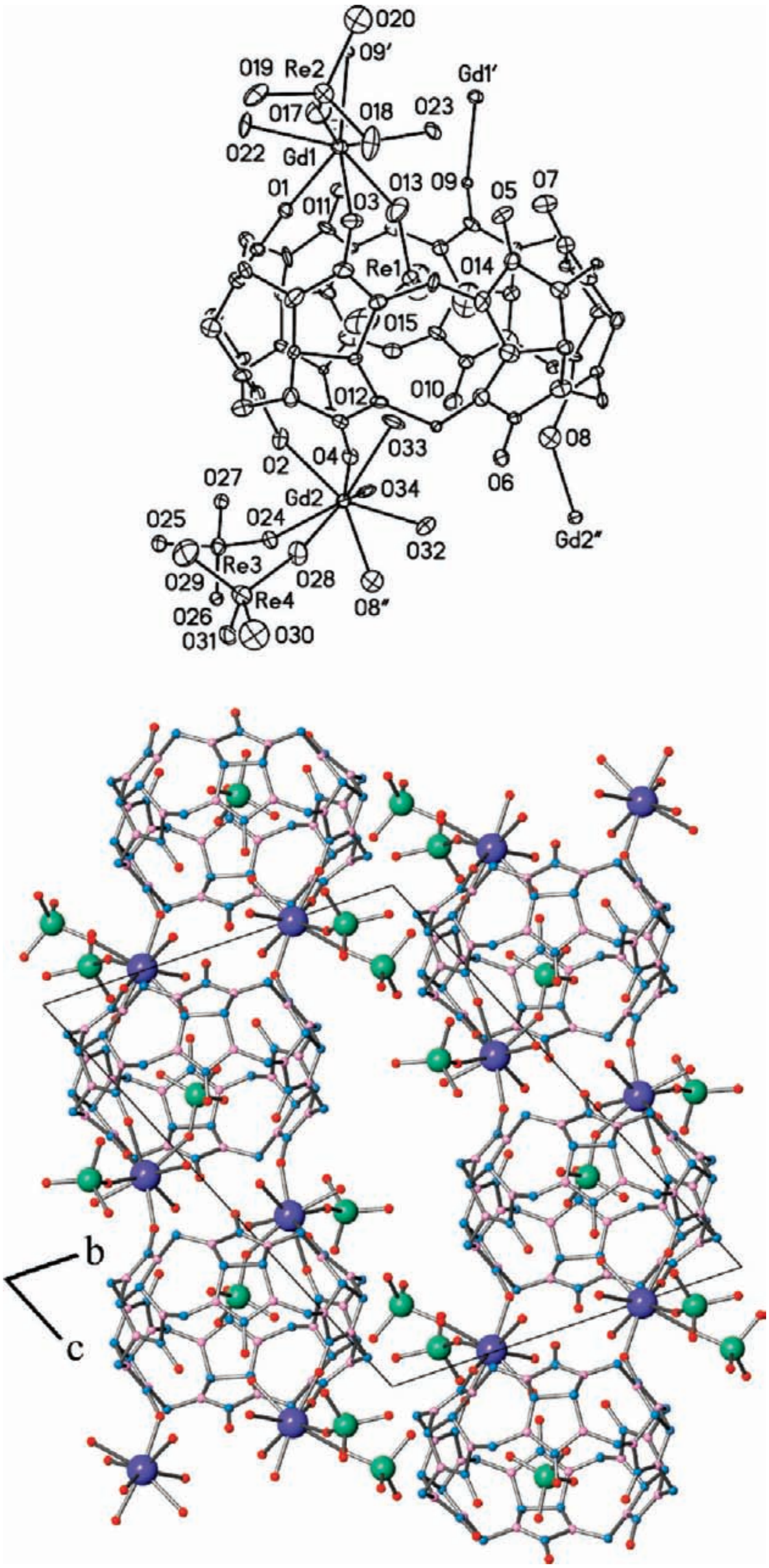

Figure 8. (Top) View of complex **10** with counterions, solvent molecule, and carbon-bound hydrogen atoms omitted. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (′) = 2 − *x*, 2 − *y*, 1 − *z*; (″) = 2 − *x*, 1 − *y*, 2 − *z*. (Bottom) Arrangement of the columns viewed down the *a* axis. Counterions, solvent molecules, and hydrogen atoms are omitted. Gadolinium is in blue and rhenium in green.

and 2.42(4) Å (range 2.328−2.468 Å) in the complexes previously reported, in which each cation is held in a bidentate fashion.[2a,e,j] There are two independent cations in the asymmetric unit in **10**; the coordination sphere of both cations is completed by two perrhenate ions, one of those bound to Gd1 being included in the CB6 cavity, and three water molecules, thus giving an eight-coordinate environment of square antiprismatic geometry in both cases, with the two carbonyl groups from the same ligand in the same face and that from the other ligand in the other face. The average Gd−O(ReO_3) bond length of 2.40(4) Å is close to the value of 2.490(8) Å in the uranyl−gadolinium complex; the bond length with the included anion, Gd1−O13, seems larger than the others by about 0.08 Å, but this is not significant due to the large standard deviations in this rather low-quality crystal structure. Atoms Gd1 and Gd2 are located at 1.630(12) and 1.540(12) Å from the mean O_6 plane of the associated bidentate portal, these values being intermediate between those associated to bidentate and tridentate portals in complex **8** and slightly smaller than that for the bridging cation in **9**. The resulting distance between the two cations, 9.121(2) Å, albeit smaller than in **9**, does not permit perrhenate bridging. Instead, hydrogen bonding between the aqua ligand O33 of Gd2 and the perrhenate atom O15 can be inferred from their being separated by 2.92(4) Å. The polymeric chains in **10** are directed along the $[01\bar{1}]$ direction, and in the absence of CH···O interactions, they are stacked so as to minimize the CB6−CB6 contacts (packing index 0.75).

Two ytterbium ion complexes of CB6, **11** and **12**, were obtained in this study. The former crystallized during an attempt at the synthesis of a mixed uranyl−ytterbium complex, and the latter is isomorphous to the lutetium ion complex **13**. In spite of the absence of direct coordination of CB6 to Yb^{3+}, complex **11** is particularly interesting, since it is the first instance of encapsulation of an uncoordinated perrhenate ion in CB6. The Yb^{3+} ion is located on a 2-fold symmetry axis, and it is surrounded by eight aqua ligands, giving a square antiprismatic geometry. This group is located above one portal of CB6, to which it is connected by four hydrogen bonds (Figure 9). Two perrhenate counterions are connected to the aquated cation by hydrogen bonds mediated by solvent water molecules. The third perrhenate anion is located on the 2-fold axis and is included in the CB6 cavity, while its oxygen atoms are involved in hydrogen bonds with aqua ligands. The absence of perrhenate bonding to the cation results in a different position of the former in the macrocycle, with respect to that in the complexes previously described, which will be discussed later. Hydrogen-bonded columns of alternate $[Yb(H_2O)_8]^{3+}$ cations and CB6−ReO_4^- assemblies are running along the *b* axis, and they are shifted by half the *b* parameter with respect to one another, so as to give the usual bumps-to-hollows pattern (packing index 0.75). These columns are further connected by hydrogen bonds through the water molecules and the free perrhenate anions.

The isomorphous ytterbium and lutetium complexes **12** and **13** are molecular species in which one metal ion only is coordinated to one tridentate CB6 molecule (Figure 10). Two independent such complex molecules are present in the asymmetric unit (corresponding to Ln1 and Ln2), as well as one $[Ln(H_2O)_8]^{3+}$ cation (Ln = Yb, Lu), three nitrate and six perrhenate anions (two of them encapsulated). The average Ln−O(CB) bond length is 2.35(11) Å for both compounds, with a marked tendency for the bond involving the central carbonyl group to be shorter than the others, by about 0.2 Å; such an effect was discernible, but much less pronounced, with the larger lanthanides. The cation is also closer to the mean O_6 plane than in all of the preceding cases, with displacements of 0.715(4) and 0.750(4) Å in **12** and 0.714(4) and 0.751(5) Å in **13**. The Ln−O(CB) bond lengths are larger than in the uranyl−lutetium complex, where CB6 is bidentate [2.303(5) Å] but equal to the average value in the ytterbium complexes, all with bidentate CB6 also, 2.35(5) Å.[2a,j] The average Ln−O(ReO_3) bond lengths of 2.325(7) Å for Yb and 2.302(13) Å for Lu are slightly shorter than the distance of 2.362(6) Å in the uranyl−lutetium complex, but no other comparable distance is to be found in the CSD. The coordination sphere of the cations bound to CB6 is completed by four aqua ligands, so that all cations are in eight-coordinate environments of square antiprismatic geometry, with two out of the three coordinated carbonyl groups pertaining to the same square face and the third to the other face. The two independent $[Yb(CB6)(ReO_4)(H_2O)_4]^{2+}$ units are facing each other through the complexed portals, and dimerization by hydrogen bonding occurs. The $[Ln(H_2O)_8]^{3+}$ cation is itself located between the portals of two CB6 molecules, where it is held by hydrogen bonds. Columns of alternate dimers and aquated cations are thus formed along the *a* axis, which are separated by half the unit cell parameter along the *c* axis and shifted along the *b* axis, so as to give the usual bumps-to-hollows match (packing index 0.76 and 0.75 in **12** and **13**, respectively).

CB7 Complex. Although solid-state encapsulation of complex species such as $[SnCl_4(H_2O)_2]$,[27] ferrocene,[28] and oxaliplatin[29] in CB7 has been reported, as well as inclusion of organic cations,[30] the crystal structures of metal complexes of CB7 with carbonyl bonding are reduced, up to now, to those of some uranyl complexes.[4a,c] Complex **14**, which is thus the first to be characterized with a lanthanide ion, is a very large assembly uniting three different ytterbium−CB7 units. The first comprises two CB7 molecules bridged by one cation, with two partially included (but not coordinated) $[Yb(ReO_4)(NO_3)(H_2O)_5]^+$ cations. The second is built from one bidentate CB7, one coordinated cation which is disordered over two positions related by a mirror plane, and one coordinated and included ReO_4^- anion, and the third is a simple hydrogen-bonded group of one CB7 and one strongly disordered $[Yb(H_2O)_8]^{3+}$ cation. Only the first unit, which is the most interesting one and the less plagued by disorder, will be discussed at length. The bridging atom Yb1 is located on the mirror plane (*x* 1/4 *z*) and is bound to two carbonyl

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(27) Lorenzo, S.; Day, A.; Craig, D.; Blanch, R.; Arnold, A.; Dance, I. *CrystEngComm* **2001**, *3*, 230.

(28) (a) Jeon, W. S.; Moon, K.; Park, S. H.; Chun, H.; Ko, Y. H.; Lee, J. Y.; Lee, E. S.; Samal, S.; Selvapalam, N.; Rekharsky, M. V.; Sindelar, V.; Sobransingh, D.; Inoue, Y.; Kaifer, A. E.; Kim, K. *J. Am. Chem. Soc.* **2005**, *127*, 12984. (b) Rekharsky, M. V.; Mori, T.; Yang, C.; Ko, Y. H.; Selvapalam, N.; Kim, H.; Sobransingh, D.; Kaifer, A. E.; Liu, S.; Isaacs, L.; Chen, W.; Moghaddam, S.; Gilson, M. K.; Kim, K.; Inoue, Y. *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 20737.

(29) Jeon, Y. J.; Kim, S. Y.; Ko, Y. H.; Sakamoto, S.; Yamaguchi, K.; Kim, K. *Org. Biomol. Chem.* **2005**, *3*, 2122.

(30) Liu, S.; Zavalij, P. Y.; Lam, Y. F.; Isaacs, L. *J. Am. Chem. Soc.* **2007**, *129*, 11232.

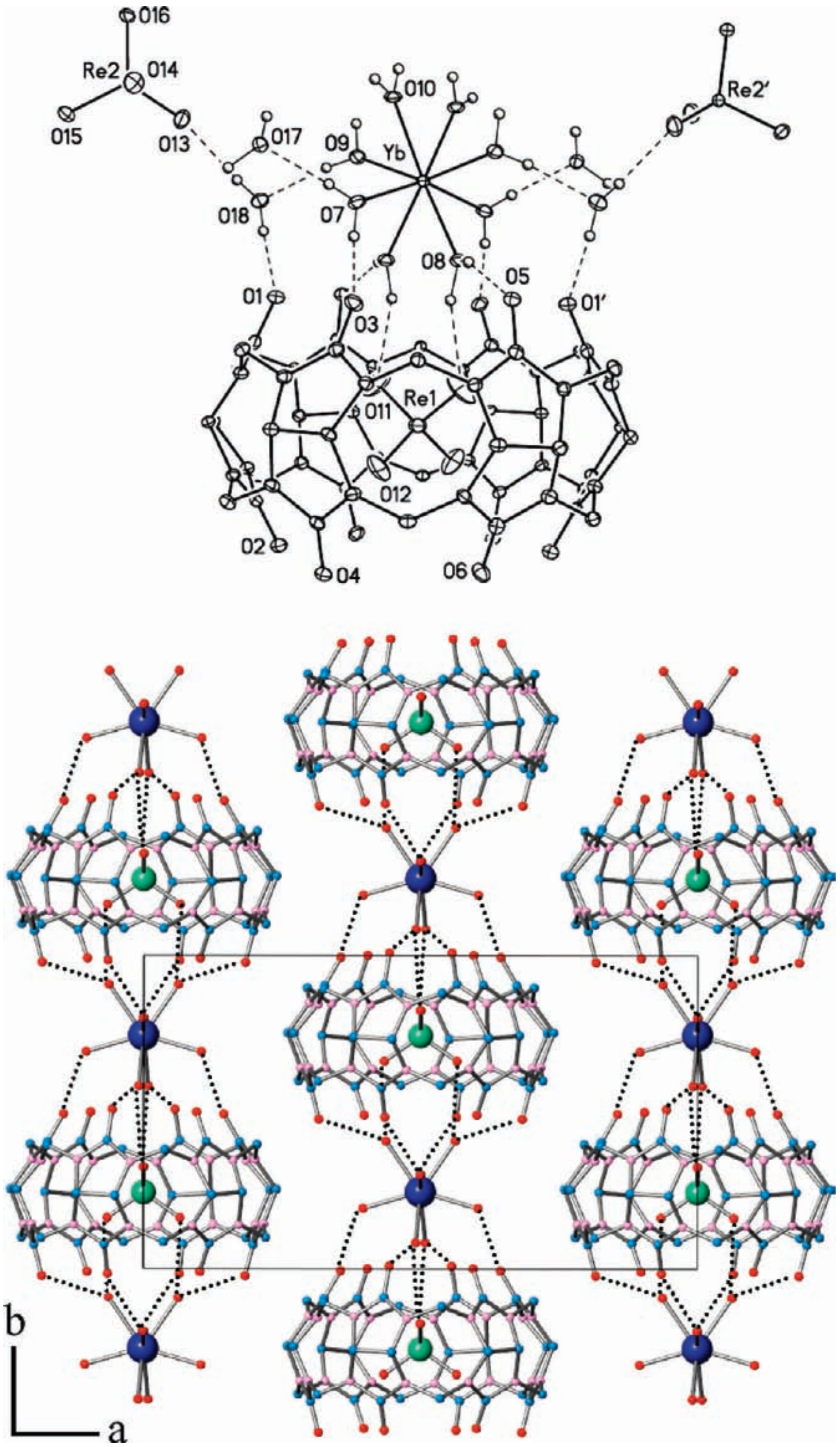

Figure 9. (Top) View of complex **11** with carbon-bound hydrogen atoms omitted. Hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: (′) = −*x*, *y*, 1/2 − *z*. (Bottom) Arrangement of the columns viewed down the *c* axis. Counterions, solvent molecules, and hydrogen atoms are omitted. Hydrogen bonds are represented as dotted lines. Ytterbium is in blue and rhenium in green.

groups from each of the two symmetry-related CB7 molecules, with an average bond length of 2.30(2) Å, comparable to that measured in complex **12** (Figure 11). Four additional aqua ligands make an eight-coordinate environment of quite regular square antiprismatic geometry, with the four carbonyl oxygen atoms defining one face and the four aqua ligands the other (dihedral angle 0.09°). The atom Yb2 is bound to a bidentate nitrate and a monodentate perrhenate in trans positions and five aqua ligands roughly arranged in an equatorial plane. The geometry around Yb2 can, however, be seen as square antiprismatic, with one face defined by the nitrate atoms O22 and O23 and the aqua ligands O25 and O26 and the other by the perrhenate atom O18 and the three remaining aqua ligands (dihedral angle 1.8°). The $[Yb(ReO_4)(NO_3)(H_2O)_5]^+$ cation is not coordinated to CB7 but is located so that the perrhenate group is included

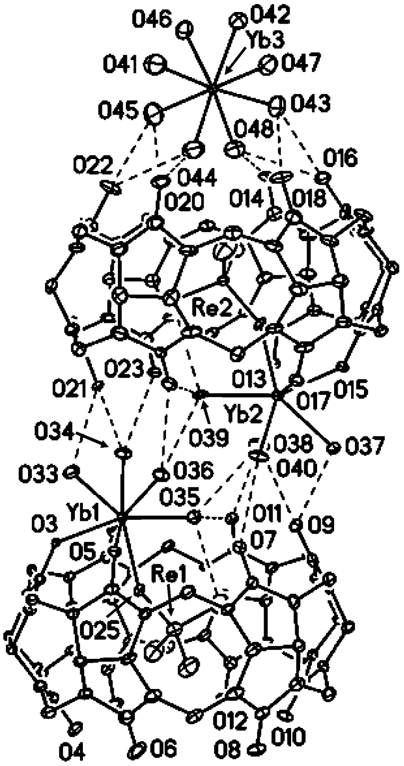

Figure 10. View of the hydrogen-bonded assembly in **12** with counterions, solvent molecules, and hydrogen atoms omitted. Possible hydrogen bonds are represented as dashed lines. Displacement ellipsoids are drawn at the 30% probability level. Compound **13** is isomorphous to **12**.

in the cavity and the mean plane of the five aqua ligands is approximately parallel to the CB7 molecule, thus looking like a lid over the macrocycle aperture. Although the aqua protons have not been found, the presence of hydrogen bonds, simple or bifurcated, between the ligands and the carbonyl groups can be inferred from the O···O contacts, in the range 2.65−3.08 Å. Yb1 and Yb2 are displaced by 1.540(4) and 1.465(3) Å, respectively, from the mean O_6 planes of the associated portals, and the Yb1···Yb2 distance is 9.5891(6) Å. These values preclude perrhenate bridging, but a hydrogen bond between the aqua ligand O16 of Yb1 and one of the perrhenate oxygen atoms is likely, with an O···O distance of 2.749(19) Å. Notwithstanding the presence of only one bridging cation instead of two, the overall geometry of this complex is analogous to that in the tetranuclear complex **9**; the replacement of coordination bonds by hydrogen bonds for the terminal cation leaves the intermetallic distance nearly unchanged. The packing of the three units comprising this compound and the numerous counterions and water molecules is very intricate. Although the CB7 molecules of the bridged unit make dihedral angles of ca. 98 and 100° with the other CB7 molecules, no significant CH···O interaction is present.

ReO_4^- Coordination and Encapsulation. Perrhenate anions are rather weak ligands, and as indicated above, few f-element complexes with coordinated perrhenates have been crystallographically characterized.[7,8,23] It is thus particularly notable that perrhenate coordination is observed both in the uranyl−lanthanide complexes previously reported and in nine out of the present lanthanide complexes, among which are all of the CB6 and CB7 complexes. The nitrate ions present in the lanthanide salts used as reactants are either completely or at least partially displaced by the perrhenate anions in excess under the hydrothermal conditions used. Perrhenate encapsulation is never observed with CB5, whereas it is ubiquitous with CB6. The perrhenate size is likely too large for CB5, and it is replaced in this case by the nitrate anion, which fits nicely in the cavity. The diameters of the portals of CB5, CB6, and CB7 are given as 2.4, 3.9, and 5.4 Å (van der Waals radii excluded), respectively, and the equatorial internal diameters as 4.4, 5.8, and 7.3 Å.[1b,d] The usual N−O bond length in the nitrate ion is 1.24(6) Å (average from the CSD), so that its smallest width, which is indeed parallel to the CB5 plane in structures **1**−**4** due to the bridging nature of the bonding to the cations, is ca. 1.86 Å, or 4.86 Å when the van der Waals radii are taken into account. These values seem large with respect to the estimated CB5 dimensions, but the elongation of the macrocycle along the largest nitrate width amounts to ca. 0.4 Å only, which indicates little strain. Some deformation of the portal in the transition state during anion encapsulation is, however, very likely.[1d] The shortest contacts between the nitrate ion and CB5 in **1** involve atom O11, which is bound to Ce, and are at 2.592(17) and 2.674(17) Å with atoms O9 and C25 of one carbonyl group in the narrower portal; all other contacts are larger than 2.8 Å. It is to be noted that, although perrhenate seems too large to fit into CB5 (or its inclusion complex much less stable than that with nitrate), a crystallochemical analysis indicated that perbromate [with an average Br−O bond length of 1.60(2) Å, slightly smaller than the average Re−O of 1.70(5) Å] and sulfate [S−O 1.47(3) Å], but also periodate [larger than perrhenate, I−O 1.72(6) Å], could, on geometrical grounds only, be encapsulated by CB5.[31] This leaves open the question of pertechnetate encapsulation in CB5 [Tc−O 1.68(6) Å], although it is likely to behave as the similarly sized perrhenate. The perrhenate anion tetrahedron has a side length of ca. 2.77 Å and a height of ca. 2.26 Å, that is, 5.77 and 5.26 Å, respectively, when van der Waals radii are taken into account. These values fit the equatorial cavity size of CB6, although in this case also, deformation during the encapsulation process is likely. In the case of CB7, little deformation may be necessary. Depending on the coordination mode of CB6, different positions of ReO_4^- in the cavity are observed. Perrhenate is bridging two cations across the CB6 cavity in three cases, in which the latter is tridentate at both portals (with Ce^{3+} in **6** and **8** and with Pr^{3+} in **7**). In these cases, CB6 presents a strong ellipsoidal distortion,[32] as illustrated in Figure 12 for compound **6**, in which the largest difference in the distances between diametrically opposed oxygen atoms (such as O1···O7) amounts to ca. 2.3 Å and the oxygen atoms are separated into two groups of three, the coordinated ones being in very close contact. The coordinated perrhenate oxygen atom is also in close contact with these three coordinated oxygen atoms at each

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(31) Virovets, A. V.; Blatov, V. A.; Shevchenko, A. P. *Acta Crystallogr., Sect. B* **2004**, *60*, 350.

(32) Samsonenko, D. G.; Virovets, A. V.; Lipkowski, J.; Gerasko, O. A.; Fedin, V. P. *J. Struct. Chem.* **2002**, *43*, 664.

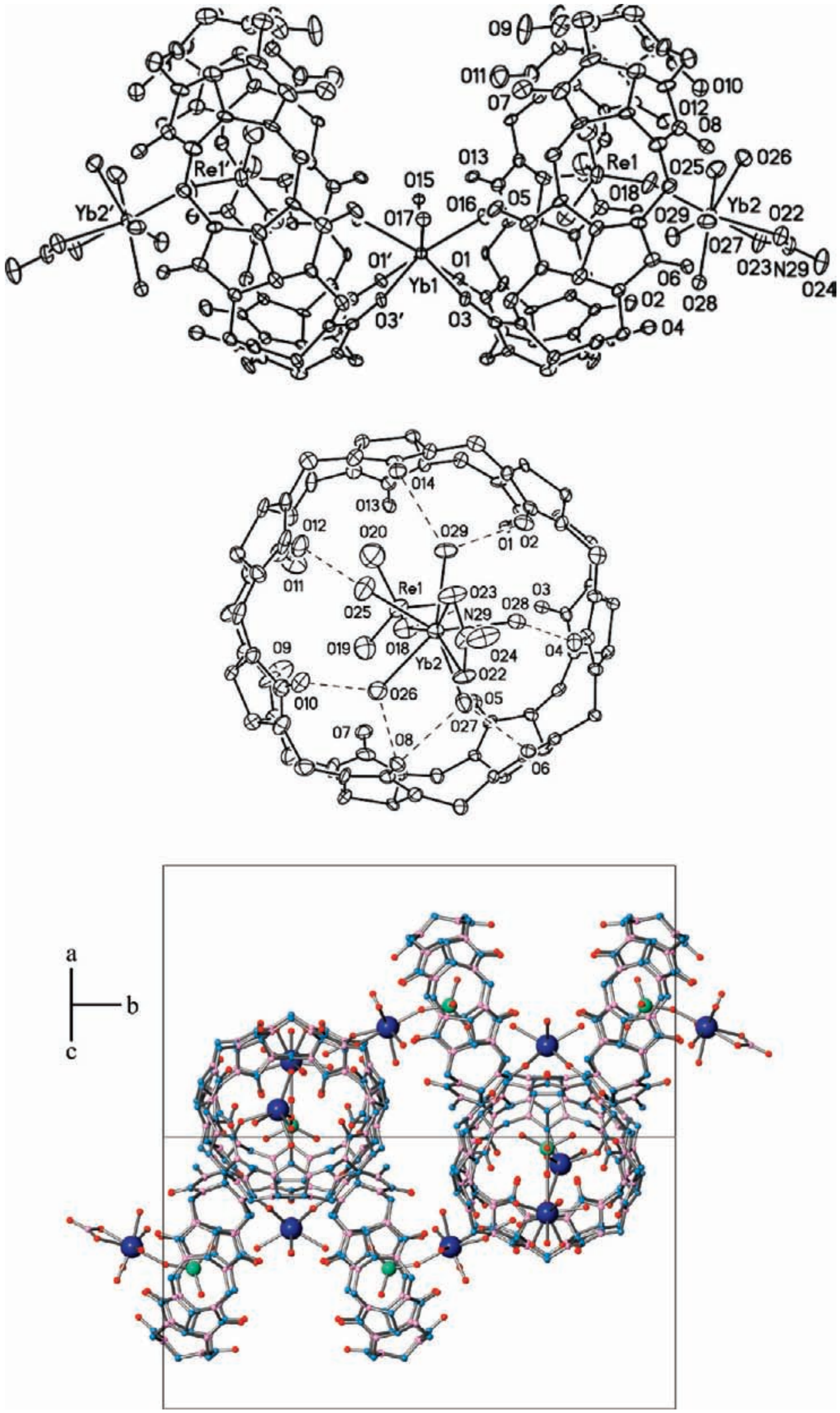

Figure 11. (Top) View of the trinuclear ytterbium complex in **14** with hydrogen atoms omitted. Displacement ellipsoids are drawn at the 30% probability level. Symmetry code: (′) = x, 3/2 − y, z. (Middle) View showing the location of the $[Yb(ReO_4)(NO_3)(H_2O)_5]^+$ cation above the macrocycle portal. Possible hydrogen bonds are represented as dashed lines. (Bottom) View of the arrangement of the different motifs in the packing. Counterions, solvent molecules, and hydrogen atoms are omitted. Only one position of the disordered ytterbium atom is shown. Ytterbium is in blue and rhenium in green.

portal. The shortest contacts between the perrhenate oxygen atoms and CB6 in **6** are O27···O1 and O28···O2, 2.794(10) and 2.874(10) Å, respectively. When CB6 is only bidentate, as in compound **9**, the perrhenate ion is no longer bridging; the ellipsoidal elongation is smaller, with a maximum difference between O···O separations for diametrically opposed oxygen atoms of ca. 0.80 Å, which suggests that it is more an effect of coordination than of encapsulation. In

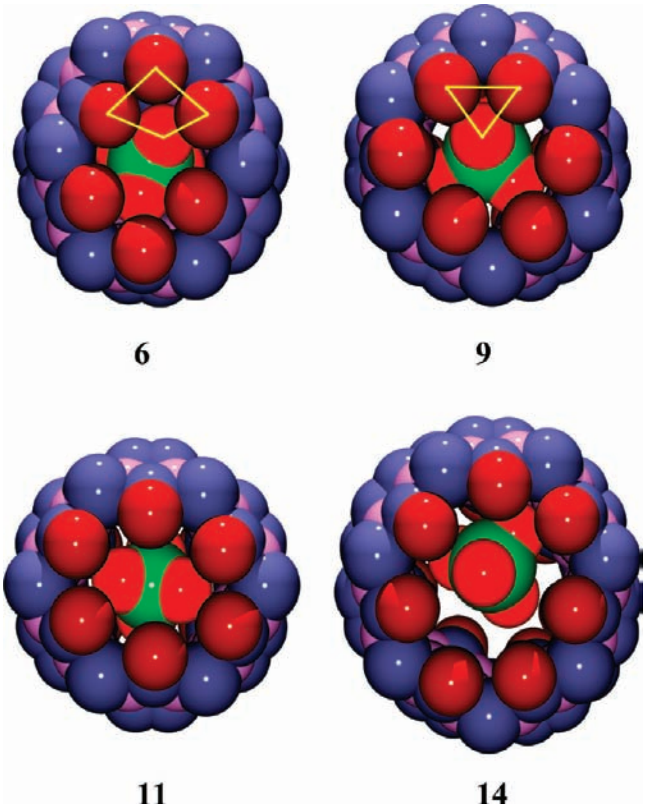

Figure 12. Spacefill representation of perrhenate inclusion in CB6 (compounds **6**, **9**, and **11**) and CB7 (**14**). Hydrogen atoms are omitted. The yellow polygons represent the lanthanide coordination sites in **6** and **9**; only the perrhenate oxygen atom pointing upward is coordinated in **14**.

this case, the only contacts shorter than 3 Å are between O20 and O6 [2.79(2) Å] and O8 [2.85(2) Å]. In compound **11**, where perrhenate is not coordinated and is only involved in hydrogen bonds with aqua ligands, its position is very different, with two oxygen atoms instead of one pointing toward the cavity entrance. Interestingly, the shortest contacts involve carbon atoms of the C═O groups, in particular O12···C10 at 3.023(9) Å. The difference between the largest and smallest O···O distances involving diametrically opposed oxygen atoms is, however, large, at 1.66 and 1.19 Å for the two portals. In the case of CB7, ReO_4^- is obviously too small to fill the cavity. The only short contacts are between the noncoordinated perrhenate atom O20 and one nitrogen [3.022(17) Å] and one carbon atom [3.06(3) Å]. Obviously, when not severely constrained by coordination, ReO_4^- orients itself so as to be nearer to the less electron-rich part of the cavity,[1e] as could be expected. Complexes between CBs and a polyoxovanadate have recently been described.[33] The latter anion is too large to fit into the cavity, and it is instead located outside. It is, however, interesting that ion−dipole interactions involving the electron-deficient carbon sites, with distances comparable to the present ones, have been found in these compounds. Similar interactions are likely present in compounds **11** and **14**.

Conclusion

Although the interest of this work does not consist primarily in the study of lanthanide complexes of CBs, which have been already widely investigated,[2] some novel structures result from the use of perrhenic acid as a reactant, among which are the ytterbium−CB5 one-dimensional polymer **5**, the sinuous chain, ribbonlike assembly in the cerium−CB6 complex **8**, and the samarium−CB6 sandwich complex **9**. One of the rare examples of metal ion complexes of CB7, and the first with a lanthanide ion, **14**, is also reported, with the original association of one ytterbium penta-aqua cation to CB7 as a hydrogen-bonded lid. However, the main results concern the complexation and encapsulation of the perrhenate ion. Lanthanide complexation by ReO_4^- is ubiquitous in the CB6 and CB7 series, although nitrate ions are always present in the reacting medium. It has been shown previously that perrhenate bonding to the uranyl ion occurs under similar conditions.[5] These results may be of interest in the field of nuclear waste reprocessing due to the analogy between ReO_4^- and TcO_4^-, although, of course, these investigations have been performed in the solid state, and the observations may not be directly transposable to solutions. Of interest also in this context is the ready encapsulation of perrhenate in CB6 and CB7. A search of the CSD shows that, up to now, sulfate and perchlorate are the only tetrahedral oxoanions to be found in association with CBs in the solid state, with, in some cases, coordination of sulfate to lanthanide ions,[2a,c] but these anions are never encapsulated in the CB cavity (the higher negative charge of sulfate may be an unfavorable factor). The present lanthanide complexes, together with the uranyl−lanthanide complexes previously reported, thus provide the first examples of crystallographically characterized encapsulation of a tetrahedral oxoanion in CBs. Considering the generality of this behavior in the present series and also the underdevelopment of the studies of anion encapsulation in CBs, this phenomenon may well deserve further study and, particularly, to be investigated in solution.

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.

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(33) Fang, X.; Kögerler, P.; Isaacs, L.; Uchida, S.; Mizuno, N. *J. Am. Chem. Soc.* **2009**, *131*, 432.