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Article

Sandwich-Type Tetranuclear Lanthanide Complexes with Cucurbit[6]uril: From Molecular Compounds to Coordination Polymers

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Sandwich-type lanthanide complexes with macrocyclic ligand cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12}$, CB[6]) were synthesized under hydrothermal conditions from aqueous solutions of lanthanide(III) bromides, CB[6], and 4-cyanopyridine. According to X-ray analysis (Ln = La, Pr, Dy, Ho, Er, and Yb), the compounds with different structural types of lanthanide cores have a common fragment where the tetranuclear hydroxo complex is sandwiched between two macrocycles $\{(IN@CB[6])Ln_4(\mu_3\text{-}OH)_4(IN@CB[6])\}^{6+}$ (IN = isonicotinate). The photoluminescence (for Ln = Eu) and Fourier transform ion cyclotron resonance mass spectra (for Ln = Pr, Dy, and Er) were studied. The compounds are used for the first time as precursors for the synthesis of lanthanide−silver heterometallic coordination polymers. The chainlike crystal structure of polymers (Ln = La, Pr, and Dy) is constituted by the sandwich complexes linked via the coordination of IN nitrogen atoms to the silver atoms.

Introduction

The metal−organic frameworks composed of linking metal centers and rigid organic bridging components have received considerable attention in recent years not only because of the architectural beauty of their structures but also because of their potential applications as new materials in optoelectronic devices and gas storage and for shape-and-size-selective separations and catalysis.[1] Considerable progress has been achieved in the design and application of transition metal−organic frameworks. However, the field of coordination polymers containing lanthanide ions has been hardly explored so far, in spite of special luminescence and magnetic properties and catalytic activity expected for these compounds.[2] Synthesis of lanthanide coordination polymers in which the metallic sites are occupied by polynuclear species is of particular interest but still represents a big challenge because of a high tendency of lanthanides to form insoluble polymeric hydroxo and oxo compounds in aqueous solutions. To date, only a few examples of coordination polymers constructed from hydroxo lanthanide cluster cores are known. The use of multifunctional carboxylate ligands (one part of them prevents the core from further aggregation, and another one coordinates an adjacent lanthanide core) leads to 3D porous frameworks constructed from hydroxo lanthanide cluster cores of Er_2, Er_4, Dy_4, Ho_7, and Yb_7.[3] Recently, the rigid ligand isonicotinic acid with both O and N donor atoms has been proven to act as a linker between the lanthanide (Ln_{14} and Ln_{36}) clusters and transition-metal ions forming structures with 3D Ln−M heteroatomic coordination frameworks.[4] Infinite one-dimensional chains are formed in the structures of hexanuclear lanthanide hydroxo complexes bridged by inorganic ligands: in the structure of the Er_6 complex with an original N_2O_2 ligand and in the structure of a cyanide-bridging Yb_6−Pd heterometallic complex.[5]

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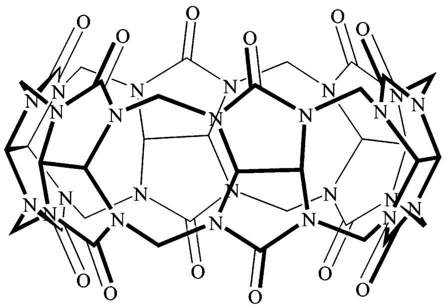
Scheme 1



cucurbit[6]uril

Recently, we have managed to isolate novel tetranuclear lanthanide(III) hydroxo complexes with the organic macrocyclic ligand cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12}$, CB[6]) from aqueous solutions of lanthanide nitrates and chlorides and 4-cyanopyridine.[6] The cucurbit[6]uril molecule resembles in shape a barrel containing oxygen atoms of carbonyl groups (portals) on the planes of the top and the bottom (Scheme 1).[7]

The formation of Ln_4 complexes results from the combined influence of the tetradentate coordination of the polycation by the portals of CB[6] and the chelating effect of the carboxylate ligands of isonicotinic acid (HIN) generated as a result of the hydrolysis of 4-cyanopyridine. The compounds have a sandwich structure with the tetranuclear lanthanide hydroxo unit $\{Ln_4(\mu_3\text{-}OH)_4\}^{8+}$ situated between two CB[6] molecules. The aromatic part of the isonicotinate anions (IN) is encapsulated into the cavity of CB[6], so that the nitrogen atom of the anion can be coordinated by metal ions. The compounds are soluble in water, and tetranuclear sandwich fragments remain in aqueous solutions. These factors let us propose these complexes as promising chemical precursors in the design of new coordination polymers.

Here, we report the synthesis and structural characterization of new tetranuclear lanthanide(III) hydroxo complexes (**1**−**6**) isolated from aqueous solutions of CB[6], lanthanide bromides, and 4-cyanopyridine. In the present work, these complexes are used for the first time as starting compounds for the synthesis of lanthanide−silver heterometallic coordination polymers (**7**−**9**) through the coordination of silver ions by the nitrogen atoms of IN ligands.

$$(H_3O)_3\{[La_4(OH)_8(H_2O)_2(IN)_2(IN@CB[6])_2] \times [La(H_2O)_7(HIN)][La(H_2O)_8]\}Br_9 \cdot 25H_2O \quad (1)$$

$$(H_3O)_3\{[Pr_4(OH)_8(H_2O)_4(IN@CB[6])_2] \times [Pr(H_2O)_7(HIN)]_2\}Br_{11} \cdot 26H_2O \quad (2)$$

$$(H_3O)_4[Dy_4(OH)_5(H_2O)_4(\mu_2\text{-}IN)(IN@CB[6])_2]Br_8 \cdot 25H_2O \quad (3)$$

$$(H_3O)_2[Ho_4(OH)_5(H_2O)_4(\mu_2\text{-}IN)(IN@CB[6])_2]Br_6 \cdot 27H_2O \quad (4)$$

$$(H_3O)_4[Er_4(OH)_5(H_2O)_4(\mu_2\text{-}IN)(IN@CB[6])_2]Br_8 \cdot 23H_2O \quad (5)$$

$$(H_3O)_4[Yb_4(OH)_6(H_2O)_4(IN@CB[6])_2]Br_8 \cdot 35H_2O \quad (6)$$

$$(H_3O)_3[La_4(OH)_8(H_2O)_3(IN@CB[6])_2\{Ag(H_2O)_2(HIN)\} \times \{Ag(H_2O)_2(IN)\}][Ag(H_2O)_2(CB[6])](NO_3)_7 \cdot 31H_2O \quad (7)$$

$$[Pr_4(OH)_8(H_2O)_3(IN@CB[6])_2\{Ag(H_2O)_2(HIN)\} \times \{Ag(H_2O)_2(IN)\}][Ag(H_2O)_2(CB[6])](NO_3)_4 \cdot 28H_2O \quad (8)$$

$$[Dy_4(OH)_8(H_2O)_3(IN@CB[6])_2\{Ag(H_2O)_2(HIN)\} \times \{Ag(H_2O)_2(IN)\}][Ag(H_2O)_2(CB[6])](NO_3)_4 \cdot 28H_2O \quad (9)$$

Experimental Section

General Data. The starting compounds $LnBr_3 \cdot xH_2O$ (Ln = La, Pr, Dy, Ho, Er, and Yb) and 4-cyanopyridine (99%) were of commercial quality and used without further purification; cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12} \cdot 10H_2O$)[7b] was synthesized according to known procedures. Elemental analysis was carried out by the microanalytical services of the Institute of Inorganic Chemistry (Karlsruhe, Germany). The IR spectra were recorded using KBr pellets on an IFS-28 (Bruker) spectrophotometer in the 4000−300 cm^{-1} region.

High-resolution electrospray ionization (ESI) Fourier transform ion cyclotron resonance (FT-ICR) mass spectra were recorded with an Apex II, Bruker Daltonics, mass spectrometer.[8] The samples were transferred into the gas phase by electrospraying their freshly prepared aqueous solutions at concentrations on the order of 0.1 mM and at spraying rates of ~200 μL/h. The electrospray tip was typically held at a potential of 3−4 kV. The ions were pretrapped in a hexapole ion guide for 2−5 s in order to increase ion intensity and guided into a commercial Infinity cell (Bruker Daltonics) where they were detected under ultrahigh vacuum conditions (at 3×10^{-10} mbar) by means of

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standard ICR techniques. All of the spectra were calibrated against $Cs_{n+1}I_n^+$ cluster cations spectra. The m/z difference between calculated and experimental peaks typically never exceeded m/z 0.1 and is presumably caused by Coulomb repulsion effects of the highly charged clusters as m/z values of measured singly charged clusters showed a better agreement with the calculated masses. The absolute intensities are arbitrary; they change from spectrum to spectrum and strongly depend on the spraying conditions.

Photoluminescence (PL) measurements were performed on a Spex Fluorolog-3 spectrometer equipped with a 450 W xenon light source, double excitation and emission monochromators, and a thermoelectrically cooled Hamamatsu R928 photomultiplier as a detector. Aqueous solutions of the lanthanide complexes were measured in a standard 10 mm cuvette in a 90° geometry. Sample crystals were dispersed in viscous polyfluoroester (ABCR GmbH), layered between two 1-mm-thick quartz plates and mounted on a coldfinger of an optical closed-cycle cryostat (Leybold) operating at 14−293 K. PL was collected at a ~30° angle relative to the excitation light beam. All emission spectra were corrected for the wavelength-dependent response of the spectrometer and detector (in relative photon flux units). PL quantum yield, φ_{PL}, of the metal complexes in aqueous solutions was determined relative to that of the fluorescence of rhodamine 6G in methanol ($\varphi_{PL} = 0.95$).

Preparation of Compounds

$(H_3O)_3\{[La_4(OH)_8(H_2O)_2(IN)_2(IN@CB[6])_2][La(H_2O)_7(HIN)][La(H_2O)_8]\}Br_9 \cdot 25H_2O$ (1). A solution of $LaBr_3 \cdot 6H_2O$ (0.30 g, 0.62 mmol) in water (1.5 mL), cucurbit[6]uril (0.010 g, 0.009 mmol), and 4-cyanopyridine (0.040 g, 0.38 mmol) were placed in a glass tube. The sealed tube was treated as follows: (1) heating from 20 to 130 °C for 5 h, (2) storage at 130 °C for 12 h, (3) slow cooling to room temperature for 48 h. After three days, colorless needlelike crystals were filtered off and dried in the air for 12 h. Yield: 0.018 g (82% based on CB[6]). Anal. calcd for $C_{102}H_{194}Br_9N_{53}O_{87}La_6$: C, 23.99; H, 3.83; N, 14.53. Found: C, 23.60; H, 3.41; N, 14.68. IR (KBr, cm^{-1}): 3408(s), 2930(w), 2856(w), 1722(s), 1667(w), 1611(s), 1565(s), 1489(s), 1423(s), 1372(s), 1326(s), 1292(m), 1239(s), 1191(s), 1145(s), 1067(w), 984(w), 966(s), 820(w), 797(s), 758(s), 708(w), 675(s), 626(s), 566(w), 378(s).

The syntheses of **2**−**6** and **10** were carried out similarly to that of **1**.

$(H_3O)_3\{[Pr_4(OH)_8(H_2O)_4(IN@CB[6])_2][Pr(H_2O)_7(HIN)]_2\}Br_{11} \cdot 26H_2O$ (2). Pale-green needlelike crystals. Yield: 0.019 g (86% based on CB[6]). Anal. calcd for $C_{96}H_{195}Br_{11}N_{52}O_{87}Pr_6$: C, 22.20; H, 3.78; N, 14.02. Found: C, 22.24; H, 3.61; N, 14.03. IR (KBr, cm^{-1}): 3400(s), 3009(w), 2930(w), 2852(w), 1722(s), 1667(w), 1611(s), 1565(s), 1489(s), 1423(s), 1372(s), 1326(s), 1292(m), 1240(s), 1192(s), 1145(s), 1067(w), 984(w), 966(s), 820(w), 797(s), 758(s), 710(w), 676(s), 627(s), 566(w), 473(w), 400(m), 381(s). FT-ICR-MS($\{Pr_5\}=\{Pr_4(OH)_8(H_2O)_4(IN)_2(CB[6])_2\}\{Pr(H_2O)_7(HIN)\}^{5+}$): m/z 789.5 $[\{Pr_5\} - 11H_2O - HIN + Br]^{4+}$, 809.5 $[\{Pr_5\} - 11H_2O - HIN + Br + HBr]^{4+}$, 1091.0 $[\{Pr_5\} - 9H_2O - HIN + 2Br]^{3+}$, 1575.9 $[\{Pr_5\} - 12H_2O - HIN - 2IN + 4Br + OH]^{2+}$, or $[Pr_5(OH)_7O(CB[6])_2Br_4]^{2+}$, 1584.9 $[\{Pr_5\} - 11H_2O - HIN - 2IN + 4Br + OH]^{2+}$, 1627.0 $[\{Pr_5\} - 11H_2O - HIN + 2Br + OH]^{2+}$, 1659.0 $[\{Pr_5\} - 11H_2O - HIN + 3Br]^{2+}$.

$(H_3O)_4[Dy_4(OH)_5(H_2O)_4(\mu_2\text{-}IN)(IN@CB[6])_2]Br_8 \cdot 25H_2O$ (3). Pale-green needlelike crystals. Yield: 0.014 g (80% based on CB[6]). Anal. calcd for $C_{90}H_{159}Br_8N_{51}O_{68}Dy_4$: C, 24.95; H, 3.70; N, 16.49. Found: C, 24.72; H, 3.81; N 16.35. IR (KBr, cm^{-1}): 3424(s), 3257(w), 2930(w), 2853(w), 1722(s), 1649(s), 1600(s), 1552(m), 1498(s), 1486(s), 1418(s), 1373(s), 1327(s), 1292(m), 1238(s), 1191(s), 1143(s), 1062(m), 1013(w), 984(w), 968(s), 864(w), 820(w), 797(s), 759(s), 713(w), 683(m), 632(m), 557(w), 473(w), 448(w), 379(s). FT-ICR-MS($\{Dy_4\}=\{Dy_4(OH)_5(H_2O)_4(IN)_3(CB[6])_2\}^{4+}$): m/z 790.3 $[\{Dy_4\} + 2H_2O + Br - IN]^{4+}$, 800.9 $[\{Dy_4\}+ 2H_2O]^{4+}$, 821.1 $[\{Dy_4\} + 2H_2O + HBr]^{4+}$ or $[\{Dy_4\} + 3H_2O + Br - OH]^{4+}$, 831.6 $[\{Dy_4\} + 2H_2O + HIN]^{4+}$, 1086.4 $[\{Dy_4\} + 3H_2O + 2Br - IN]^{3+}$, 1094.5 $[\{Dy_4\} + 2H_2O + Br]^{3+}$, 1100.5 $[\{Dy_4\} + 3H_2O + Br]^{3+}$, 1108.5 $[\{Dy_4\} + 2H_2O + IN]^{3+}$, 1121.4 $[\{Dy_4\} + 2H_2O + HBr + Br]^{3+}$, 1135.5 $[\{Dy_4\} + 2H_2O + HBr + IN]^{3+}$, 1579.7 $[\{Dy_4\} + 2OH + Br - IN]^{2+}$, 1620.1 $[\{Dy_4\} + H_2O + OH + 2Br - IN]^{2+}$, 1641.2 $[\{Dy_4\} + H_2O + Br + OH]^{2+}$, 1681.6 $[\{Dy_4\} + 2H_2O + 2Br]^{2+}$.

$(H_3O)_2[Ho_4(OH)_5(H_2O)_4(\mu_2\text{-}IN)(IN@CB[6])_2]Br_6 \cdot 27H_2O$ (4). Pale-orange needlelike crystals. Yield: 0.012 g (67% based on CB[6]). Anal. calcd for $C_{90}H_{157}Br_6N_{51}O_{68}Ho_4$: C, 25.86; H, 3.79; N, 17.09. Found: C, 25.04; H, 3.64; N 16.73. IR (KBr, cm^{-1}): 3420(s), 3005(w), 2938(w), 2857(w), 1722(s), 1653(s), 1605(s), 1552(m), 1486(s), 1419(s), 1373(s), 1328(s), 1293(m), 1237(s), 1191(s), 1147(s), 1063(m), 1012(w), 984(w), 969(s), 884(w), 865(w), 820(w), 802(s), 772(s), 760(s), 714(w), 680(m), 652(m), 632(m), 559(w), 541(w), 474(w), 446(w), 376(s).

$(H_3O)_4[Er_4(OH)_5(H_2O)_4(\mu_2\text{-}IN)(IN@CB[6])_2]Br_8 \cdot 23H_2O$ (5). Pale-pink needlelike crystals. Yield: 0.018 g (97% based on CB[6]). Anal. calcd for $C_{90}H_{155}Br_8N_{51}O_{66}Er_4$: C, 25.05; H, 3.62; N, 16.55. Found: C, 24.87; H, 3.68; N, 16.67. IR (KBr, cm^{-1}): 3496(s), 2933(w), 1722(s), 1614(s), 1563(m), 1532(m), 1489(s), 1456(s) 1422(s), 1372(s), 1328(s), 1292(m), 1238(s), 1191 (s), 1145(s), 1052(m), 1011(w), 984(w), 969(s), 835(m), 820(w), 798(s), 758(s), 712(w), 680(m), 633(m), 573(w), 474(w), 432(w), 381(s). FT-ICR-MS ($\{Er_4\} = \{Er_4(OH)_5(H_2O)_4(IN)_3(CB[6])_2\}^{4+}$): m/z 752.1 $[\{Er_4\} - 4H_2O + OH - IN]^{4+}$, 779.1 $[\{Er_4\} + 2H_2O + OH - IN]^{4+}$, 783.6 $[\{Er_4\} + 3H_2O + OH - IN]^{4+}$, 1071.5 $[\{Er_4\} + 3H_2O + OH + Br - IN]^{3+}$, 1085.5 $[\{Er_4\} + 3H_2O + OH]^{3+}$, 1092.4 $[\{Er_4\} + 3H_2O + 2Br - IN]^{3+}$, 1106.5 $[\{Er_4\} + 3H_2O + Br]^{3+}$, 1127.4 $[\{Er_4\} + 3H_2O - OH + 2Br]^{3+}$.

$(H_3O)_4[Yb_4(OH)_6(H_2O)_4(IN@CB[6])_2]Br_8 \cdot 35H_2O$ (6). Colorless needlelike crystals. Yield: 0.013 g (70% based on CB[6]). Anal. calcd for $C_{84}H_{176}Br_8N_{50}O_{77}Yb_4$: C, 22.67; H, 3.99; N, 15.74. Found: C, 22.83; H, 3.65; N, 15.56. IR (KBr, cm^{-1}): 3410(s), 3125(w), 3008(w), 2935(w), 2852(w), 1723(s), 1654(m), 1611(s), 1554(m), 1491(s), 1457(s), 1420(s), 1374(s), 1328(s), 1292(m), 1235(s), 1191(s), 1147(s), 1064(m), 984(w), 968(s), 888(s), 820(w), 798(s), 759(s), 715(w), 681(m), 652(w) 635(m), 545(w), 480(w), 437(w), 376(s).

$(H_3O)_3[La_4(OH)_8(H_2O)_3(IN@CB[6])_2\{Ag(H_2O)_2(HIN)\}\{Ag(H_2O)_2(IN)\}][Ag(H_2O)_2(CB[6])](NO_3)_7 \cdot 31H_2O$ (7). A solution of **1** (0.0060 g) in water (1 mL) was carefully layered by an aqueous solution of 0.5 M $AgNO_3$ (0.2 mL) in a glass tube. In three days, colorless polyhedral-like crystals were filtered off and dried in the air for 12 h. Yield: 0.0032 g (71% based on **1**). Anal. calcd for $C_{132}H_{222}Ag_3N_{83}O_{116}La_4$: C, 27.78; H, 3.92; N, 20.37. Found: C, 27.84; H, 3.60; N, 20.56. IR (KBr, cm^{-1}): 3443(s), 3002(w), 2930(w), 2852(w), 1724(s), 1636(w), 1611(s), 1560(s), 1479(s), 1419(m), 1384(s), 1377(s), 1327(s), 1295(s), 1235(s), 1192(s), 1148(m), 1057(w), 1029(w), 984(w), 966(s), 820(w), 802(s), 759(s), 676(s), 633(m), 554(w), 453(w), 371(s).

The syntheses of **8** and **9** were carried out similarly to that of **7** from aqueous solutions of **2** (0.0060 g) and **3** (0.0070 g), correspondingly.

$[Pr_4(OH)_8(H_2O)_3(IN@CB[6])_2\{Ag(H_2O)_2(HIN)\}\{Ag(H_2O)_2(IN)\}][Ag(H_2O)_2(CB[6])](NO_3)_4\cdot 28H_2O$ (8). Colorless polyhedral-like crystals. Yield: 0.0040 g (96% based on **2**). Anal. calcd for $C_{132}H_{207}Ag_3N_{80}O_{101}Pr_4$: C, 29.26; H, 3.85; N, 20.68. Found: C, 29.15; H, 4.00; N, 20.63. IR (KBr, cm^{-1}): 3438(s), 3004(w), 2930(w), 2854(w), 1725(s), 1607(s), 1560(m), 1478(s), 1419(s), 1384(s), 1375(s), 1325(s), 1294(m), 1236(s), 1190(s), 1146(s), 1067(m), 1030(w), 984(w), 965(s), 820(w), 801(s), 760(s), 712(w), 675(m), 629(m), 559(w), 457(w), 398(w), 370(s).

$[Dy_4(OH)_8(H_2O)_3(IN@CB[6])_2\{Ag(H_2O)_2(HIN)\}\{Ag(H_2O)_2(IN)\}][Ag(H_2O)_2(CB[6])](NO_3)_4\cdot 28H_2O$ (9). Colorless polyhedral-like crystals. Yield: 0.0043 g (73% based on **3**). Anal. calcd for $C_{132}H_{207}Ag_3N_{80}O_{101}Dy_4$: C, 28.80; H, 3.79; N, 20.36. Found: C, 28.91; H, 3.71; N, 20.25. IR (KBr, cm^{-1}): 3439(s), 3006(w), 2927(w), 2853(w), 1725(s), 1608(s), 1560(m), 1482(s), 1415(s), 1384(s), 1376(s), 1325(s), 1295(m), 1235(s), 1190(s), 1146(s), 1065(m), 984(w), 965(s), 820(w), 799(s), 759(s), 677(m), 629(m), 454(w), 369(s).

For compounds **1**−**9**, the number of water molecules of crystallization estimated by X-ray diffraction analysis is in agreement with the elemental analysis data. For these complexes, water of crystallization is sometimes lost during storage (compared to the X-ray diffraction data collected from a crystal immediately after withdrawing from the solution) and can vary for different samples depending on the experimental conditions and air humidity during storage.

The compound **$(H_3O)_x[Eu_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4(H_2O)_4(IN@CB[6])_2]Br_{x+2}\cdot nH_2O$** (**10**) was carried out similarly to that of **1**. Colorless needle -like crystals. Yield: 0.015 g. IR (KBr, cm^{-1}): 3439(s), 3266(w), 2931(w), 2242(w), 1719(s), 1643(s), 1593(s), 1549(m), 1498(s), 1430(s), 1416(s), 1372(s), 1327(s), 1292(m), 1238(s), 1192(s), 1146(s), 1062(w), 1013(w), 984(w), 968(s), 865 (m), 798 (s), 770 (s), 710(w), 684 (s), 630 (m), 554 (w), 448 (w), 417 (m), 375 (s). The crystal system is monoclinic, the space group is $P2_1/c$, $a = 16.125(3)$ Å, $b = 34.096(7)$ Å, $c = 29.622(6)$ Å, $\beta = 101.29(3)°$.

The compound **$(H_3O)_5[Eu_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4(H_2O)_4(IN@CB[6])_2]Cl_7\cdot 38H_2O$** (**11**) was synthesized according to known procedures.[6b]

X-Ray Structure Determinations. The data collection was performed on a STOE IPDS II diffractometer (Mo Kα, $\lambda = 0.71073$ Å) equipped with a CCD area detector. The diffraction frames were integrated with subsequent constrained cell refinement using the SAINT package and corrected for absorption with SADABS.[9] Further experimental details are described in Table 1. Decomposition of the crystals did not occur during the data collection. The structures were solved by direct methods and refined by full-matrix least-squares method with SHELXTL.[9] The positions of hydrogen atoms of cucurbit[6]uril and organic ligands were calculated geometrically and refined using a riding model. The hydrogen atoms of the water molecules of crystallization were not located.

Results and Discussion

Syntheses and structures of tetranuclear lanthanide sandwich compounds. For the syntheses of tetranuclear lanthanide complexes, a hydrothermal approach was applied. As we

Table 1. Crystal Data and Structure Refinement for Compounds **1**−**6**

	1	2	3	4	5	6
formula	$C_{102}H_{194}Br_9N_{53}O_{87}La_6$	$C_{96}H_{195}Br_{11}N_{52}O_{87}Pr_6$	$C_{90}H_{159}Br_8N_{51}O_{68}Dy_4$	$C_{90}H_{157}Br_6N_{51}O_{68}Ho_4$	$C_{90}H_{155}Br_8N_{51}O_{66}Er_4$	$C_{84}H_{176}Br_8N_{50}O_{77}Yb_4$
fw	5107.75	5194.51	4332.96	4180.85	4315.97	4450.19
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)	150(2)
cryst syst	monoclinic	monoclinic	tetragonal	tetragonal	tetragonal	orthorhombic
space group	$P2_1/c$	$C2/c$	$I\bar{4}2d$	$I\bar{4}2d$	$I\bar{4}2d$	$P2_12_12$
a (Å)	28.640(6)	28.442(6)	45.883(7)	45.701(7)	45.675(7)	16.533(3)
b (Å)	14.509(3)	14.631(3)	45.833(7)	45.701(7)	45.675(7)	31.877(6)
c (Å)	41.545(8)	41.057(8)	14.316(3)	14.309(3)	14.291(3)	14.127(3)
β (deg)	92.07(3)	93.21(3)				
V (Å^3)	17252(6)	17058(6)	30074(9)	29885(9)	29814(9)	7445(3)
Z	4	4	8	8	8	2
D_{calcd} (Mg/m^3)	1.966	2.023	1.914	1.858	1.923	1.985
no. of reflns collected	125635	34371	87362	79471	108382	31207
no. of independent reflns	32737 [R(int) = 0.0317]	14780 [R(int) = 0.0482]	7651 [R(int) = 0.0282]	7610 [R(int) = 0.0253]	7592 [R(int) = 0.0231]	7665 [R(int) = 0.0271]
max. and min. transmission	0.4172 and 0.3877	0.5066 and 0.2610	0.4198 and 0.2714	0.4493 and 0.2975	0.4003 and 0.2547	0.3828 and 0.2460
GOF on F^2	1.431	1.029	1.039	1.069	1.059	1.171
final R indices [$I > 2\sigma(I)$][a]	R1 = 0.0572, wR2 = 0.0857	R1 = 0.0509, wR2 = 0.1313	R1 = 0.0376, wR2 = 0.0791	R1 = 0.0567, wR2 = 0.1348	R1 = 0.0377, wR2 = 0.0798	R1 = 0.0325, wR2 = 0.0604
R indices (all data)	R1 = 0.0857, wR2 = 0.0915	R1 = 0.0648, wR2 = 0.1381	R1 = 0.0499, wR2 = 0.0818	R1 = 0.0710, wR2 = 0.1400	R1 = 0.0459, wR2 = 0.0823	R1 = 0.0368, wR2 = 0.0615

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = \sigma_F^{-2}$.

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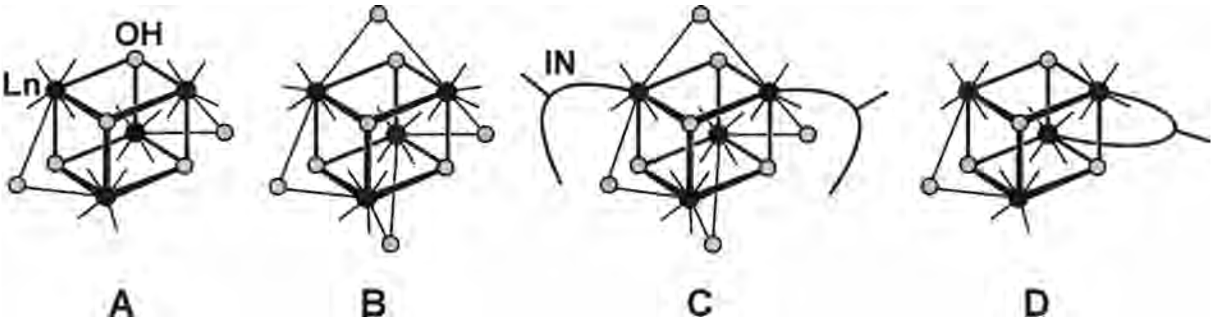
(9) Bruker Advanced X-ray Solutions: *APEX2*, version 1.08; *SAINT*, version 7.03; *SHELXTL*, version 6.12; *SADABS*, version 2.11; Bruker AXS Inc.: Madison, WI, 2004.

Scheme 2. Structural Types for Lanthanide Core in the Sandwich Complexes **1**−**6** (CB[6] Molecules and Aqua Ligands Are Not Shown): **A**, $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2\}^{6+}$; **B**, $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4\}^{4+}$; **C**, $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4(IN)_2\}^{2+}$; **D**, $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)(\mu_2\text{-}IN)\}^{6+}$



have shown earlier, a great excess of metal salt to CB[6] and a slow hydrolysis of 4-cyanopyridine under hydrothermal conditions are necessary for the isolation of tetranuclear complexes as single crystals from lanthanide(III) nitrate and chloride aqueous solutions.[6] The reactions of lanthanide(III) bromides (Ln = La, Pr, Dy, Ho, Er, Yb), cucurbit[6]uril, and 4-cyanopyridine were carried out in sealed tubes at 130 °C; after slow cooling of the sealed reactions tubes and allowing them to stand at room temperature for several days, colorless or pale-color needlelike crystals of **1**−**6** were separated. Like tetranuclear nitrate and chloride salts, the obtained product compounds are soluble in water, and the aqueous solutions turn turbid after standing for a few days at room temperature, presumably because of further hydrolysis of the compounds. The IR spectra of complexes **1**−**6** are typical of lanthanide sandwich compounds.[6]

Single-crystal X-ray analysis of obtained tetranuclear complexes **1**−**6** revealed a common structural fragment: the sandwich structure with the cubanelike $\{Ln_4(\mu_3\text{-}OH)_4\}^{8+}$ unit situated between two tetradentate cucurbit[6]uril ligands. Metal atoms are coordinated also by two bidentate isonicotinate (IN) anions whose aromatic parts are encapsulated into the cavity of each CB[6] molecule. The sandwich fragment is similar to that for the above-mentioned Ln_4 nitrate and chloride salts, and two different structural types for those complexes were revealed, depending on two or four μ_2-hydroxo ligands coordinated to the Ln_4 core (Scheme 2, types A and B).[6] For complexes **1**−**6**, both these types and new ones, with two additional terminal isonicotinate ligands (Scheme 2, type C), or with one μ_2-hydroxo and one μ_2-isonicotinate ligands (Scheme 2, type D), are found.

In the sandwich fragment of **1**, the $\{La_4(\mu_3\text{-}OH)_4\}^{8+}$ unit is coordinated (in addition to two CB[6]) by four μ_2-hydroxo ligands, two aqua ligands, and two terminal IN ligands in the monodentate mode (Scheme 2, type C). The composition of the sandwich cation is $[La_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4(H_2O)_2(IN)_2(IN@CB[6])_2]^{2+}$, and the coordination number for the La atoms is nine: three μ_3-hydroxo ligands, two μ_2-hydroxo ligands, two oxygen atoms of the CB[6] molecule, one oxygen atom of the isonicotinate anion included into the CB[6], and either one terminal water ligand (for La(2) and La(4)) or one terminal IN ligand (for La(1) and La(3)) (Figure 1).

The bond lengths in the La_4 core are presented in Table 2. The coordination of IN makes two longer La−(μ_2-OH) distances between the oxygen atom and the metal atom coordinated by IN (2.811(6) and 2.853(5) Å), whereas other La−(μ_2-OH) bond lengths lie in the range of 2.662(5)−2.795(5) Å. The external CB[6] portals of the sandwich cation are coordinated by mononuclear lanthanide complexes; at that, only one oxygen portal atom of each CB[6] is involved in the coordination (La−O(CB[6]) = 2.593(4) and 2.522(4) Å, for La(5) and La(6), correspondingly). The aqua ligands of both mononuclear complexes form hydrogen bonds with the portal of the CB[6] ligand of the neighboring sandwich cation (O···O, 2.79−2.90 Å) resulting in a chain structure (Figure 2). The water molecules of crystallization, the bromide anions, and the H_3O^+ cations (they were added to the formula to ensure the neutrality of the crystalline framework) are

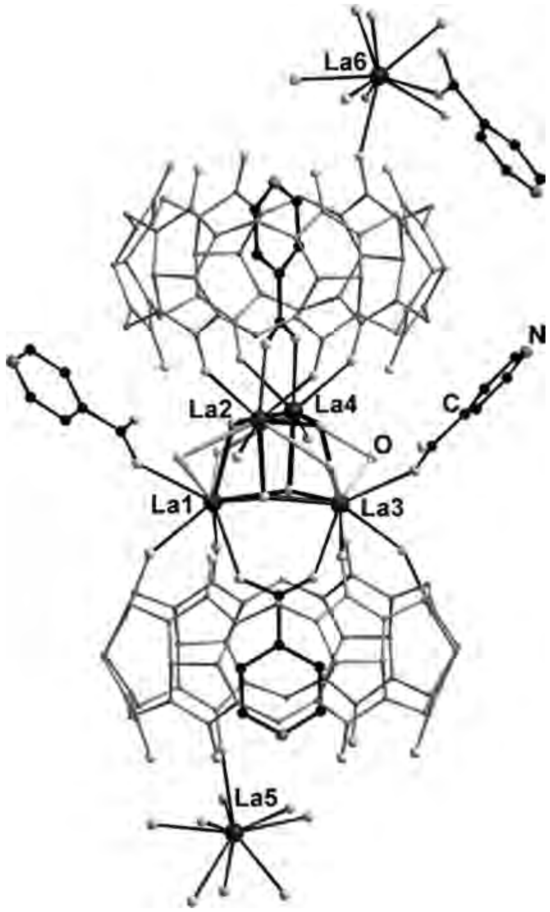


Figure 1. The structure of the $[La_4(OH)_8(H_2O)_2(IN)_2(IN@CB[6])_2][La(H_2O)_7(HIN)][La(H_2O)_8]^{6+}$ complex in **1**. Hydrogen atoms are omitted for clarity.

Table 2. The Bond Lengths (Å) in Lanthanide Core of Complexes **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
Ln−(μ_3-O)	2.423(4)−2.513(4)	2.428(4), 2.447(4)	2.322(6)−2.387(7)	2.302(11)−2.354(11)	2.283(7)−2.383(7)	2.259(6)−2.345(5)
Ln−(μ_2-O)	2.662(5)−2.853(5)	2.674(5), 2.760(5)	2.584(7)	2.582(11)	2.526(7)	2.501(6), 2.581(6)
Ln−O (CB°)	2.502(4)−2.669(4)	2.462(4)−2.552(5)	2.350(6)−2.536(7)	2.322(12)− 2.538(11)	2.342(7)−2.568(7)	2.275(6)−2.393(5)
Ln−O (IN@CB°)	2.455(4)−2.500(4)	2.420(5), 2.426(5)	2.336(6), 2.366(7)	2.312(11), 2.364(11)	2.308(7), 2.331(7)	2.292(5), 2.310(5)
Ln−O (IN)	2.603(5), 2.605(6)		2.366(7)	2.306(11)	2.325(7)	
Ln−O (H_2O)	2.572(5), 2.576(5)	2.503(6), 2.521(5)	2.382(8), 2.410(8)	2.327(11), 2.368(11)	2.367(8), 2.369(8)	2.319(5), 2.346(6)
Ln···Ln	3.8746(10)−4.0602(9)	3.7799(11)−3.8908(8)	3.5939(10)−3.8165(10)	3.5610(14)−3.7878(14)	3.5644(10)−3.7787(10)	3.5847(7)−3.7048(9)

located between the chains (here and in the further structures **2**−**6**).

Compound **2** is isostructural to the previously presented Pr_4 chloride salt;[6b] they differ only by the number of the water molecules of crystallization. There are four μ_2-hydroxo ligands coordinated to the Ln_4 core (Scheme 2, type B), and the coordination number for the Pr atoms is nine (Figure 1S, Supporting Information).

The compositions of the isotypical compounds **3**−**5** differ by the number of bromide anions or water molecules. In these sandwich compounds, metal atoms of the cubanelike $\{Ln_4(\mu_3\text{-}OH)_4\}^{8+}$ unit (Ln = Dy (**3**), Ho (**4**), Er (**5**)) are coordinated by one bridging μ_2-hydroxo and one μ_2-isonicotinate ligand, and new structural type D (Scheme 2) is realized. The structure of the sandwich complex is shown in Figure 3 (for compound **4** as an example). Each lanthanide atom is coordinated by three μ_3-hydroxo ligands, by two oxygen atoms of CB[6] molecule, by one oxygen atom of the isonicotinate anion included into CB[6], and by one water molecule, and one coordination position is occupied either by one μ_2-hydroxo ligand (for Ln(1)) or by one oxygen atom of μ_2-isonicotinate ligand (for Ln(2)). The coordination number for the Ln atoms is eight. The crystal structure of **3**−**5** has a clear layered motive along the *c* direction (Figure 4, for compound **4**, as an example). The $[Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)(\mu_2\text{-}IN)(H_2O)_4(IN@CB[6])_2]^{4+}$ sandwiches are located by pairs; the pairs are perpendicular to each other in the unit cell. Both sandwiches in one pair are located close enough to the sandwich of the neighboring perpendicular pair and connected by hydrogen bonds between their CB[6] carbonyl portals and CH and CH_2 groups of CB[6] of the perpendicular sandwich ($d_{av.}(O\cdots H{-}C) = 2.59$ Å, for **4**).

In the crystal structure of **6**, the composition of the sandwich complex is $[Yb_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(H_2O)_4(IN@CB[6])_2]^{4+}$ (structural type A, Scheme 2), and the ytterbium atoms are eight-coordinate. The same structure of sandwich fragment was found earlier for Ho_4 nitrate and Er_4 and Yb_4 chloride salts.[6] Having the same sandwich fragment, the salts differ in their crystal packing. In contrast to chain structures of nitrate (space group *Pbam*) and chloride (space group *C*2/*c*) salts, in the compound **6** (space group $P2_12_12$) the sandwiches form parquetlike layers (Figure 5).

The bond lengths in the lanthanide core of complexes **1**−**6** (Table 2) are in the normal range[3,6,10] and decrease from **1** to **6** in accordance with the decrease of the Ln radius (1.17 Å for La^{3+} and 1.01 Å for Yb^{3+}).[11]

The reaction with europium(III) bromide carried out under the same hydrothermal conditions as for **1**−**6** affords single crystals (**10**) with crystallographic parameters different from **1**−**6**. Unfortunately, the structure of the compound was solved only to $R_1 \approx 20\%$ because of high disordering of the sandwich complexes. Analysis of the X-ray data obtained for three crystals from parallel synthetic experiments demonstrates that the structure consists of the sandwich cations with the tetranuclear lanthanide core of structural type B (Scheme 2). The space group and the crystal system for **10** are identical to those for chloride salt $(H_3O)_5[Eu_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4(H_2O)_4(IN@CB[6])_2]Cl_7\cdot 38H_2O$ (**11**),[6b] and the corresponding unit cell parameters are similar (for **11**, $a = 16.0366(6)$ Å, $b = 33.8771(12)$ Å, $c = 29.4760(11)$ Å, and $\beta = 100.667(1)°$; for **10**, see the Experimental Section), which indicates that these compounds are isotypical. Figure 2S (Supporting Information) shows the structure of sandwich complexes in **10** and **11**.

Thus, the bromide salts of tetranuclear lanthanide sandwich compounds were obtained under hydrothermal synthesis, as in the case of previously presented chloride and nitrate salts. Single-crystal X-ray analysis revealed both known structural types of sandwich complexes, in which metal atoms, aqua ligands, and hydroxo bridges form $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(H_2O)_4\}^{6+}$ and $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4(H_2O)_4\}^{4+}$ cores, and new ones, with additional isonicotinate ligands bonded to the core in monodentate $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4(H_2O)_2(IN)_2\}^{2+}$ or bidentate $\{Ln_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)(H_2O)_4(\mu_2\text{-}IN)\}^{6+}$ mode. This fact demonstrates the influence of the counteranion on the formation of sandwich complexes of different types and on the manner of their crystal packing. Independently of the counteranion (nitrate, chloride, or bromide) in the compounds, the structural types with nine-coordinated lanthanide atoms are realized for the elements of the beginning of the lanthanide row (Ln = La, Pr, Eu, Gd, Tb), while the elements of the end of the row have the coordination number eight (Ln = Dy, Ho, Er, Yb), which is in good agreement with the lanthanide contraction.

Photoluminescence Spectroscopy. Because of the excellent luminescent properties of Eu(III) ions, the photoluminescence of **10** and **11** was investigated. These complexes show bright red light emission under UV photoexcitation. The low-resolution PL emission spectrum of **11** has already been presented.[6b] In this contribution, we report PL excitation

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(10) (a) Wang, R.; Zheng, Z.; Jin, T.; Staples, R. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1813. (b) Ma, B. Q.; Zhang, D. S.; Gao, S.; Jin, T. Z.; Yan, C. H.; Xu, G. X. *New J. Chem.* **2000**, *24*, 251.

(11) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley and Sons: New York, 1999; Vol. *1109*.

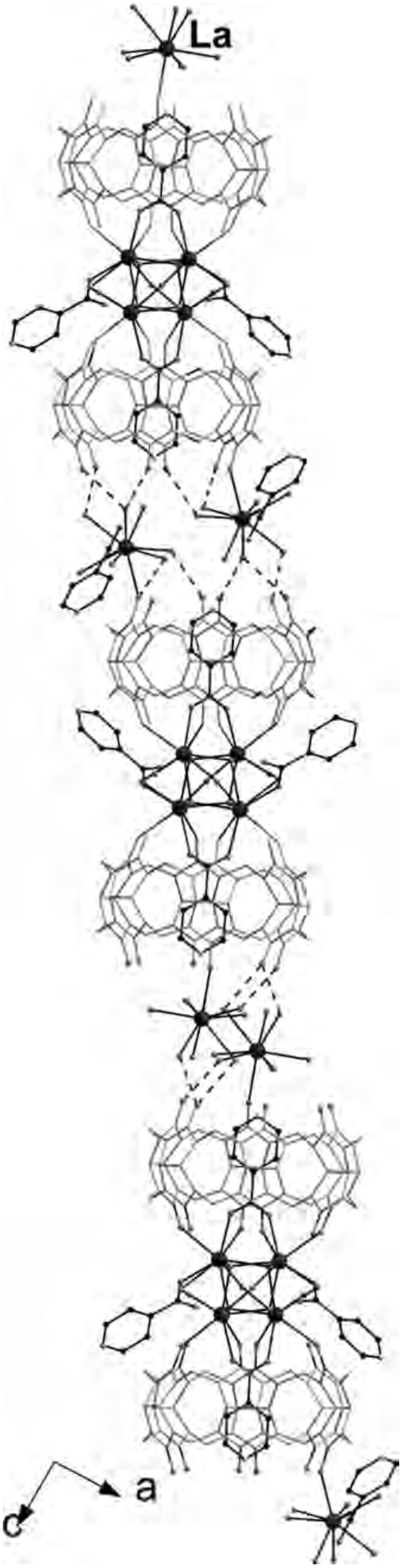

Figure 2. Fragment of the crystal structure in **1**. Dashed lines show hydrogen bonds.

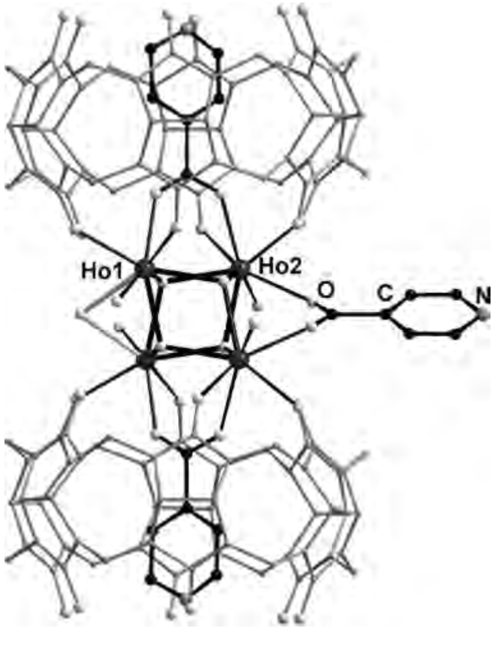

Figure 3. The structure of the $[Ho_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)(\mu_2\text{-}IN)(H_2O)_4(IN@CB[6])_2]^{4+}$ complex in **4**. Hydrogen atoms are omitted for clarity.

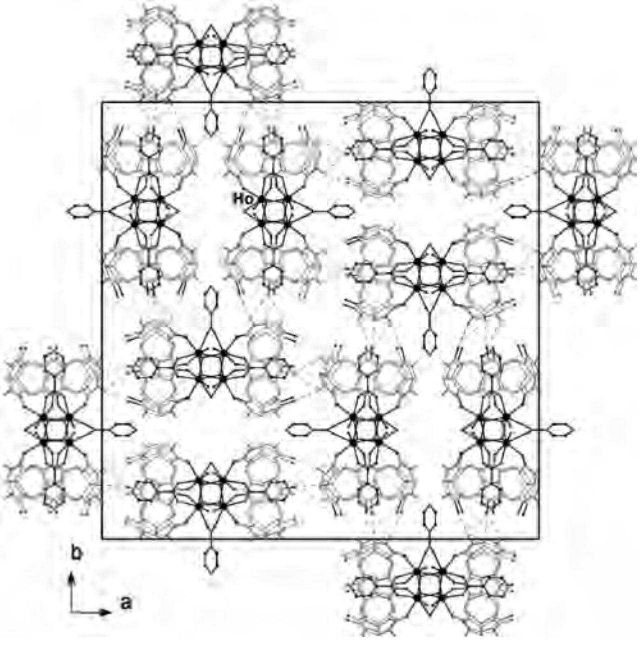

Figure 4. The layer packing of $[Ho_4(OH)_5(\mu_2\text{-}IN)(H_2O)_4(IN@CB[6])_2]^{4+}$ sandwiches in the crystal structure of **4**. Dashed lines show hydrogen bonds.

(PLE) and high-resolution emission spectra of solid samples measured at different temperatures down to 14 K as well as PL spectra of their aqueous solutions. Surprisingly, significant differences in the PL splitting patterns were found for these structurally similar complexes. This indicates the high sensitivity of electronic relaxation (PL properties) in the tetranuclear lanthanide complexes to small variations of the metal core geometry and surrounding area.

Figure 6 shows low-temperature PLE and emission spectra of crystalline samples of **10** and **11**. According to the PLE spectra, photoexcitation is the most effective in the ligand band at $\lambda_{exc} \sim 270$ nm, associated with the absorption of

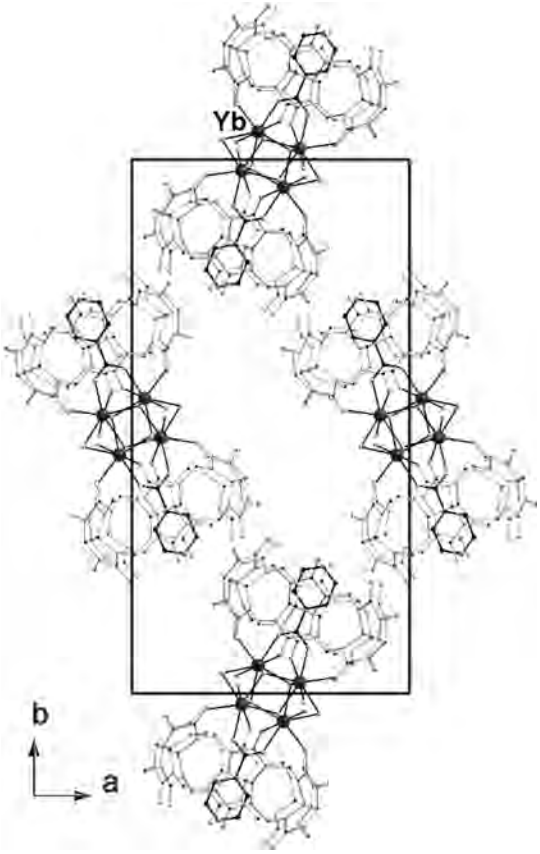

Figure 5. Parquetlike layer of $[Yb_4(OH)_6(H_2O)_4(IN@CB[6])_2]^{4+}$ sandwich cations in the structure of **6**.

cucurbit[6]uril units. This suggests an effective intramolecular energy transfer from the ligands to the tetranuclear lanthanide core. Narrow lines in the PLE spectra correspond to direct photoexcitation of f → f transitions of the lanthanide core. The strongest one at 394 nm can be assigned to the $^7F_0 \rightarrow {}^5L_6$ transition of the Eu^{3+} ion.[12] However, as typical for lanthanide complexes, oscillator strengths of f → f transitions are low, and photoexcitation via these transitions is inefficient. Because of the UV excitation range, a determination of the PL efficiency of solid samples with the aid of a conventional integrating sphere[13] was not feasible. By comparison with signals of other luminophors measured using the same apparatus, we roughly estimate $\varphi_{PL}$to be *at least* several percent for solid **10** and **11** at cryogenic temperatures. The PL depends only moderately on the temperature.

Series of emission bands within ~580−720 nm are characteristic for Eu(III) and can be assigned to $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3, 4$) transitions. High-resolution spectra reveal splittings of the emission bands into lines with a width of about 20 cm^{-1}. The appearance of the formally forbidden $^5D_0 \rightarrow {}^7F_0$ transition in the spectra of **11** as well as complex and multicomponent splittings suggest a low local symmetry for the Ln ions in the compound. This observation seems to be common for polynuclear Eu complexes.[14] In contrast to **11**, almost no signature of the $^5D_0 \rightarrow {}^7F_0$ transition, notably narrower bands, and simpler splitting patterns are observed in the emission spectra of **10** (Figure 6a)—suggesting a high local symmetry for the Eu ions. The reasons for the different PL behavior of structurally similar **10** and **11** and a possible role of the Br^- versus Cl^- anions (we remind that **10** and **11** were prepared by the same procedure from Eu(III) bromide and chloride, respectively) are not clear at the moment.

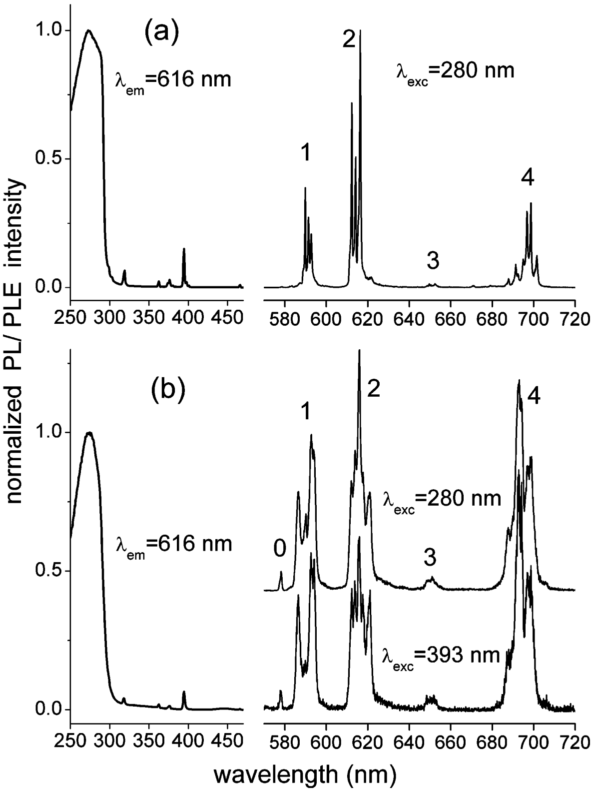

Figure 6. Normalized photoluminescence excitation (PLE) and emission spectra (left and right panels, respectively) of crystals of **10** (a) and **11** (b) measured at $T = 23$ K. The spectra were scanned with a spectral slit width of 1 and 0.2 nm, respectively. Emission bands 0−4 correspond to transitions $^5D_0 \rightarrow {}^7F_J$, $J = 0, 1, 2, 3, 4$. A broad PLE band at ~280 nm corresponds to absorption of the CB[6] ligands.

A similar but relatively weak and broad PL emission was observed from aqueous solutions of **10** and **11**, as illustrated in Figure 7 for complex **11**. The integral PL quantum yield, φ_{PL}, was determined to be $(1.2 \pm 0.3) \times 10^{-2}$ and $(2.4 \pm 0.5) \times 10^{-2}$ for **10** and **11**, respectively ($\lambda_{exc} = 394$ nm). We note further that the PL of **11** is by a factor of ~5 stronger than the corresponding PL from aqueous solutions of $EuCl_3$ or $EuBr_3$ at the same absorption (with an approximately similar metal concentration as in aqueous solutions of Ln_4 complexes).

PLE and high-resolution emission spectra of the solid sample as well as the PL spectrum of an aqueous solution of the terbium(III) complex $(H_3O)_4[Tb_4(OH)_8(H_2O)_4(IN)_2(CB[6])_2]Cl_6 \cdot 40H_2O$[6b] (**12**) were also measured. The results indicate also a low local symmetry for the Tb ions in the compound. The spectra (Figure 2S) and their description are in the Supporting Information.

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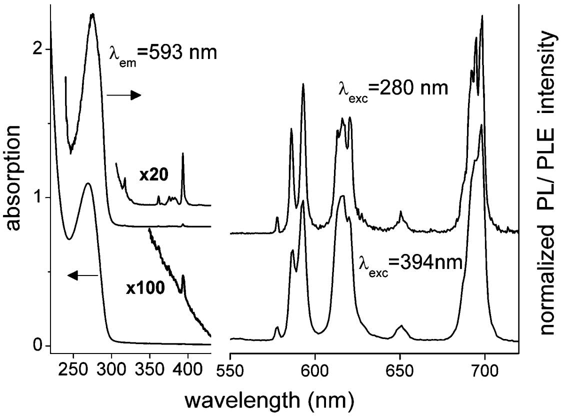

Figure 7. Absorption, photoluminescence excitation (left panel), and emission (left and right panel) spectra of **11** dissolved in water. The PLE spectrum and emission at $\lambda_{\text{exc}} = 280$ nm were scanned with a spectral slit width of 1 nm. A larger slit width of 2 nm was used for the emission spectrum at $\lambda_{\text{exc}} = 394$ nm because of the weaker signal.

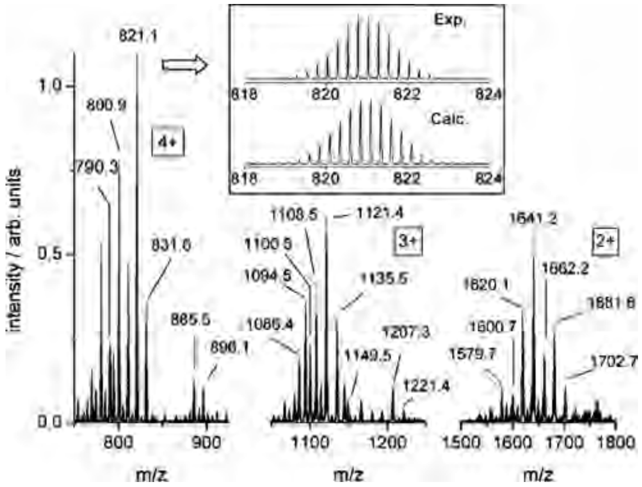

Figure 8. FT-ICR mass spectra (extracts) of different charge states (+4, +3, +2) of compound **3** electrosprayed out of water. The inset shows the isotopic resolution of the $[\{Dy_4\} + 2H_2O + HBr]^{4+}$ tetracation at around 821.1 *m/z*. The given *m/z* numbers correspond to the most abundant isotopologue of the calculated ion signal.

Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometry. Complexes **2**, **3**, and **5** were studied using FT-ICR mass spectrometry. In the spectra of **3** and **5**, FT-ICR allows identification of the intact sandwich complexes $[Ln_4(OH)_5(H_2O)_4(IN)_3(CB[6])_2]^{4+}$. In general, the mass spectra show these species as (interchanging) H_2O and HBr, OH^-, Br^-, and IN^- adducts, and therefore, +4, +3, and +2 charged cations appear. Such ligand exchange reactions were also observed for cadmium selenide clusters (see, e.g., ref 15). Figure 8 shows mass spectra of different charge states (+4, +3, and +2) for **3**; the inset shows the measured and calculated isotopic pattern of the ion signal at *m/z* 821.1 (most abundant isotopologue), which can be assigned to the $[\{Dy_4\} + 2H_2O + HBr]^{4+}$ tetracation (where $\{Dy_4\}$ is $\{Dy_4(OH)_5(H_2O)_4(IN)_3(CB[6])_2\}^{4+}$). Note that the compositions of this cation and the $[\{Dy_4\} + 3H_2O + Br - OH]^{4+}$ cation are identical and cannot be distinguished by mass spectrometrical methods. This fact also holds true for many other cations. The latter cation and the cation at *m/z* 831.6 $[\{Dy_4\} + 3H_2O + IN - OH]^{4+}$ can be interpreted as the loss of one hydroxo ligand. Some peaks (*m/z* 790.3, 1086.4, 1579.7, and 1620.1) correspond to the species resulting from the loss of one isonicotinate ligand. The loss of hydroxo and isonicotinate anions was also observed for the isostructural erbium compound **5** (mass spectra see in Figure 4S, Supporting Information). This is in contrast to the case of previously presented erbium(III) chloride salt,[6b] where we did not observe the loss of OH or IN ligands from the $[Er_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_2(H_2O)_4(IN@CB[6])_2]^{4+}$ sandwich in the ESI-MS spectrum.

In the mass spectra of compound **2** (there are two mononuclear praseodymium complexes bonded to the sandwich external CB[6] portals in the structure of **2**), by assuming only a tetranuclear $\{Pr_4\}$ core, no peaks could be assigned. However, when five Pr atoms in the species was proposed (which would be consistent with a Pr_4 core plus one Pr atom bound to one of the two CB[6] ligands), an assignment of the measured ion signals was possible. Note that an assignment by assuming $\{Pr_4(Pr)_2\}$ entities as they appear in the structure fails too. The mass spectra (Figure 5S) and the assignments of the ion signals for **2** are in the Supporting Information.

To summarize the results of the mass spectrometric study, we can conclude that in the cases of the Dy (**3**) and Er (**5**) compounds the tetranuclear sandwich complexes exist in solution and can be transferred into the gas phase by electrospray. For the Pr (**2**) compound, molecular ions comprising five Pr atoms were observed.

Lanthanide Coordination Polymers. Tetranuclear lanthanide sandwich complexes are soluble in water; moreover, sandwich fragments, according to the mass spectrometric data, remain in aqueous solutions. The nitrogen atom of the isonicotinate anion encapsulated into the CB[6] cavity is located in the center of the CB[6] portal and is accessible to coordination by metal ions. These factors make sandwich complexes very promising precursors for the synthesis of coordination polymers.

The syntheses were carried out by careful layering of a $AgNO_3$ aqueous solution on a solution of a sandwich compound (**1**−**6**) in a narrow glass tube. In a few days, polyhedral-like crystals for Ln = La (**7**), Pr (**8**), and Dy (**9**) were separated with a good yield. The crystals are stable in the air for several days and insoluble in water. For syntheses with Ln = Ho, Er, and Yb, amorphous powders were obtained. Also, the chloride salts of tetranuclear lanthanide sandwich compounds can be used as precursors for the synthesis of coordination polymers. Starting from the praseodymium(III) sandwich chloride salt,[6b] we isolated crystals similar in parameters to **7**−**9** (the crystal system is monoclinic, the space group is $P2_1/c$, $a = 33.617(2)$ Å, $b = 22.178(1)$ Å, $c = 29.288(6)$ Å, $\beta = 111.71(4)°$).

Structures determined for **7**−**9** are listed in Table 3. The compounds are isotypical; they differ by the number of nitrate anions and the water molecules. The chainlike crystal structure is constituted by sandwich complexes linked via the coordination of the nitrogen atoms of the isonicotinate ligands to the silver atoms. The composition and structure of the sandwich complexes in **7**−**9** are the same for all three

Table 3. Crystal Data and Structure Refinement for Compounds **7**−**9**

	7	**8**	**9**
formula	$C_{132}H_{222}Ag_3N_{83}O_{116}La_4$	$C_{132}H_{207}Ag_3N_{80}O_{101}Pr_4$	$C_{132}H_{207}Ag_3N_{80}O_{101}Dy_4$
fw	5707.18	5418.03	5504.39
T (K)	150(2)	150(2)	150(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	33.812(3)	33.550(7)	33.275(7)
b (Å)	22.175(3)	22.231(4)	22.164(4)
c (Å)	29.278(5)	29.254(6)	29.204(6)
β (deg)	112.120(11)	111.53(3)	112.15(3)
V (Å^3)	20336(5)	20297(7)	19949(7)
Z	4	4	4
D_{calcd} (Mg/m^3)	1.864	1.773	1.833
no. of reflns collected	107676	72754	135919
no. of independent reflns	37446 [R(int) = 0.0208]	32514 [R(int) = 0.0337]	37718 [R(int) = 0.0247]
max. and min. transmission	0.9407 and 0.7899	0.7293 and 0.6284	0.9113 and 0.7034
GOF on F^2	1.057	1.394	1.357
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.0532, wR2 = 0.1102	R1 = 0.0490, wR2 = 0.0617	R1 = 0.0447, wR2 = 0.0628
R indices (all data)	R1 = 0.0903, wR2 = 0.1175	R1 = 0.0703, wR2 = 0.0653	R1 = 0.0672, wR2 = 0.0671

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $w = \sigma_F^{-2}$.

Table 4. The Bond Lengths (Å) in Lanthanide Core of Complexes **7**−**9**

	7	**8**	**9**
Ln−(μ_3-O)	2.426(4)−2.549(4)	2.384(3)−2.496(3)	2.293(3)−2.431(3)
Ln−(μ_2-O)	2.653(4)−3.037(4)	2.606(4)−2.957(4)	2.469(3)−2.973(3)
Ln−O (CB°)	2.513(4)−2.559(5)	2.472(3)−2.517(3)	2.395(3)−2.443(3)
Ln−O (IN@CB°)	2.471(4)−2.479(4)	2.421(3)−2.451(3)	2.327(3)−2.352(3)
Ln−O (IN)	2.462(4)	2.417(4)	2.308(3)
Ln−O (H_2O)	2.522(5)−2.567(4)	2.476(4)−2.535(3)	2.359(3)−2.419(3)
Ln···Ln	3.8864(6)−4.0946(9)	3.8185(8)−4.0153(9)	3.6697(8)−3.8723(8)

compounds independently of the structural type of starting compound. Therefore, only the structural description of **8**, representative of coordination polymers **7**−**9**, is presented. The bond lengths in the Ln_4 core are listed in Table 4.

As shown in Figure 9, the tetranuclear praseodymium complex is situated between two tetradentate CB[6] ligands. The structural type of the complex can be regarded as B (Scheme 2), in which one of the aqua ligands (at Pr(2) in Figure 9) is substituted by an oxygen atom belonging to the bridging isonicotinate ligand. This IN ligand links the neighboring sandwiches in a chain. The coordination of IN makes longer the Pr−(μ_2-OH) distance between the oxygen atom and the metal atom coordinated by IN (2.957(4) Å), whereas other Pr−(μ_2-OH) bond lengths lie in the range of 2.606(4)−2.790(3) Å. A similar prolongation of one of the La−(μ_2-OH) and Dy−(μ_2-OH) bonds is observed in complexes **7** and **9**. The coordination number for the Pr atoms is nine. Note that the coordination number for the Dy atoms in isostructural coordination polymer **9** is nine too, in spite of the fact that, in starting sandwich compound **3**, the dysprosium atoms are eight-coordinate. Both of the nitrogen atoms encapsulated into CB[6] isonicotinate ligands are coordinated by silver atoms. The silver atoms Ag(1) and Ag(2) are four-coordinate and have distorted tetrahedral coordination geometry. The bond distances and angles for Ag(1) and Ag(2) coordination environments in **8** are presented in Table 5. In addition to the IN ligand encapsulated into CB[6], each of the silver atoms is coordinated with two aqua ligands. The fourth position in the Ag(1) coordination sphere is occupied by the nitrogen atom N(1) of the terminal isonicotinic acid ligand. The coordination environment of Ag(2) is completed by the nitrogen atom N(4) of a bridging isonicotinate ligand. This IN ligand links neighboring sandwiches by coordination of a carboxylic oxygen atom to the lanthanide atom (Pr(2)) of the tetranuclear core, resulting in a zigzag chainlike structure of the compound (Figure 10). The chains $\{[Pr_4(\mu_3\text{-}OH)_4(\mu_2\text{-}OH)_4(H_2O)_3(IN@CB[6])_2\{Ag(H_2O)_2(HIN)\}\{Ag(H_2O)_2(IN)\}]^{3+}\}_\infty$ are arranged in the crystal structure of **8** along the b axis; the angle between two neighboring sandwiches in the chain is about 45°. These complexes are the first examples of a polynuclear lanthanide−silver heterometallic coordination polymer. For mononuclear lanthanide aqua complexes, only two recently published examples are known (Ln = Nd(III) and Eu(III)).[16] In these homochiral isostructural compounds, the Ag centers also have tetrahedral coordination geometry and are connected with the Ln atoms through the isonicotinate and acetonate ligands.

An interesting feature of the **7**−**9** crystal structures is the presence of silver complexes of the composition $[Ag(H_2O)_2(CB[6])]^+$ located between the chains (Figure 11). This is one of the rare examples[17] of the direct coordination of CB[6] portals by a transition metal. The coordination by s and f elements is more usual for CB[6] while the other metals are connected with CB[6] through the hydrogen bonds.[18] The silver atom is 0.353(2) Å below the mean plane of the six carbonyl oxygen atoms of the portal, and it is coordinated to three portal oxygen atoms with Ag−O distances of 2.501(3), 2.544(4), and 2.589(4) Å. Two water molecules are bound to the metal ion with distances of 2.565(3) and 2.348(4); one of them (the nearest one) is situated inside of the cavity. Thus, the silver atom has a slightly distorted pyramidal coordination environment with the oxygen atom of the encapsulated water molecule at the top of the pyramid.

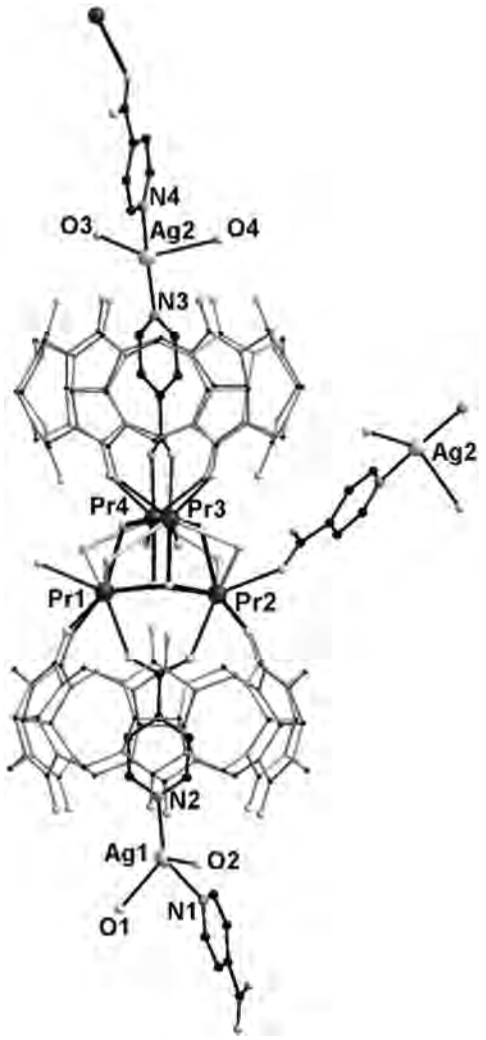

Figure 9. Fragment of the $\{[Pr_4(OH)_8(H_2O)_3(IN@CB[6])_2\{Ag(H_2O)_2(HIN)\}\{Ag(H_2O)_2(IN)\}]^{3+}\}_\infty$ chain in the structure of **8**. Hydrogen atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Ag(1) and Ag(2) Coordination Environments in **8**

Ag(1)−O(1)	2.398(5)	N(1)−Ag(1)−N(2)	135.39(17)
Ag(1)−O(2)	2.620(5)	O(1)−Ag(1)−O(2)	93.29(17)
Ag(1)−N(1)	2.235(6)	N(1)−Ag(1)−O(1)	88.83(19)
Ag(1)−N(2)	2.158(4)	O(1)−Ag(1)−N(2)	132.91(16)
Ag(2)−O(3)	2.546(4)	N(3)−Ag(2)−N(4)	156.41(17)
Ag(2)−O(4)	2.802(5)	O(3)−Ag(2)−O(4)	105.00(17)
Ag(2)−N(3)	2.123(5)	N(3)−Ag(2)−O(3)	102.80(17)
Ag(2)−N(4)	2.181(6)	O(3)−Ag(2)−N(4)	96.59(16)

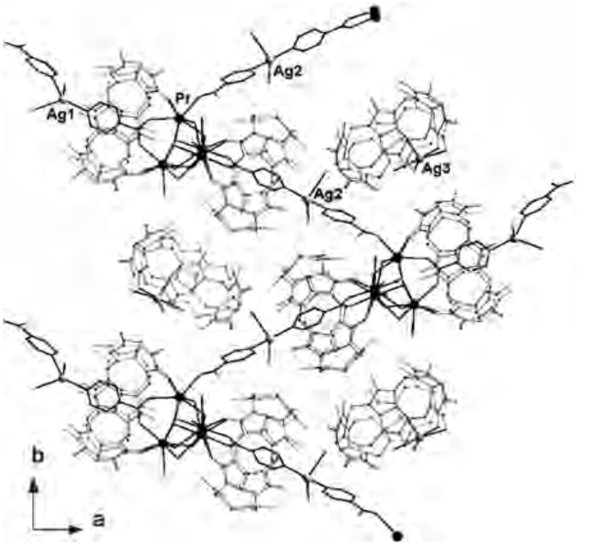

Figure 10. Crystal packing in the structure of **8** projected onto the *ab* plane. The water molecules of crystallization and the nitrate anions are omitted for clarity.

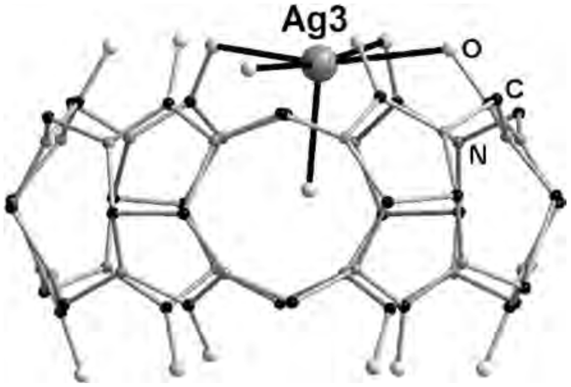

Figure 11. The structure of the $[Ag(H_2O)_2(CB[6])]^+$ complex in **8**. Hydrogen atoms are omitted for clarity.

Conclusions

In summary, sandwich-type tetranuclear lanthanide complexes with cucurbit[6]uril were synthesized under hydrothermal conditions from aqueous solutions of lanthanide(III) bromides, CB[6], and 4-cyanopyridine. The structural analysis of obtained compounds and the comparison with that for previously presented sandwich chloride and nitrate salts allow us to define a common sandwich fragment in their structures. It consists of the cubanelike $\{Ln_4(\mu_3\text{-}OH)_4\}^{8+}$ unit situated between two macrocyclic CB[6] molecules, and two chelate isonicotinate ligands are included into the CB[6] cavities. This sandwich fragment, $\{(IN@CB[6])Ln_4(\mu_3\text{-}OH)_4(IN@CB[6])\}^{6+}$, is invariable in the structures of all of the compounds independently of the lanthanide atom or counteranion in the structure. Coordination to the sandwich of additional hydroxo- or isonicotinate ligands allows for different structural types of complexes; four of them were revealed for the Ln_4 bromide salts. The sandwich fragments remain in aqua solution and can be transferred into the gas phase by electrospray. Photoluminescence emission from aqueous solutions of the Eu_4 sandwich complex is by a factor of ∼5 stronger than that of $EuCl_3$ or $EuBr_3$.

The bromide salts of tetranuclear lanthanide sandwich compounds proved to be promising precursors for the synthesis of coordination heterometallic polymers. We have successfully synthesized $Ln_4{-}Ag$ (Ln = La, Pr, and Dy) polymers constructed from sandwich complexes bonded in chains through the coordination of the silver atom to the nitrogen atom of the IN ligand. The sandwich fragment $\{(IN@CB[6])Ln_4(\mu_3\text{-}OH)_4(IN@CB[6])\}^{6+}$ remains in the coordination polymers. These results provide a perspective toward using sandwich compounds as building blocks in the design of heterometallic polylanthanide hydroxo-complex-based coordination polymers. We are also investigating the synthesis of compounds in which these sandwich species would be linked by other organic ligands with versatile coordination modes. The use of other transition metals could lead to 4f−3d mixed-metal functional materials with interesting magnetic and luminescence properties.

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Supporting Information Available: Figures 1S−5S, description of PLE spectra of **12**, FT-ICR mass spectra of **2** and **5**, IR spectra of **1**−**9**, and crystallographic data of **1**−**9** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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