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Uranyl-Lanthanide Heterometallic Complexes with Cucurbit[6]uril and Perrhenate Ligands

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The reaction of uranyl and lanthanide nitrates with cucurbit[6]uril (CB6) in the presence of perrhenic acid and under hydrothermal conditions yields the novel heterometallic uranyl-lanthanide molecular complexes $[UO_2Ln(CB6)(ReO_4)_2(NO_3)(H_2O)_7](ReO_4)_2$ (Ln = Sm, Eu, Gd, Lu). Both metal cations are bound to carbonyl groups of the same CB6 portal, one for UO_2^{2+} and two for Ln^{3+}. The uranium atom is also bound to one monodentate perrhenate ion and three aquo ligands, while the lanthanide is bound to one monodentate perrhenate and one nitrate ions, and four aquo ligands. Not only are these complexes rare examples of ReO_4^- bonding to f element ions, but the perrhenate bound to Ln is included in the CB6 cavity, thus providing the first case of inclusion of a tetrahedral oxoanion in this macrocycle.

Coordination complexes uniting uranyl and lanthanide ions in the same molecular unit are extremely rare, and the first examples, obtained under hydrothermal conditions with 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*′′,*N*′′′-tetraacetic acid (DOTA) and oxalato ligands, were reported only very recently.[1] In this case, the lanthanide ion (Gd or Eu) occupies the N_4O_4 site of the macrocycle, as usual, and the uranyl ion, bound to carboxylate oxygen atoms directed outward and to oxalate groups, connects the $[Ln(DOTA)(H_2O)]^-$ units to form a two-dimensional framework. Ligands that do not display two different coordination sites seem at first less suitable for the complexation of both of these cations, which present very different coordination geometry requirements (equatorial for uranyl and spherical for lanthanides). Attempts to use various polycarboxylic acids, for example, consistently give crystalline solids containing only the uranyl ion. Cucurbiturils (CBs) may not appear very promising to achieve this particular heterometallic coordination, although their lanthanide complexes have been much investigated,[2] and several uranyl complexes were recently described.[3] In the case of uranyl complexation in particular, a molecular capsule in which one portal of cucurbit[5]uril (CB5) is closed by a uranyl ion bound to the five oxygen donors could be isolated, as well as capsules closed by one uranyl ion on the one side and one alkali-metal ion on the other.[3b] It thus appeared tempting to try to replace the latter ion by a lanthanide, but, unfortunately, this resulted in lanthanide complexes only being obtained up to now with CB5. However, quite unexpectedly, uranyl-lanthanide heterometallic complexes could be synthesized from cucurbit[6]uril (CB6)[4] and crystallographically characterized.[5] These complexes comprise perrhenate ions as both ligands and counterions, resulting from the use of perrhenic acid as a useful reactant promoting CB dissolution without forming polymers with uranyl ions and CB molecules, in contrast to sulfuric acid.[3b]

Four isomorphous compounds of the general formula $[UO_2Ln(CB6)(ReO_4)_2(NO_3)(H_2O)_7](ReO_4)_2 \cdot 4H_2O$ with Ln = Sm (**1**), Eu (**2**), Gd (**3**), and Lu (**4**) were obtained. The asymmetric unit comprises one uranyl cation, one lanthanide cation, one CB6 unit, four perrhenate ions, one nitrate ion, and water molecules, both coordinated and free; complex **1** is represented in Figure 1. Both cations are bound to oxygen atoms of the same CB6 portal, uranium to only one donor and the lanthanide to two donors. The uranyl coordination sphere is completed by three aquo ligands and one perrhenate ion (the latter is possibly affected by some unresolved disorder, as suggested by the highest residual electron density peaks being located near the rhenium atom in all compounds). The U−O(CB6), U−O(ReO_4), and U−O(aquo) bond lengths

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averaged over all four complexes are 2.357(7), 2.379(6), and 2.391(18) Å, respectively. The former is in agreement with the values in previous uranyl complexes with monodentate CB6, which are in the range 2.337(6)−2.545(6) [mean value 2.41(7)] Å, and also with the values with pentadentate CB5, in the range 2.342(10)−2.421(18) [mean value 2.40(2)] Å.[3] Only four crystal structures with uranyl-bonded perrhenate ions are present in the Cambridge Structural Database (CSD, version 5.29),[6] with an average U−O bond length of 2.37(3) Å for terminal perrhenates, which matches the present value.[7] Uranyl perrhenates devoid of organic ligands have also recently been reported, with U−O bond lengths in the range 2.362(7)−2.433(9) Å.[8] The uranium coordination geometry in **1**−**4** is pentagonal-bipyramidal, with, curiously, the two bulkiest ligands in cis positions (with a possible intramolecular CH···O17 contact at 2.5−2.6 Å), and the equatorial plane (root-mean-square deviation 0.04−0.08 Å) is nearly perpendicular to the mean plane of CB6, with a dihedral angle of 82−87°. The lanthanide ion is bound to two adjacent carbonyl groups, as usual,[2] with average bond lengths of 2.393(2), 2.383(1), 2.373(1), and 2.303(5) Å for **1**−**4**, respectively. The values for Sm, Eu, and Gd are slightly smaller than the average values of 2.43(4), 2.39(6), and 2.38(4) Å, respectively, in previously characterized complexes.[2a−c,e] The Ln^{3+} cation is also bound to a perrhenate ion that is located in the CB6 cavity, with Ln−O bond lengths of 2.520(7), 2.504(7), 2.490(8), and 2.362(6) Å in **1**−**4**, displaying a linear variation that spans a larger range than that of the bonds with carbonyls. As in the case of uranyl, few examples of lanthanide-bonded

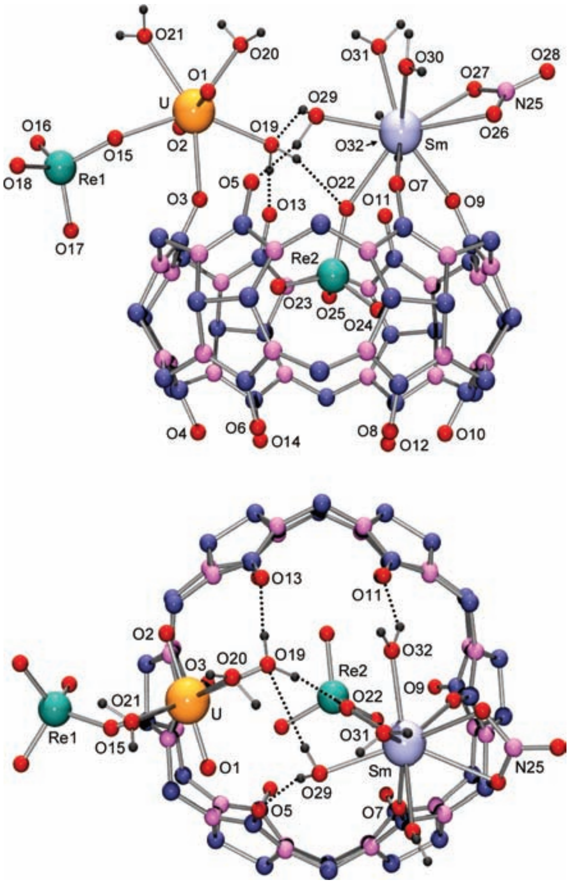

Figure 1. Two views of complex **1**. Counterions, solvent molecules, and carbon-bound hydrogen atoms are omitted. Atoms are represented as spheres of arbitrary radii. Hydrogen bonds are shown as dotted lines. Selected bond lengths (Å) and angles (deg): U−O1 1.757(8), U−O2 1.760(8), U−O3 2.369(7), U−O15 2.372(8), U−O19 2.403(7), U−O20 2.356(11), U−O21 2.388(10), U···Sm 5.9345(7), Sm−O7 2.395(7), Sm−O9 2.391(6), Sm−O22 2.520(7), Sm−O26 2.711(7), Sm−O27 2.543(7), Sm−O29 2.407(7), Sm−O30 2.465(6), Sm−O31 2.412(7), Sm−O32 2.394(7), Re1−O15 1.784(8), Re1−O16 1.690(7), Re1−O17 1.693(8), Re1−O18 1.704(8), Re2−O22 1.776(8), Re2−O23 1.709(8), Re2−O24 1.708(9), Re2−O25 1.709(8); O1−U−O2 177.9(4), O3−U−O15 72.9(3), O3−U−O19 68.6(3), O19−U−O20 72.2(4), O20−U−O21 72.5(5), O21−U−O15 74.1(4), Re1−O15−U 147.6(5), O7−Sm−O9 82.3(2), O7−Sm−O22 73.5(3), O9−Sm−O22 73.3(3), O26−Sm−O27 48.5(2), Re2−O22−Sm 151.6(5).

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(4) Synthesis of **1**: CB6·5H_2O (30 mg, 0.028 mmol), $UO_2(NO_3)_2$·6H_2O (28 mg, 0.056 mmol), $Sm(NO_3)_3$·6H_2O (25 mg, 0.056 mmol), $HReO_4$ (76.5% solution in water, 70 mg, 0.279 mmol), and demineralized water (1.4 mL) were placed in a 15 mL tightly closed glass vessel and heated at 180 °C under autogenous pressure (ca. 1.1 MPa), yielding colorless/light-yellow crystals of complex **1** within 5 days (18 mg, 24% yield on the basis of CB6). Anal. Calcd for $C_{36}H_{58}N_{25}O_{44}Re_4SmU$: C, 16.15; H, 2.18; N, 13.08. Found: C, 16.43; H, 2.31; N, 13.21. Compounds **2**−**4** were obtained under similar conditions from the corresponding lanthanide salts, with yields of 33 and 27% for **2** and **3**, respectively, and only a small quantity of crystals for **4**. Anal. Calcd for $C_{36}H_{58}EuN_{25}O_{44}Re_4U$ (**2**): C, 16.14; H, 2.18; N, 13.07. Found: C, 16.27; H, 2.28; N, 13.12. Anal. Calcd for $C_{36}H_{58}GdN_{25}O_{44}Re_4U$ (**3**): C, 16.10; H, 2.18; N, 13.04. Found: C, 16.27; H, 2.30; N, 13.12.

(5) Crystallographic data were collected at 100(2) K on a Nonius Kappa CCD area detector diffractometer[12] and processed with HKL 2000.[13] Absorption effects were corrected with SCALEPACK.[13] The structure of **3** was solved by direct methods and used as a starting point for the other structures. All were refined by full-matrix least squares on F^2 with *SHELXTL*.[14] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen atoms were found on a Fourier difference map, except for those of one aquo ligand in **3** and **4** and one solvent water molecule in all cases. The carbon-bound hydrogen atoms were introduced at calculated positions. The highest residual electron density peaks are located near rhenium atoms and may be indicative of unresolved disorder. The drawings were done with ORTEP-3/POV-Ray.[15] Crystal data for **1**: $C_{36}H_{58}N_{25}O_{44}Re_4SmU$, $M = 2678.25$, monoclinic, space group $P2_1/n$, $a = 12.3227(2)$ Å, $b = 25.4575(8)$ Å, $c = 20.8405(7)$ Å, $\beta = 90.738(2)°$, $V = 6537.2(3)$ Å^3, $Z = 4$. Refinement of 1000 parameters on 12 373 independent reflections out of 146 088 measured reflections ($R_{int} = 0.035$) led to R1 = 0.046, wR2 = 0.124, $S = 1.035$, $\Delta\rho_{min} = -2.31$, and $\Delta\rho_{max} = 3.83$ e Å^{-3}. Crystal data for **2**: $C_{36}H_{58}EuN_{25}O_{44}Re_4U$, $M = 2679.86$, monoclinic, space group $P2_1/n$, $a = 12.3179(3)$ Å, $b = 25.4574(8)$ Å, $c = 20.8257(7)$ Å, $\beta = 90.794(2)°$, $V = 6529.9(3)$ Å^3, $Z = 4$. Refinement of 1000 parameters on 12 383 independent reflections out of 176 827 measured reflections ($R_{int} = 0.050$) led to R1 = 0.044, wR2 = 0.112, $S = 1.048$, $\Delta\rho_{min} = -6.59$, and $\Delta\rho_{max} = 2.67$ e Å^{-3}. Crystal data for **3**: $C_{36}H_{58}GdN_{25}O_{44}Re_4U$, $M = 2685.15$, monoclinic, space group $P2_1/n$, $a = 12.3177(5)$ Å, $b = 25.4330(5)$ Å, $c = 20.8372(8)$ Å, $\beta = 90.859(2)°$, $V = 6527.1(4)$ Å^3, $Z = 4$. Refinement of 1000 parameters on 12 351 independent reflections out of 153 063 measured reflections ($R_{int} = 0.089$) led to R1 = 0.049, wR2 = 0.136, $S = 1.041$, $\Delta\rho_{min} = -1.22$, and $\Delta\rho_{max} = 3.29$ e Å^{-3}. Crystal data for **4**: $C_{36}H_{58}LuN_{25}O_{44}Re_4U$, $M = 2702.87$, monoclinic, space group $P2_1/n$, $a = 12.2658(4)$ Å, $b = 25.7983(9)$ Å, $c = 20.5848(8)$ Å, $\beta = 90.627(2)°$, $V = 6513.4(4)$ Å^3, $Z = 4$. Refinement of 1000 parameters on 12 334 independent reflections out of 145 913 measured reflections ($R_{int} = 0.063$) led to R1 = 0.037, wR2 = 0.098, $S = 1.016$, $\Delta\rho_{min} = -4.54$, and $\Delta\rho_{max} = 1.63$ e Å^{-3}.

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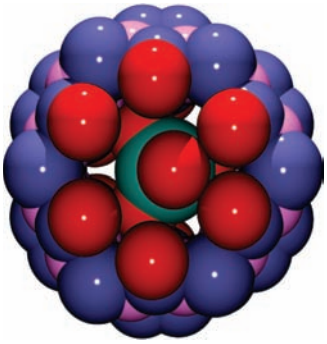

Figure 2. Spacefill representation of perrhenate inclusion in the CB6 cavity in complex **1**. The uranium and samarium atoms are omitted.

perrhenates have been reported up to now.[9] Although this is the first occurrence of perrhenate encapsulation in a CB, other instances of second-sphere inclusion of coordinated anions such as chloride, nitrate, or isonicotinate have been reported.[2f−i] The lanthanide coordination sphere in **1**−**3** is completed by one asymmetric bidentate nitrate ion and four aquo ligands, giving a nine-coordinate environment of capped square-antiprismatic geometry with the sets of atoms O7, O9, O27, O30 and O22, O29, O31, O32 defining the two faces (dihedral angle 3.58−3.89°) and O26, associated with the largest bond length, in the capping position. In complex **4**, the nitrate ion is monodentate and the coordination polyhedron is a square antiprism.

The two metal cations are thus held side-by-side on the same CB6 portal and are separated by one (O5) or two (O11 and O13) uncoordinated carbonyl groups. The resulting species is strongly asymmetric, but the macrocycle does not show severe distortion; it may, however, be noted that, in the complexed portal, the O···O distances are alternately long (3.60−3.87 Å) and short (3.02−3.36 Å), with the shortest distance, between the chelating atoms O7 and O9, decreasing from 3.15 Å for Sm to 3.02 Å for Lu. The uncomplexed portal is less distorted, with O···O distances in the range 3.23−3.67 Å. The included perrhenate anion is oriented so that the three uncoordinated oxygen atoms are pointing toward three groups of methylene bridges of CB6, which is possibly the origin of the slight trigonal distortion of the latter. As can be seen in Figure 2, ReO_4^- fits snugly in the macrocycle cavity while being inclined so that the coordinating atom O22 is close to O7 and O9, with these three atoms building a tripod on which the lanthanide is nestled. The aquo ligands are involved in hydrogen bonds, both intra- and intermolecular, as usual in such complexes, but no significant intercucurbituril CH···O hydrogen bonds are observed in the packing.

Up to now, these heterobimetallic complexes could be isolated reproducibly for lanthanide ions in the middle and end of the 4f series (although a mixture with lanthanide-only complexes was obtained in some experiments), but repeated attempts with lighter cations (Ce, Pr, and Nd) gave only the lanthanide complexes as crystals, which display a wide range of structures and will be reported elsewhere. A more thorough investigation with varying experimental conditions and/or in solution would be required to clarify this point, which may be indicative of a size effect.

In summary, the complexes reported herein present several different elements of novelty. They constitute only the second group of uranyl-lanthanide heterometallic complexes ever characterized, while differing from the first examples by the absence of different coordination sites, thus opening novel perspectives for the search of suitable ligands, not necessarily heterofunctional, that may give materials interesting for their luminescence properties. Further, they provide novel cases of bonding of the weakly coordinating perrhenate anions to both uranyl and lanthanide cations, which remains a very rare occurrence. This is of interest in the field of nuclear waste reprocessing because ReO_4^- is analogous to the pertechnetate ion TcO_4^-, which contains the long-lived β-emitter ^{99}Tc and is known to be coextracted with UO_2^{2+}.[7,10] The examples of perrhenate complexation to uranyl previously reported involve the additional ligands triphenylphosphine oxide,[7a] tri-*n*-butylphosphine oxide, and triisobutyl phosphate[7c] or bis(diphenylphosphino)methane dioxide,[7b] and the present complexes are thus the first with a ligand that does not contain the P=O functionality. Particularly notable is the replacement of nitrate by perrhenate in the coordination sphere of both cations, complete for uranium and partial only for lanthanides, because the PUREX (Plutonium-URanium EXtraction) process involves dissolution of the irradiated nuclear fuel in nitric acid (in previous studies, uranium trioxide UO_3 was reacted with $HReO_4$ to give $UO_2(ReO_4)_2 \cdot H_2O$, further used as a starting material, so that no other anion was present[7]). Last, these complexes are the first examples of inclusion of a group VII oxoanion, and more generally of a tetrahedral anion, in CBs, which confirms the potential of these macrocycles as anion complexants.[2f,g] Considering the interest in finding sequestering agents for these oxoanions,[11] this finding deserves further exploration.

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

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