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Crystal structure determination of 4f–5f heterometallic complexes

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The reaction of $[UO_2Cl_4]^{2-}$ with *t*Bu-calix[6]arene (H_6L) in the presence of lanthanum triflate in pyridine leads to the formation of $[U\{(H_2L)LaCl_2(NC_5H_5)_4\}_2]$ (1); in the course of the reaction, the uranyl cations (UO_2^{2+}) are transformed into U(+VI) alkoxides (1) and "UO_6" oxides at the centre of the decametallic cluster $[ULa_9O_8Cl_{15}(O_3SCF_3)_6(NC_5H_5)_9]^{4-}$ (2); complexes 1 and 2 are the first 4f–5f heterometallic complexes to be reported.

From a coordination chemistry point of view, the parent unsubstituted calixarenes can be considered as large flexible polyalkoxide ligands which size and flexibility vary with the number of their phenolic units.[1] The potential of this class of macrocycles for the design of new metal complex architectures is fascinating, especially if their numerous binding sites can be used to coordinate several metal centres on the same ligand or to stabilise polymetallic species.[2] An interesting feature of calixarenes is the possibility of directing their reactivity towards transition metals by the addition of alkali metal ions to the reaction mixture.[3] For example, the addition of caesium is necessary to make *t*Bu-calix[6]arene (H_6L) react with $[UO_2Cl_4]^{2-}$.[4] In order to test whether a similar influence was to be observed from the addition of other types of metals, we decided to study the effect of a lanthanide cation on the same reaction. We report herein the spectacular influence of La^{3+} on the coordination of H_6L towards uranyl that leads to the formation of $[U\{(H_2L)LaCl_2(NC_5H_5)_4\}_2]$ (**1**). In the course of the reaction, the U=O bond is activated and the uranyl cations (UO_2^{2+}) are been transformed into U(+VI) alkoxides (**1**) and "UO_6" oxides at the centre of the decametallic cluster $[ULa_9O_8Cl_{15}(O_3SCF_3)_6(NC_5H_5)_9]^{4-}$ (**2**). Complexes **1** and **2** are the first 4f–5f heterometallic complexes to be reported.†

When $[HNC_5H_5]_2[UO_2Cl_4]$ was treated with H_6L in pyridine, no reaction was observed.[4] Likewise, $[HNC_5H_5]_2[UO_2Cl_4]$ remained inert upon addition of $[La(O_3SCF_3)_3]$ to its pyridine solution.[5] However, when even small amounts of $[La(O_3SCF_3)_3]$ were added to the mixture of $[HNC_5H_5]_2[UO_2Cl_4]$ and H_6L in pyridine at room temperature, the pale yellow colour immediately changed to a deep red. The solution was allowed to stand and after 30 days, red crystals suitable for X-ray crystallography were obtained, amongst other reaction products. The structure was solved and revealed that the lanthanum–uranium heterotrimetallic complex $[U\{(H_2L)LaCl_2(NC_5H_5)_4\}_2]$ (**1**) had been produced by the reaction (Fig. 1).‡ **1** is a trimetallic complex organised around a U(+VI) centre that is coordinated by two calixarenes in a 1,2,3-alternate conformation. The two macrocycles bind the actinide cation through three adjacent phenolate groups of one of their half cones. Formally speaking **1** is a uranium hexa-alkoxide reminiscent of the complex $[U(H_3L)_2]$ formed by the reaction of UCl_4 and H_6L.[6] Compared to $[U(H_3L)_2]$, each macrocycle in **1** is further coordinated to a lanthanum cation through the central phenolate group of its second half cone. The coordination sphere of the lanthanide is completed by two chlorides and three pyridine molecules. The pyridine bearing N(1D) is included in the half cone designed by the phenolic faces of O(1), O(2) and O(6), thus the calixarene is both a first and second sphere ligand of the lanthanide cation.[7] The coordination geometries around the metal centres are a distorted octahedron for the actinide and a distorted pentagonal bi-pyramid for the lanthanide. *t*Bu-calix[6]arene in **1** is a bridging ligand acting as a chelating tridentate ligand on one side and a unidentate ligand on the other. This new binding feature further expands the versatility and potential of calix[6]arenes as metal receptors.

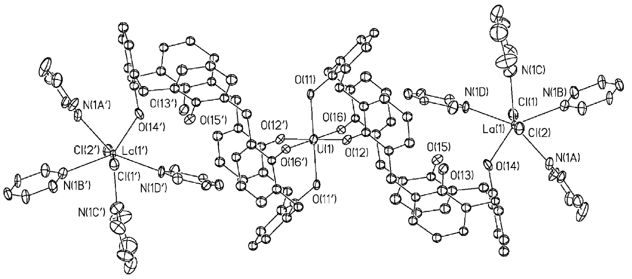

Fig. 1 Molecular structure of compound **1** (ellipsoids drawn at the 15% probability level). The uranium atom lies on an inversion centre. All *t*Bu groups and hydrogen atoms or solvent molecules have been omitted for clarity. Selected bond lengths (Å): U–O 2.12(3), La–O 2.258(5), La–N 2.51(7), La–Cl 2.57(2).

The formation of **1** implies that at least some of the $[UO_2]^{2+}$ has been fully deoxygenated in the course of the reaction to form the U(+VI) cation. Such examples of the activation of the two very strong U=O double bonds of the uranyl unit are scarce in the literature. To the best of our knowledge they have only been reported in the reduction of UO_2Cl_2 by means of NaS_2PMe_2 and in the synthesis of $[UO(O\textit{t}Bu)_4]$.[8] Interestingly, the possibility of the direct transformation of UO_2Cl_2 into uranium hexa-alkoxides by use of thermal disproportionation was also mentioned by Bradley and co-workers as early as 1959.[9] In the absence of any traces of water, pyridine *N*-oxide or decomposed H_6L in the NMR spectra of the reaction mixture from which **1** was isolated, we came to the conclusion that some sort of uranium oxide had to be formed in order to balance the deoxygenated U(+VI). In order to grow single crystals from the otherwise insoluble reaction products, the synthesis of **1** was repeated in diluted conditions.[10] The solution was allowed to stand at room temperature and after 180 days, colourless crystals suitable for X-ray crystallography were isolated amongst those of **1** and some unreacted $[HNC_5H_5]_2[UO_2Cl_4]$ and H_6L.[11] The crystal structure was solved, revealing $[ULa_9O_8Cl_{15}(O_3SCF_3)_6(NC_5H_5)_9]^{4-}$ (**2**);§ a heterodecametallic mixed uranium–lanthanum oxide (Fig. 2). The charge and stoichiometry of **2** was unequivocally confirmed by the presence of four pyridinium cations in the lattice.

2 is organised around a "UO_6" moiety where the uranium centre sits on the C_2 axis of symmetry that also passes through La(1), N(1) and Cl(1) (Fig. 3). The arrangement of the donor atoms around the actinide cation is a distorted trigonal prism. All six O^{2-} ligands coordinated to uranium have a tetrahedral coordination geometry and further bind three lanthanum cations. The latter are of two sorts; the cations of the first group [La(1), La(3) and La(3′)] are coordinated by two μ_4-O^{2-} ligands of the "UO_6" centre and by four μ-Cl^- and a pyridine molecule; those of the second group [La(2), La(4), La(5) and their symmetry equivalents] are coordinated by two μ_4-O^{2-} ligands of the "UO_6" centre but also by one almost planar μ_3-O^{2-} [O(4)]

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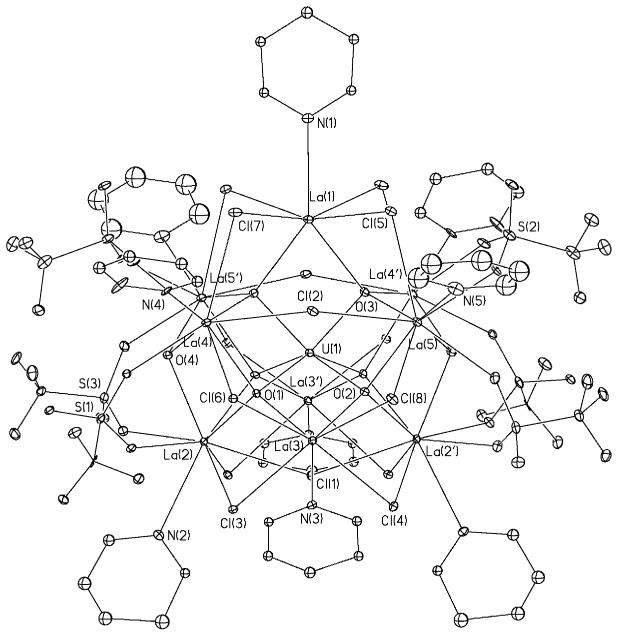

Fig. 2 Molecular structure of compound **2** (ellipsoids drawn at the 10% probability level). All hydrogen atoms or solvent molecules have been omitted for clarity. Selected mean bond lengths (Å): U–O 2.18(2), La–O 2.45(5), La–O(triflate) 2.58(1), La–N 2.75(3), La–Cl 2.95(6).

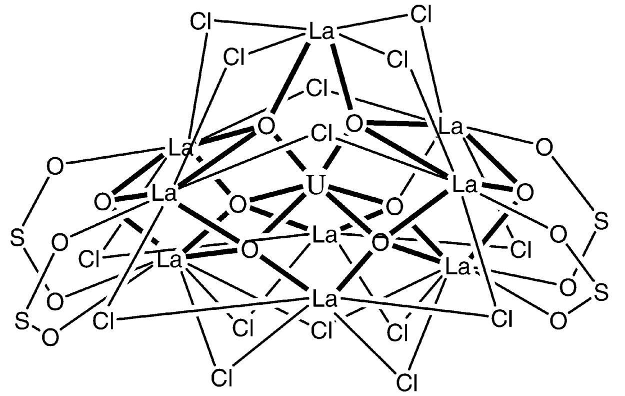

Fig. 3 Simplified molecular structure of the polymetallic core of **2**.

that binds three lanthanide cations in a triangular fashion, three μ-Cl$^-$, two bridging triflate group and a pyridine molecule: The first group has a coordination number of seven and the second of nine; the respective coordination geometry being a capped and a tricapped trigonal prism. **2** is a large molecular object that resembles a sphere with a diameter of about 2 nanometers. The synthesis of high-nuclearity aggregates of lanthanide cations is a challenge for coordination chemists. There are only a few reports in the literature of clusters containing nine or more f-metals as in **2**.[12] Much larger polyoxometalates have been described for the d-metals.[13]

In conclusion, we have demonstrated the spectacular influence of the lanthanum cation on the reaction of H_6L towards $[UO_2Cl_4]^{2-}$. The U=O bond has been activated at room temperature affording **1** and **2**: the first 4f–5f heterometallic complexes to be reported. The syntheses of **1** and of the previously reported $[Cs][UO_2Cl_2]_2[H_2L]$,[4] show that the coordination of a calixarene can be forced onto uranium by means of ligand exchange reactions. The work presented in this contribution further reinforces the idea that a rich chemistry can be developed at the boundary between macrocycle, supramolecular and coordination chemistries.[14]

Notes and references

† General: All experiments were carried out in a glove box under dried N_2. Pyridine was dried over K (**CAUTION!**) and distilled prior use.

Synthesis of **1** and **2**: $[HNC_5H_5]_2[UO_2Cl_4]$ (0.200 g, 0.349 mmol) was treated with H_6L (0.136 g, 0.140 mmol) at room temperature in pyridine (10 mL). $[La(O_3SCF_3)_3]$ (0.451 g, 0.770 mmol) was added to the pale yellow solution and its colour immediately changed to a deep red. After 48 hours the mixture was filtered and left standing at room temperature for several days. The easily recognisable red crystals of **1** were physically separated from the colourless needles of **2** and from unreacted $[HNC_5H_5]_2[UO_2Cl_4]$ and H_6L.[11] For **1** and **2** the approximate recovered yield was 10%.[15] ^{1}H NMR ([D$_5$]pyridine) for complex **1**: δ 7.022 (br., 24 H, ArH), 4.24, 3.67, 3.02 (d, $J = 15$ Hz, 3 × 8 H, Ar–CH$_2$–Ar), 1.14 (18H, *t*Bu), 1.06, 0.96 (2 × 36 H, *t*Bu), 0.76 (18 H, *t*Bu).

‡ Crystal data for $\mathbf{1}\cdot19(NC_5H_5)$: $C_{267}H_{295}Cl_4La_2N_{27}O_{12}U$, $M = 4731.95$), $0.12 \times 0.12 \times 0.12$ mm^3, triclinic, $P\bar{1}$, $Z = 1$, $a = 15.646(3)$, $b = 16.759(3)$, $c = 23.203(5)$ Å, $\alpha = 89.79(3)$, $\beta = 79.67(3)$, $\gamma = 87.41(3)°$, $V = 5979(2)$ Å^3, $\rho_{calc} = 1.314$ g cm^{-3}, $F(000) = 2456$, $2\theta_{max} = 51.26°$, graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), $\mu_{Mo} = 1.137$ cm^{-1}, $T = 100$ K. The structure was solved by direct methods[16] and refined on F^2.[17] Of the 26187 reflections measured, 17157 were found to be independent ($R_{int} = 0.133$), 7013 of which were considered as observed [$I > 2\sigma(I)$]. All reflections were used in the refinement of the 709 parameters, leading to a final R_1 of 0.1180 and a R_{all} of 0.2744. wR_{obs} and wR_2 were respectively equal to 0.2305 and 0.3085. The goodness-of-fit parameter S was 1.021 and the maximum residual density 1.076 e Å^{-3}.

§ Crystal data for $[H(NC_5H_5)_2]_2[HNC_5H_5]_2[\mathbf{2}]\cdot3(NC_5H_5)$: $C_{96}H_{94}Cl_{15}F_{18}La_9N_{18}O_{26}S_6U$, $M = 4470.22$, $0.10 \times 0.08 \times 0.06$ mm^3, monoclinic, $C2/c$, $Z = 4$, $a = 19.865(4)$, $b = 29.031(6)$, $c = 25.276(5)$ Å, $\beta = 99.33(3)°$, $V = 14384(2)$ Å^3, $\rho_{calc} = 2.064$ g cm^{-3}, $F(000) = 8488$, $2\theta_{max} = 51.44°$, graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), $\mu_{Mo} = 4.187$ cm^{-1}, $T = 100$ K. The structure was solved by direct methods[16] and refined on F^2.[17] Of the 22931 reflections measured, 12517 were found to be independent ($R_{int} = 0.113$), 5874 of which were considered as observed [$I > 2\sigma(I)$]. All reflections were used in the refinement of the 623 parameters, leading to a final R_1 of 0.0586 and a R_{all} of 0.1636. wR_{obs} and wR_2 were respectively equal to 0.0890 and 0.1163. The goodness-of-fit parameter S was 0.909 and the maximum residual density 1.036 e Å^{-3}. CCDC reference numbers 151550 and 151551. See http://www.rsc.org/suppdata/dt/b2/b200199n/ for crystallographic data in CIF or other electronic format.

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5 In this case, some degree of ligand exchange between the metals should not be neglected. However, the major part of the uranyl salt could be recovered and microcrystals of **2** were never isolated from this reaction.
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10 An NMR tube was charged with 0.005 g of H_6L in pyridine (10 mL). One equivalent of $[HNC_5H_5]_2[UO_2Cl_4]$ and two of $[La(O_3SCF_3)_3]$ were added. The tube was allowed to stand at room temperature and after 180 days, crystals of **2** suitable for X-ray crystallography could be recovered.
11 No matter what stoichiometry was used for the reaction (including a large excess of $[La(O_3SCF_3)_3]$), some unreacted $[HNC_5H_5]_2[UO_2Cl_4]$ and H_6L were always recovered along with **1** and **2** (easily recognisable from the measurement of the crystal cell of the microcrystals) at the end of the reaction. The presence of the unreacted material prevented the isolatation of the very unstable heterometallic complexes in their elementally pure form. Furthermore, the repeated FAB and electro-spray mass analysis performed on freshly prepared samples only afforded peaks corresponding to degradation products of high molecular weight.
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14 The formation of red coloured complexes is also observed upon addition of the triflate salts of Sm, Yb, Ba to the mixture of $[HNC_5H_5]_2[UO_2Cl_4]$ and H_6L. Microcrystalline powders have been obtained but no monocrystals suitable for an X-ray analysis or analytically pure samples of these very unstable compounds have yet been isolated.

15 The formation of microcrystals of **1** could also be observed when $[U(H_3L)_2]$ was mixed with $LaCl_3$ in NMR tube scale reactions.[6]

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