Bulky cation and four different polyiodide anions in [Lu(Db18c6)(H2O)3(Thf)6]4(I3)2(I5)6(I8)(I12)
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$$[\text{Lu(Db18c6)(H2O)3(Thf)6}]_{4}(\text{I3})_{2}(\text{I5})_{6}(\text{I8})(\text{I12})$$

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**SHORT COMMUNICATION**

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**Bulky cation and four different polyiodide anions in**

\[ \text{[Lu(Db18c6)(H}_2\text{O})_2\text{(Thf)}_4\text{I}_7\text{(I}_3\text{)}_2\text{(I}_5\text{)}_6\text{(I}_8\text{)}\text{(I}_12\text{)}_2]^{3-} \]

Christine Walbaum,\textsuperscript{[a]} Ingo Pantenburg,\textsuperscript{[a]} Peter Junk,\textsuperscript{[b]} Glen B. Deacon,\textsuperscript{[b]} and Gerd Meyer\textsuperscript{[a]}*

**Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of his 65th Birthday**

**Keywords:** Bulky cation; Crown ether; Crystal structure; Lutetium; Polyiodides

Black single crystals of \([\text{Lu(Db18c6)(H}_2\text{O})_2\text{(Thf)}_4\text{I}_7\text{(I}_3\text{)}_2\text{(I}_5\text{)}_6\text{(I}_8\text{)}\text{(I}_12\text{)}_2]^{3-}\) were obtained from Lu, I$_2$, and Db18c6 (dibenzo-18-crown-6) in Thf solution. In the bulky cation, Lu$^{3+}$ is surrounded by nine oxygen atoms, six of Db18c6 and three of water molecules to which two Thf are attached each. Meanwhile, four polyiodide anions, (I$_2$)$_3$, (I$_3$)$_2$, (I$_5$)$_6$, and (I$_8$)$_2$ and (I$_{12}$)$_2$, in a 2:6:1:1 ratio form a three-dimensional network and leave space for the bulky cations.

**Results and Discussion**

The reaction of elemental lutetium and iodine in Thf followed by the addition of dibenzo-18-crown-6 (Db18c6) resulted in a solution from which black single crystals of [cation]$^{3+}$[I$_{12}$]$^{3-}$ grew after a prolonged period of time.\textsuperscript{[5]} A crystal structure determination reveals that this simple formula needs to be rewritten as follows, [Lu(Db18c6)(H$_2$O)$_2$(Thf)$_4$I$_7$(I$_3$)$_2$(I$_5$)$_6$(I$_8$)(I$_{12}$)$_2$].

![Figure 1](image-url) The cation [Lu(Db18c6)(H$_2$O)$_2$(Thf)$_4$I$_7$]$^{3+}$ in the crystal structure of 1.

The bulky cation [Lu(Db18c6)(H$_2$O)$_2$(Thf)$_4$I$_7$]$^{3+}$ (Fig. 1) consists of a central Lu$^{3+}$ cation surrounded by six oxygen atoms of Db18c6 and three water molecules in a tristar-like arrangement, a motif reminiscent of that seen in the simple molecular structure of [Sm(Db18c6)I$_3$].\textsuperscript{[6]} The Lu-O distances range from 226 to 255 pm (Db18c6) and 220-231 pm (water). Coordination numbers of (about) nine seem to be typical for crown ether—lanthanide(III) complexes, as is also attested by similar coordination environments in...
The asymmetric unit contains 28 iodine atoms which are arranged, the centre of symmetry of space group P21/c taken into account, in a fashion that Fig. 2 depicts.

The triiodide anion, \((I_3)^-\), is slightly asymmetric and almost linear (I25-I26: 287.7(11), I26-I27: 177.5(4); all distances here and in the following are given in units of picometres, pm, and angles in degrees). Through a long distance of 383.4(15) pm (I25-I11) it is weakly connected to one of the pentaiodide anions.

The crystal structure contains three crystallographically independent V-shaped pentaiodide anions, \((I_5)^-\), of the form \([I_2−I−I_2]−\) with typical bond distances and angles. These are for \#1: I1-I2: 280.8(13), I2-I3: 306.8(15), I3-I4: 315.7(14), I4-I5: 273.7(13), I1-I2-I3: 177.5(4), I2-I3-I4: 91.6(1), I3-I4-I5: 174.9(1); #2: I11-I12: 284.5(11), I12-I13: 305.2(14), I13-I14: 310.9(14), I14-I15: 279.7(14), I11-I12-I13: 177.9(4), I12-I13-I14: 102.0(3), I13-I14-I15: 177.2(4); #3: I10-I11: 275.9(14), I11-I12: 317.9(14), I12-I13: 308.0(10), I13-I14: 280.4(11), I12-I13-I14: 174.6(1), I12-I13-I14: 84.0(1), I12-I13-I14: 174.4(1). Two of the \(I_5^-\) anions may be seen as being connected via distances of 360.1(15) (I11-I15) to dimers. The third \(I_5^-\) anion shows a distance in the same range (I20-I18: 362.2(15)) to the octaiodide anion.

The centrosymmetric octaiodide anions, \((I_8)^2^-\) = \([I_2−I−I_2]^−\) are Z-shaped and show bond distances and angles that are comparable to similar compounds. The reaction mixture was stirred over night at room temperature. A black solution was separated from a red precipitate via a filter canula. To the black solution dibenzo-18-crown-6 (0.11 g, 0.3 mmol) was added causing the immediate precipitation of a brown solid. The reaction mixture was filtered and, after a few weeks, black polyhedral crystals grew from the mother liquor, a reason why we cannot report analytical data.

**Figure 2.** The four different polyiodide anions in the crystal structure of [Lu(Db18c6)(H2O)3(Thf)12][I3][I5][I6][I12], with their atomic numbering scheme. Atoms that do not belong to the asymmetric unit are drawn in a lighter pink.

**Figure 3.** A space-filling model of the anionic polyiodide network, in which the bulky cations fit clearly well, in the unit cell of 1 projected along [010].

**Conclusions**

The reaction of lutetium metal and elemental iodine in Thf with the addition of Db18c6 resulted in black single crystals of [Lu(Db18c6)(H2O)3(Thf)12][I3][I5][I6][I12] with both an unusual cation coordination and four different polyiodide anions forming a three-dimensional network in which the large cations are encapsulated.

**Experimental Section**

**Synthesis of 1:** Iodine (1.13 g, 4.5 mmol) and 20 mL Thf were added to a Schlenk flask under a nitrogen atmosphere which already contained lutetium powder (0.18 g, 1 mmol). The reaction mixture was stirred overnight at room temperature. A black solution was separated from a red precipitate via a filter canula. To the black solution dibenzo-18-crown-6 (0.11 g, 0.3 mmol) was added causing the immediate precipitation of a brown solid. The reaction mixture was filtered and, after a few weeks, black polyhedral crystals grew from the filtrate. These are very sensitive and loose Thf and iodine when taken out of the mother liquor, a reason why we cannot report analytical data other than the crystal structure.
Single crystals of 1 were selected from the mother liquor and were mounted on a glass fibre in silicone oil. The crystal quality was checked on a single-crystal X-ray diffractometer (Bruker X8 APEX II CCD) and a complete intensity data set was collected using graphite-monochromated Mo-Kα radiation (λ= 71.073 pm). The data set was corrected for absorption (SADABS), then merged to 25697 unique reflections using the Bruker Apex II program suite.[11] Further programs used are the WinGX suite of programs,[12] including SIR-92[13] and SHELXL-97[14] for structure solution and refinement. The last refinement cycles included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms. The positions of the hydrogen atoms were calculated with the riding model and their isotropic thermal parameter fixed to be 1.2 times that of the parent atom.

Crystallographic data for the crystal structure of 1 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 767937. Copies of the data can be obtained, free of charge, on application to CHGC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Crystal data for 1: \( \text{C}_3\text{H}_{15}\text{I}_3\text{La}_4\text{Lu}_4\text{O}_{60} \), 11194.54 g mol\(^{-1}\); diffractometer Bruker X8 APEX II CCD, \( T = 123(2) \text{K} \); 2\( \theta \)\(_{\text{max}}\) = 50.00°; one \( \varphi \)- and two \( \omega \)-scans, 704 images; \( -13 \leq h \leq 13, -17 \leq k \leq 17, -16 \leq l \leq 16 \); \( \rho_{\text{calc}} = 2.477 \text{ g cm}^{-3} \); 16270 measured reflections of which 3807 were symmetrically independent; \( R_{\text{int}} = 0.0478 \); \( F(000) = 10200 \); \( \mu = 7.123 \text{ mm}^{-1} \).

Monoclinic, \( P2_1/c \) (no. 14), \( a = 2132.80(8), b = 2871.52(9), c = 2658.64(9) \text{ pm}, \beta = 112.792(2)^\circ \); \( V = 15011.1(9) \text{ pm}^3 \); \( Z = 2 \); R values: \( R_{\text{wp}}/R_{\text{wp}} \) for 3699 reflections with \( |I| > 2\sigma(I) \): 0.0999 / 0.2159, for all data: 0.1012 / 0.2156; \( S_{\text{all}} = 1.227 \).

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