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

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

Christine Walbaum,^[a] Ingo Pantenburg,^[a] Peter Junk,^[b] Glen B. Deacon,^[b] and Gerd Meyer^{[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 [Lu(Db18c6)(H₂O)₃(Thf)₆]₄(I₃)₂(I₅)₆(I₈)(I₁₂) were obtained from Lu, I₂ and Db18c6 (dibenzo-18-crown-6) in Thf solution. In the bulky cation, Lu³⁺ 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, (I₃)⁻, (I₅)⁻, (I₈)²⁻ and (I₁₂)²⁻, in a 2:6:1:1 ratio form a three-dimensional network and leave space for the bulky cations.

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Introduction

The vast majority of polyiodides are triiodides. These can easily be made deliberately by the addition of elemental iodine to solutions which contain iodide anions and an appropriate cation. The triiodide anion, I₃⁻, is a linear 22 electron species (sometimes slightly bent due to packing effects) with three-centre-four-electron bonding obeying the Gillespie-Nyholm VSEPR concept; it is, therefore, a species in its own right. Higher polyiodide assemblies are loose connections between iodide, iodine and triiodide and may be put together, on paper, in a construction-kit manner. However, their distinction is not always beyond arbitrariness, often a matter of taste and follows selfmade rules, mostly based on distances.

Nevertheless, a large number of polyiodide anions have been observed in solids,^[1, 2] and one has the impression that their design depends upon size and shape of the counter-cation(s). Therefore, we are in the process of testing cations of different charge, size and shape. Recent work has especially focussed on lanthanide ions in combination with various crown ethers. The number of respective reports in the literature is rather limited and all but one contain triiodide as the polyiodide anion.^[3] Surprisingly, the “exception”, [Pr(B15c5)₂]₂I₂₁,^[3f] may be understood as having one of the rare higher anionic aggregates, I₂₁³⁻; the world record is still held by I₂₉³⁻.^[4] We now report the isolation of [Lu(Db18c6)(H₂O)₃(Thf)₆]₄(I₃)₂(I₅)₆(I₈)(I₁₂), a salt which contains both an exceptional cation and, in addition to I₃⁻, three higher polyiodide anions, I₅⁻, I₈²⁻, and I₁₂²⁻.

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⁺(I₁₄)³⁻ **1** grew after a prolonged period of time.^[5] A crystal structure determination reveals that this simple formula needs to be rewritten as follows, [Lu(Db18c6)(H₂O)₃(Thf)₆]₄(I₃)₂(I₅)₆(I₈)(I₁₂).

Figure 1. The cation [Lu(Db18c6)(H₂O)₃(Thf)₆]³⁺ in the crystal structure of **1**.

The bulky cation [Lu(Db18c6)(H₂O)₃(Thf)₆]³⁺ (Fig. 1) consists of a central Lu³⁺ 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)I₃].^[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

$[\text{La}_2(\text{Db18c6})_2(\text{OH})_2\text{I}_2](\text{I}(\text{I}_3))^{[3c]}$ and $[\text{Dy}_2(\text{Db18c6})_2\text{Cl}_4][\text{Dy}_2(\text{CH}_3\text{CN})_2\text{Cl}_8]$,^[7] for example. So far, in our description, the cation would be rather usual; what makes it unusually big is the addition of six Thf molecules, two at each of the three water molecules of the complex cation, see Fig. 1.

The asymmetric unit contains 28 iodine atoms which are arranged, the centre of symmetry of space group $\text{P2}_1/\text{c}$ taken into account, in a fashion that Fig. 2 depicts.

Figure 2. The four different polyiodide anions in the crystal structure of $[\text{Lu}(\text{Db18c6})(\text{H}_2\text{O})_3(\text{Thf})_6]_4(\text{I}_3)_2(\text{I}_5)_6(\text{I}_8)(\text{I}_{12})$ with their atomic numbering scheme. Atoms that do not belong to the asymmetric unit are drawn in a lighter pink.

The **triiodide** anion, $(\text{I}_3)^-$, is slightly asymmetric and almost linear (I25-I26: 287.7(11), I26-I27: 296.2(11), I25-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, $(\text{I}_5)^-$, of the form $[\text{I}_2-\text{I}-\text{I}_2]$ with typical bond distances and angles.^[8] 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: I20-I21: 275.9(12), I21-I24: 317.9(14), I24-I23: 308.0(10), I23-I22: 280.4(11), I20-I21-I24: 174.6(1), I21-I24-I23: 84.0(1), I24-I23-I22: 174.4(1). Two of the I_5^- anions may be seen as being connected via distances of 360.1(15) (I1-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, $(\text{I}_8)^{2-} = [\text{I}_2-\text{I}-\text{I}_2-\text{I}-\text{I}_2]$ are Z-shaped and show bond distances and angles that are comparable to similar compounds.^[9] (I16-I17: 284.8(10), I17-I18: 300.1(10), I18-I19: 343.0(13), I19-I19': 273.5(16), I16-I17-I18: 176.9(4), I17-I18-I19: 85.4(4), I18-I19-I19': 171.6(1)).

The centrosymmetric **dodecaiodide** anion, $(\text{I}_{12})^{2-}$, is formally built up by two $(\text{I}_5)^-$ anions that are bridged by an iodine molecule (bold) resulting in a chain like structure, $[\text{I}_2-\text{I}-\text{I}_2-\text{I}_2-\text{I}_2-\text{I}-\text{I}_2]$, with distances and angles of I6-

I7: 279.0(12), I7-I8: 309.3(11), I8-I9: 299.3(11), I9-I10: 279.0(12), I10-I28: 347.1(13), I28-I28': 271.3(17); I6-I7-I8: 173.8(4), I7-I8-I9: 99.4(3), I8-I9-I10: 179.2(4), I9-I10-I28: 80.2(4), I10-I28-I28': 169.8(4). This motif is well known from the isotopic compounds $[\text{M}(\text{Db18c6})]_2\text{I}_{12}$ with $\text{M} = \text{K}, \text{Rb}, \text{Tl}$.^[10] The shortest intermolecular distance of 386.0(12) pm is observed between the $(\text{I}_{12})^{2-}$ anion and an $(\text{I}_8)^{2-}$ anion (I6-I16).

The four polyiodide anions $(\text{I}_3)^-$, $(\text{I}_5)^-$, $(\text{I}_8)^{2-}$, and $(\text{I}_{12})^{2-}$, in a ratio of 2:6:1:1, fill the three-dimensional space rather well, as Fig. 3 depicts, with no I—I distance between neighbouring anions longer than 400 pm, and leave space for four of the cations per formula unit as described above.

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 $[\text{Lu}(\text{Db18c6})(\text{H}_2\text{O})_3(\text{Thf})_6]_4(\text{I}_3)_2(\text{I}_5)_6(\text{I}_8)(\text{I}_{12})$ 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 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 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-K α radiation ($\lambda = 71.073$ 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**: C₁₇₆H₃₁₂I₅₆Lu₄O₆₀, 11194.54 g mol⁻¹; diffractometer Bruker X8 APEX II CCD, T = 123(2) K; $2\theta_{\max} = 50.00^\circ$; one ϕ - and two ω -scans, 704 images; $-13 \leq h \leq 13$, $-17 \leq k \leq 17$, $-16 \leq l \leq 16$; $\rho_{\text{calc}} = 2.477$ g cm⁻³; 16270 measured reflections of which 3807 were symmetrically independent; $R_{\text{int}} = 0.0478$; $F(000) = 10200$; $\mu = 7.123$ mm⁻¹. Monoclinic, $P2_1/c$ (no. 14), $a = 2132.80(8)$, $b = 2871.52(9)$, $c = 2658.64(9)$ pm, $\beta = 112.792(2)^\circ$, $V = 15011.1(9)$ 10⁶ pm³, $Z = 2$; R values: R_1/wR_2 for 3699 reflections with $[I_0 > 2\sigma(I_0)]$: 0.0999 / 0.2159, for all data: 0.1012 / 0.2156; $S_{\text{all}} = 1.227$.

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