Synthesis and crystal structure of Li[{Ca$_7$(μ_3-OH)$_8$I$_6$(thf)$_{12}$}$_2$(μ-I)]·3THF, a unique H-bound dimer of a Ca$_7$-cluster on the way to sol–gels
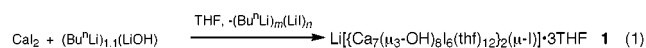
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In analogy to transition metal clusters, a mixed ligand Ca-cluster, consisting of two Ca$_7$-units linked *via* H-bonds, has been synthesised and structurally characterised, its thermal decomposition leading to the formation of sol–gels is also described.

In recent years, alkaline earth metal compounds have been increasingly studied owing to their application in different research fields, especially in the search for new precursors for superconductors and complex metal oxides. In this context, inorganic polymers of different dimensionality have been structurally characterised.[1] Furthermore, the synthesis of alkaline earth metal alkoxides has led to higher aggregated cage compounds such as the dimer [IBa(BHT)(THF)$_3$]$_2$·2THF,[2] (BHT = OC$_6$H$_2$Bu$^t_2$-2,6-Me-4), the cubane like compounds [Ba(μ_3-OBu^t)(OBu^t)(Bu^{t}OH)$_2$]$_4$,[3] and [Mg$_4$(μ_3-OMe)$_4$(OMe)$_4$-(MeOH)$_8$],[4] the large cluster [Ca$_9$(OCH$_2$CH$_2$OMe)$_{18}$(HOCH$_2$-CH$_2$OMe)$_2$][5] or the CO$_3^{2-}$-insertion product [Mg$_9$(μ_5-CO$_3$)-(O$_2$COMe)$_8$(μ_3-OMe)$_8$(MeOH)$_{13}$]·MeOH·C$_7$H$_8$.[6] Anionic N-donor ligands also yield clusters such as the THF-solvated hexamer [(THF)MgNPh]$_6$[7] or the solvent free cubane [BaNP(NMe$_2$)$_2$NP(NMe$_2$)$_2$NSiMe$_3$]$_4$.[8] The presence of alkoxy- or N-donor-groups and the resulting possibility of oxolation, that is the formation of oxygen bridges by hydrolysis, makes them potential precursors for sol–gel synthesis.

This work reports on the synthesis of a Ca$_7$-cluster forming dimers by hydrogen bonding [eqn. (1)].

$$\text{CaI}_2 + (\text{Bu}^n\text{Li})_{1.1}(\text{LiOH}) \xrightarrow{\text{THF, -(Bu}^n\text{Li)}_m(\text{LiI)}_n} \text{Li}[\{\text{Ca}_7(\mu_3\text{-OH})_8\text{I}_6(\text{thf})_{12}\}_2(\mu\text{-I})]\cdot3\text{THF} \quad \mathbf{1} \quad (1)$$

The reaction of CaI$_2$ in THF with a hexane solution containing Bu^{n}Li and LiOH yields the ionic cage compound Li[{Ca$_7$(μ_3-OH)$_8$I$_6$(THF)$_{12}$}$_2$(μ-I)]·3THF **1**.† Colorless prismatic crystals suitable for single crystal analysis which crystallise in the trigonal space group $R(\bar{3})$ (No. 148) were obtained by cooling a THF solution to –20 °C.‡ Attempts to synthesise **1** from the reaction of CaI$_2$ with LiOH failed probably owing to the stability and low solubility of the latter in THF. However, it has been shown that some mixed-anion compounds (RLi)$_m$(XLi)$_n$ (R = alkyl; X = halide, hydroxide or alkoxide) are synthetically useful reagents owing to their enhanced reactivity compared to the pure components RLi or XLi.[9] In the synthesis of **1**, partial hydrolysis of a Bu^{n}Li solution obviously leads to a soluble mixed-anion compound which was titrated to be 1.1 M in Bu^{n}Li and 1 M in LiOH. With this reagent, the synthesis of **1** is reproducible with yields of up to 87%. Addition of further equivalents of (Bu^{n}Li)$_m$(LiOH)$_n$, leads to the formation of sol–gels, fewer equivalents lower the yield of **1**.

This cluster compound is synthesised in a similar way as for transition metal clusters. For the latter, a reaction scheme includes, for instance, a metal chloride as metal source, a chalcogenide reagent such as Se(SiMe$_3$)$_2$ and a ligand compound to protect the outer cluster sphere, the driving force being the formation of a stable, volatile side product SiMe$_3$Cl. For **1**, CaI$_2$ is used as the metal source with (Bu^{n}Li)$_m$(LiOH)$_n$ as the reagent to form LiI and also as bridging ligand source. LiI is partially included in the structure of **1**. The ligands which complete the outer coordination sphere are provided by THF and part of the iodide. Unreacted Bu^{n}Li and LiI remain in solution, mainly forming the species (Bu^{n}Li)$_1$(LiI)$_1$ as determined by titration.

The molecule consists of two neutral Ca$_7$-clusters of composition [Ca$_7$(μ_3-OH)$_8$I$_6$(THF)$_{12}$] **1a**, linked together by μ-bridging iodide ions which form hydrogen bonds to an OH-group of each cluster unit (Fig. 1). To the best of the author's knowledge, this structural feature is unique for an alkaline earth metal cluster compound with mixed ligands.

The structure of the Ca$_7$-subunits can be described as two (Ca–O)$_4$ heterocubanes sharing a vertex or as a body-centered Ca-icosahedron with the outer six-membered Ca-ring missing. An alternative description is that of two Ca$_4$-tetrahedra sharing a vertex, each of the eight triangular faces of the two tetrahedra being μ_3-bridged by a hydroxy anion. The central calcium atom
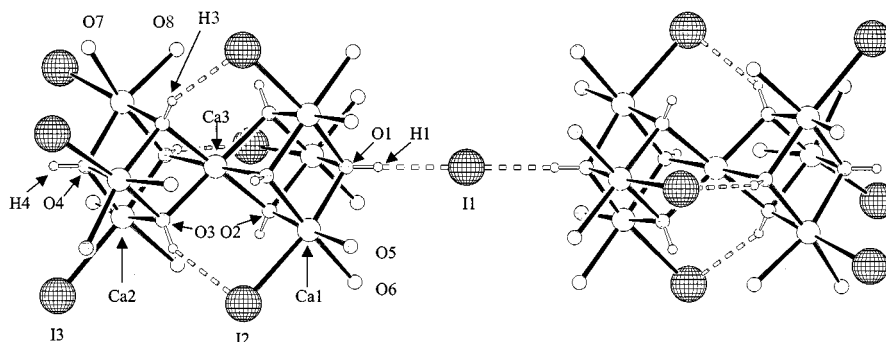

Fig. 1 Crystal structure of **1** along the horizontal C_3 axis passing through Ca3, O1, H1 and I1. Selected bond lengths (Å) and angles (°): Ca1–I2 3.151(1), Ca2–I3 3.147(1), Ca1–O2 2.312(5), Ca1–O1 2.354(4), Ca1–O5 2.413(6), Ca1–O6 2.411(6), Ca1–Ca3 3.557(2), Ca1–Ca1 3.592(3), Ca2–O3 2.322(5), Ca2–O4 2.346(4), Ca2–O8 2.425(7), Ca2–O7 2.438(7), Ca2–Ca3 3.553(3), Ca2–Ca2 3.595(3), Ca3–O3 2.365(5), Ca3–O2 2.388(5), H1–I1 2.68(2), H3–I2 2.87(7); I2–Ca1–Ca3 87.17(5), I2–Ca1–Ca1 131.40(5)–133.93(5), I3–Ca2–Ca3 145.59(6), I3–Ca2–Ca2 100.69(6)–138.28(4), Ca3–Ca1–Ca1 59.68(3), Ca1–Ca1–Ca1 (Ca2–Ca2–Ca2) 60.0, Ca3–Ca2–Ca2 59.61(3), Ca2–Ca3–Ca2 60.77(6), Ca1–Ca3–Ca2 178.87(4), O1–H1–I1 180, O3–H3–I2 149.12.

Ca3 is placed on a three fold axis $(0, 0, z; c)$ and features an octahedral coordination sphere of six OH-groups as next neighbours. At a longer distance range, it is surrounded by six Ca-atoms, Ca1, Ca2 and their symmetry equivalents, in form of a trigonal antiprism. The Ca–Ca-distances within the tetrahedra lie between 3.553(3) and 3.594(3) Å. Ca1 and Ca2 of the Ca_7-cluster also reach coordination number six, their coordination spheres being completed by three terminal ligands, two THF molecules and one iodide anion per calcium. The Ca–I distances are 3.154(2) Å (Ca1-I2) and 3.147(2) Å (Ca2-I3) and thus only slightly longer than in $CaI_2(THF)_4$ [Ca–I 3.106(2) Å] or ICa(clox)(THF)$_4$ [Ca–I 3.108(3) Å; clox = $OCPh_2CH_2C_6H_4Cl$-4],[2] and correspond to the sum of the Shannon ionic radii [Ca^{2+}(coord. 6) 1.00 Å, I^- 2.20 Å].[10] Ca–O bond lengths to the terminally bound THF-molecules in the range of 2.414(6) to 2.433(7) Å are observed, corresponding to literature data [Ca–O(THF) 2.33–2.454 Å].[2] The Ca–O(OH) distances can be divided into the shorter Ca–O bond lengths Ca1–O and Ca2–O and their symmetry equivalents [2.312(5)–2.354(4) Å] and the longer Ca–O bond lengths of the central Ca3-atom to the hydroxy groups [2.366(5)–2.393(5) Å]. They correspond, on average, to the Shannon ionic radii sum (2.35 Å). The hydroxy groups act as μ_3-ligands.

The threefold axis through Ca3 also passes through O4 and O1 $(0, 0, z; c)$ and the μ-iodide ligand I1 which, additionally, is placed on an inversion center $(0, 0, 0; a)$. Hydrogen bonding occurs along this threefold axis between the two Ca_7-clusters [I1–O1 3.682(6) Å, I1–H1 2.70(7) Å; H–I–H 180° (due to symmetry).] Other H-bonds are formed within the Ca_7-cluster between I2 and H3 [2.89(6) Å], slightly longer than that above as is also the case for the corresponding I2–O3 distance [3.771(6) Å] and the O3–H3–I2 angle is bent to 149.26°. H–I hydrogen bonds described in the literature are of the same order of magnitude, such as in [$trans$-(py)$_4$Mg(OH$_2$)$_2$]I$_2$·2py with I–O(H) 3.438(7)–3.669(9) Å (2.4–2.7 Å),[11] or in [Mg(HO-Me)$_6$]I$_2$·2tmeda with I–O 3.377(5)-4.209(5) Å and [(tmeda)SrI$_2$-(HOMe)$_3$]·0.5tmeda with I–O(H) 3.516(9)–3.555(7) Å (2.5–3.0 Å).[12] The IR spectrum of **1** in Nujol on CsI plates shows a sharp band for free OH at 3640 cm^{-1} (O4–H4, O2–H2), along with broader bands at 3550, 3300 and 3200 cm^{-1}, indicating hydrogen bonding.

μ_3-Capped Ca_3-triangles as in **1** can be found in the alkoxide aggregate [Ca$_9$(OCH$_2$CH$_2$OMe)$_{18}$(HOCH$_2$CH$_2$OMe)$_2$][5] in which the coplanar Ca-atoms occupy octahedral holes between two close-packed oxygen layers. A similar tetrahedral feature as in the building units for **1** was found in [Ba(μ_3-OBu^t)(O-Bu^t)(Bu^{t}OH)$_2$]$_4$,[3] where the tetrahedron is formed by Ba-atoms, and the triangle capping OH-groups are formally replaced by OBu^t. The same ligand (OBu^t and Bu^{t}OH) acts as a terminal ligand on the alkaline earth metal, whereas in **1**, different ligands are found on almost every position. Another tetra-hedrally built compound is the solvent free [{BaNP(N-Me$_2$)$_2$NP(NMe$_2$)$_2$NSiMe$_3$}$_4$] which consists of a RN-capped Ba-tetrahedron and forms, on hydrolysis, a white gel of composition Ba(OH)$_2$·xH$_2$O. **1** is soluble in THF or other solvents and may also act as a precursor for sol–gels. The capping hydroxy groups can undergo elimination of water with the hydroxy groups of neighbouring cluster molecules, forming oxo bridges between the clusters. This oxolation leads to gels in the classical way. Isolated and washed crystals of **1** decompose in THF after heating to form a white gel. Furthermore, the crystals lose solvent after a short period of time, and thermal treatment (DTA and thermogravimetry) shows the elimination of all the THF at 70 °C followed by water at 110 °C. Other polymerisation mechanisms are envisageable, such as elimination of terminally bound THF and saturation of the thus empty coordination site on calcium by a terminal iodide ligand of a neighbouring molecule to yield a μ-I-bridge, or elimination of iodide by addition of an excess of Bu^{n}Li. Further investigations on the use of **1** as a sol–gel precursor are under way.

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