

Oxygen Donor Stabilized Alkaline Earth Metal Iodides

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Abstract: Alkaline earth metal iodides show ionic behavior in water, but their bonding situation is not that clear in less polar solvents. The alkaline earth metal iodide adducts, *i.e.* $[\text{Ml}_2(\text{thf})_5]$ ($\text{M} = \text{Sr}$ and Ba), $[\text{CaI}_2(\text{L})_4]$ ($\text{L} = \text{thf}$, H_2O), $[\text{Ba}(\text{OH})\text{I}(\text{H}_2\text{O})_4]$ and $[\text{CaI}_2(\text{dme})(\text{diglyme})]$ ($\text{dme} = \text{dimethoxy ethane}$; $\text{diglyme} = \text{diethylene glycol dimethyl ether}$) are presented in this context and their bonding situation is discussed.

Keywords: Alkaline earth metals · Covalency · Iodides · Ionicity · Structure elucidation

Introduction

Taking into account the differences in electronegativity of the elements between alkali or alkaline earth metals on one hand and halogens on the other, the alkali and alkaline earth metal halides can be classified as ionic in the solid state and in aqueous solution. In the gas phase however, the binding situation has to be re-evaluated. Thus, a single NaI fragment in the gas phase reveals a resonance behavior of the bond which converts from covalent into ionic [1]. *Ab initio* calculations confirm the covalent character of the bonds in the alkaline earth metal halides and pseudo-halides of the heavier homologues, such as BaBr_2 , that exhibit bent structures in the gas phase,

whereas a linear arrangement is expected from the classical VSEPR model [2]. This has only recently led to a reformulation of the VSEPR model by Gillespie and Robinson [3] in order to include such exceptional structures and to allow their explanation and prediction.

Results and Discussion

We have used the principle of systematically and stepwise ‘cutting out’ structural fragments from a solid state structure with chemical scissors before: With oxygen donor ligands for instance, a complete structural genealogy tree for BaI_2 was obtained, starting with a three-dimensional structure and ‘cutting’ it down *via* two- and one-dimensional compounds to the zero-dimensional $[\text{BaI}_2(\text{thf})_5]$ [4]. Similarly, this systematic approach could be applied to barium triflate (triflate = CF_3SO_3^-) [5], and it was possible to transfer the principle to CaI_2 and SrI_2 . Here, the molecular structures of *trans*- $[\text{CaI}_2(\text{thf})_4]$ and *cis*- $[\text{CaI}_2(\text{H}_2\text{O})_4]$, *cis*- $[\text{Ba}(\text{OH})\text{I}(\text{H}_2\text{O})_4]$, *trans*- $[\text{Ml}_2(\text{thf})_5]$ ($\text{M} = \text{Sr}$, Ba) as well as *trans*- $[\text{CaI}_2(\text{dme})(\text{diglyme})]$ will be presented and compared.

Trans- $[\text{CaI}_2(\text{thf})_4]$ (1) and *cis*- $[\text{CaI}_2(\text{H}_2\text{O})_4]$ (2)

In principle, one would expect similar structures for two compounds written as $[\text{CaI}_2(\text{L})_4]$. In the case of THF as ligand L , only the *trans*-compound has been observed so far. $[\text{CaI}_2(\text{thf})_4]$ (1) was obtained when crystallizing CaI_2 from a saturated

THF solution at -20°C , in analogy to a species known from literature [6]. With the sterically bulky ligands THF in equatorial and the iodide ions in axial positions, the alkaline earth metal ion reaches a coordination number of six, and the molecules are arranged in a parallel fashion without further strong contacts between the units (Fig. 1a). When the four THF ligands are replaced by water molecules, the *cis*-compound of $[\text{CaI}_2(\text{H}_2\text{O})_4]$ (2) is obtained. The $\text{I}-\text{Ca}-\text{I}$ angle is now $90.7(1)^\circ$ compared to 180° in $[\text{CaI}_2(\text{thf})_4]$ (1) (Fig. 1b). The water molecules can interact with the μ_4 -bridging iodide ligands of the neighbor units in order to build an overall three-dimensional network *via* hydrogen bonding, as predicted by our established rules for the prediction of the dimensionality of a compound [7]. The $\text{Ca}-\text{I}$ bonds in 1 are 3.106 \AA , but are much longer in 2 with $3.194\text{--}3.240 \text{ \AA}$, indicating the further implication of iodide in hydrogen bonding for compound 2. The *trans* $\text{O}-\text{Ca}-\text{O}$ angle deviates strongly from 180° at $167.6(5)^\circ$, probably due to repulsive interactions between H_2O and iodide. Also, the *trans* $\text{O}-\text{Ca}-\text{I}$ angles are at $174.7(5)^\circ$ and $175.0(4)^\circ$ far from linear. The main interesting feature is the fact that both anions are in vicinal positions, *i.e.* to obtain the *cis*-compound, and the question arises why such a structure is more favorable even though the two negative charges must repel each other. Interestingly enough, the *trans*-version of compound 2 exists as well [8], with very similar bond length and angles as in compound 1; the four THF ligands of 1 being replaced formally by H_2O . It is however unclear, why and when the *cis*-form

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crystallizes rather than the *trans*-version. From the synthetic point of view, *cis*-**2** is obtained when crystallizing from diethyl ether in the presence of water whereas the *trans* compound is obtained from aqueous solution.

[Ba(OH)I(H₂O)₄] (3)

A *cis*-arrangement is also found in the compound [Ba(OH)I(H₂O)₄] (**3**) prepared by us [9] as well as Kellersohn *et al.* [10]. Comparing the chemical formulae, one iodide of the *cis*-**2** compound has formally been replaced by an OH⁻ group in the barium compound. In both compounds the

two anions (two I⁻ in **2**, and one I⁻ and one OH⁻ in **3**) are in *cis*-positions to each other, forming angles of 90.7° and 66.6°, respectively. The larger barium cation completes its coordination number of nine (capped square antiprism) by direct contacts to the neighboring units, leading to two-dimensional layers with the water molecules acting as bridging ligands (Fig. 1c).

These layers are linked *via* H-bonds to a three-dimensional network. Its Ba–I distance is slightly longer than the ionic radii sum, due to the iodide being involved in intramolecular H-bonding to OH and intermolecular H-bonding to H₂O of neigh-

boring sheets. For the same reasons, an elongation is also observed for the Ba–O distances.

Comparison of [Ba₂(thf)₅] (4) and [SrI₂(thf)₅] (5)

[Ba₂(thf)₅] (**4**) and [SrI₂(thf)₅] (**5**) were both obtained from a concentrated THF-solution by cooling it to –20 °C. In **4**, molecular Ba₂ is stabilized by five THF molecules (Fig. 2a).

Two iodide atoms surround the barium cation almost linearly with an I–Ba–I angle of 178°, whereas in the gas phase, free molecular BaI₂ has an I–Ba–I angle of between

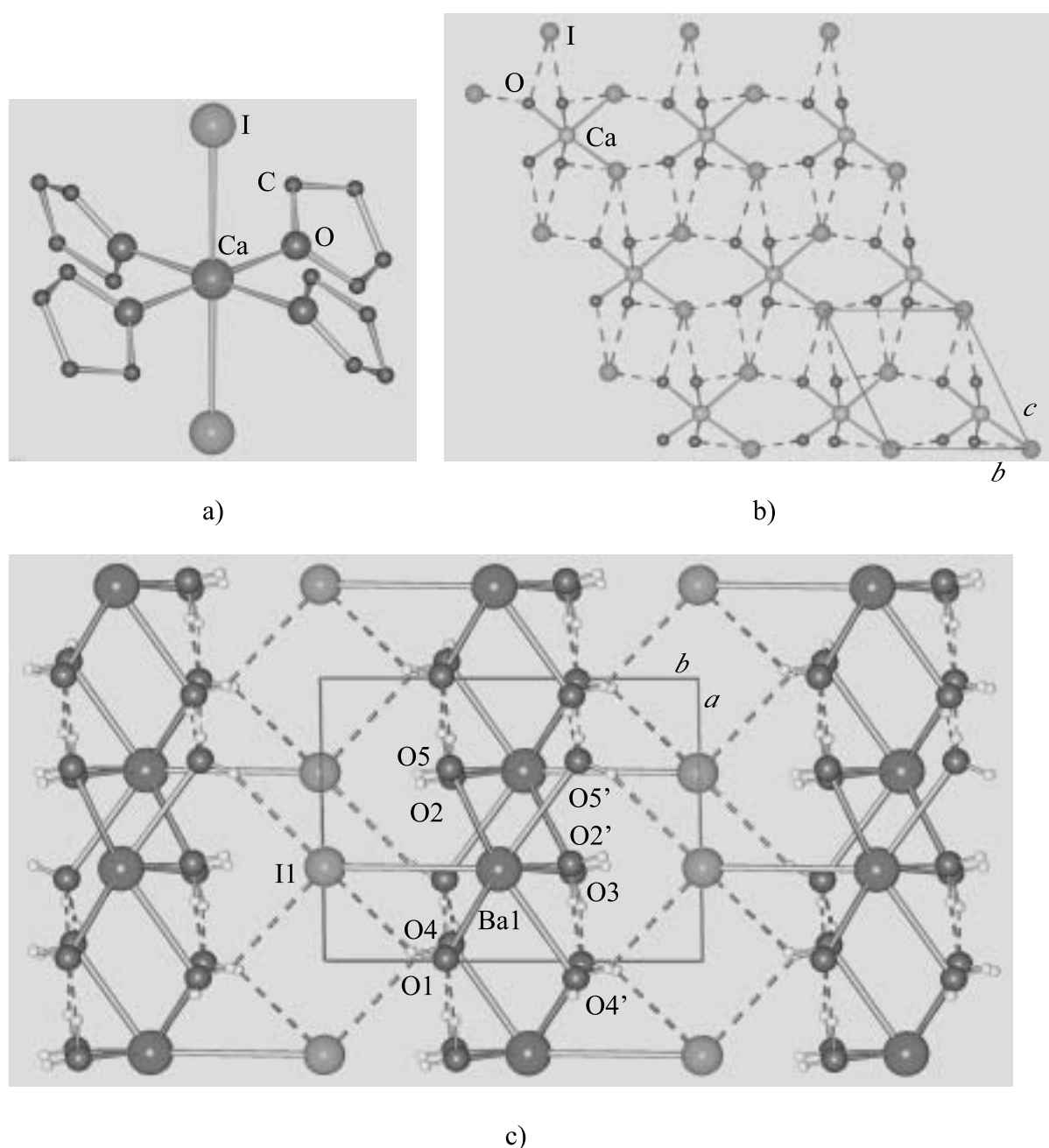


Fig. 1. Molecular unit of [Ca₂(thf)₄] (**1**) (a); three-dimensional network formed by *cis*-[Ca₂(H₂O)₄] (**2**) (b), for a) and b), H-atoms omitted for clarity; packing of the layered structure of **3** showing interlayer H–I interactions (c)

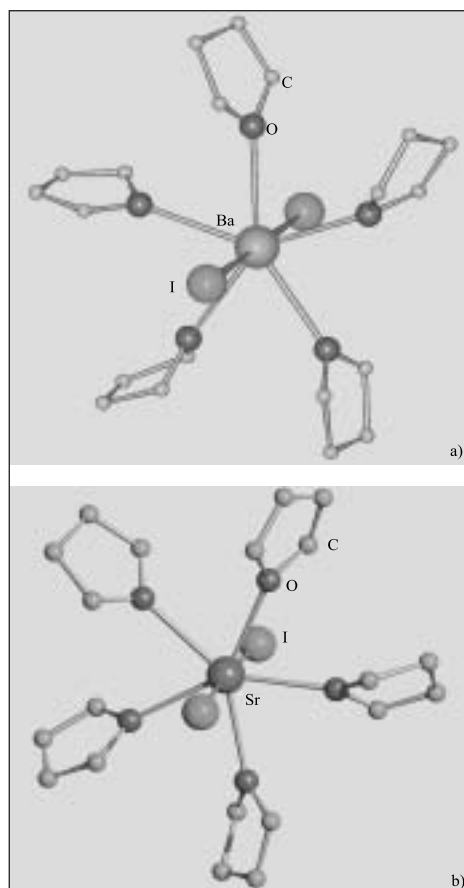


Fig. 2. Molecular structure of $[\text{BaI}_2(\text{thf})_5]$ (**4**), and $[\text{SrI}_2(\text{thf})_5]$ (**5**), H-atoms omitted

102° and 105° [2]. The THF donor ligands complete the coordination sphere of barium, occupying the equatorial positions of a slightly distorted pentagonal bipyramid. The coordination number for barium is seven, and that for iodide is one. The structure of compound **5** is very similar but with an I–Sr–I angle of 176° (Fig. 2b) [11]. In both compounds $[\text{MI}_2(\text{thf})_5]$ with $\text{M} = \text{Ba}$ and Sr , the alkaline earth metal cation possesses an almost perfect pentagonal bipyramidal coordination sphere, with the halides in axial and the THF molecules in equatorial positions. The M–I bonds are in both cases slightly shorter than the sum of the ionic radii by Shannon [12], the one for strontium in **5** being smaller than the one for barium due to its smaller ionic radius. This is also reflected by the shorter M–O bonds. The O–M–O angles have with an average of about 72° the ideal value for this geometry, whereas the I–M–I angle is smaller in the case of strontium than for the barium compound, possibly indicating a more covalent M–I bond for the former. This could also be a consequence of stronger steric interaction of the shorter bonded iodide with the THF molecules in the case of the strontium compound.

Both compounds are zero-dimensional, and the $[\text{MI}_2(\text{thf})_5]$ units in the crystal are arranged in a parallel fashion with the iodides pointing towards each other between layers of these units, and no further contacts between the units are observed.

Similar coordination chemistry and structures are known from the lanthanide ions, *i.e.* the samarium compounds $[\text{SmI}_2(\text{thf})_5]$ [13] and $[\text{SmI}_2(\text{thf})_5]^+$ [14], in which the metal cation is surrounded by two halides and five THF molecules in order to form a pentagonal bipyramidal arrangement.

Structure of $[\text{CaI}_2(\text{dme})(\text{diglyme})]$ (**6**)

The calcium ion, as seen in compound **2**, seems to be too small to host more than four bulky THF molecules as ligands, whereas strontium and barium cations are able to fix five of them in the above-mentioned iodides **4** and **5**. However, we wanted to test other etheral ligands in order to investigate if they would stabilize and favor the molecular or the ionic form of CaI_2 as well. Polyethers like DME and diglyme were therefore tested on CaI_2 . The resulting compound obtained from a solution of CaI_2 in a 1:1 mixture of both ethers reveals the structure of $[\text{CaI}_2(\text{dme})(\text{diglyme})]$ (**6**). The calcium cation reaches a coordination number of seven and is coordinated by two iodide in axial and five oxygen atoms of the polyether ligands in equatorial positions of a severely distorted pentagonal bipyramid. The Ca–I bond lengths of 3.089(1) and 3.139(1) Å compare well with the Ca–I distances in $[\text{CaI}_2(\text{thf})_4]$ and are shorter than the sum of Shannon radii (Fig. 3) [12].

The I–Ca–I angle ($176.52(3)^\circ$) is very similar to the one observed in $[\text{SrI}_2(\text{thf})_5]$. The Ca–O bonds range from 2.415(3) to 2.467(3) Å, and the O–Ca–O angles of neighboring oxygen atoms vary considerably from the ideal value of 72° in a regular pentagonal bipyramid with values between $66.94(9)^\circ$ (one of the bite angles of diglyme), and $80.7(1)^\circ$ (one of two angles be-

tween DME and diglyme). The coordination number of seven for the calcium ion in the form of a pentagonal bipyramid is therefore only possible for calcium with distortion, one oxygen O5 being 0.33 Å out of the least square plane formed by the five oxygen atoms O1 to O5. A similar coordination sphere for calcium has only been observed with crown ethers comprising five oxygen atoms, such as 15-crown-5 and its derivatives, as well as in $[\text{Ca}(\text{dme})(\text{H}_2\text{O})_3](\text{DME})\text{I}_2 \cdot \text{DME}$ [15]. No single crystal data is available for the former compounds, so it is not known whether the calcium atom would sit exactly in the middle of such a macrocyclic ligand [16].

Conclusions

In the Table, all six compounds are compared to each other, summarizing the most important facts. In the case of organic solvents which are at the same time ligands, one seems to obtain more molecular-type species like in **1**, **4**, **5**, and **6**, whereas in the presence of water, it seems difficult to predict under which conditions which of the compounds, the more molecular *trans*- or the more ionic *cis*-compound, will form. Compounds **1**, **4**, **5** and **6** are well soluble in organic solvents, whereas **2** and **3**, both *cis*-compounds regarding the anions, are not. The former four compounds possess defined units in the solid state, without further contacts to each other, whereas the latter two are hydrogen bonded or otherwise linked in the three directions of space and form a three-dimensional network. The zero-dimensional compounds behave like molecular compounds on which substitution reactions can take place in a classical way and have found their application as starting materials in reactions described elsewhere to yield supramolecular polymers and cluster compounds of alkaline earth metals [11][17][18].

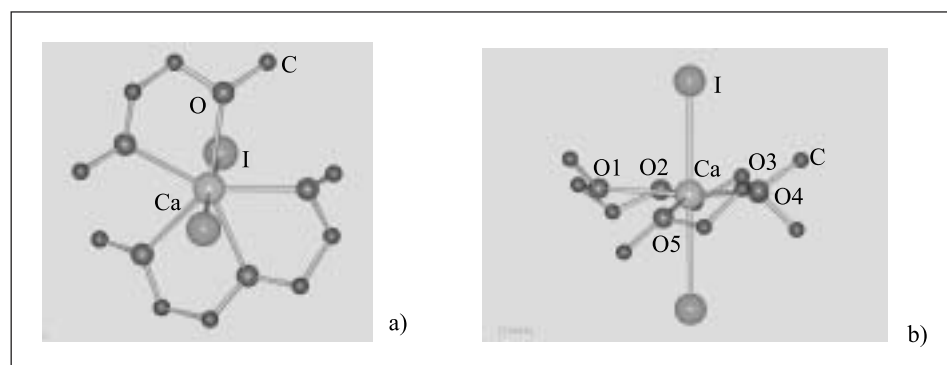


Fig. 3. Views of $[\text{CaI}_2(\text{dme})(\text{diglyme})]$ (**6**) a) General arrangement of **6**; b) O5 of **6** is strongly out of plane; H-atoms omitted for clarity

Table. The most important structural parameters for the crystal structures of $[\text{Ca}_2(\text{thf})_4]$ (1), $[\text{Ca}_2(\text{H}_2\text{O})_4]$ (2), $[\text{Ba}(\text{OH})(\text{H}_2\text{O})_4]$ (3), $[\text{Ba}_2(\text{thf})_5]$ (4), $[\text{Sr}_2(\text{thf})_5]$ (5), and $[\text{Ca}_2(\text{dme})(\text{diglyme})]$ (6)

	1	2	3	4	5	6
M–I [Å]	3.106	3.194(4), 3.240(4)	3.6928(8)	3.374, 3.3822	3.229	3.0895(9), 3.1391(9)
M–O [Å]	2.34	2.42(2) – 2.49(2)	2.815(2) – 2.863(8)	2.696 – 2.741	2.562 – 2.618	2.415(3) – 2.467(3)
I–M–I [°]	180	90.7(1)		178.61	176.34	176.52(3)
I–M–O [°]	90 av.	87.7(4) – 94.4(4)	66.61(5) – 125.79(5)	86.10 – 93.12	85.63 – 92.26	82.90(7) – 97.52(8)
O–M–O [°]		81.7(6) – 92.7(7)				66.94(9) – 80.73(10)
Space group	P2 ₁ /c	P-1	P-1	P2 ₁ /c	P4 ₃ 2 ₁ 2	P2 ₁ /n

Experimental

Synthesis and single crystal data have been published previously [19].

Acknowledgements

I thank Prof. A.F. Williams and Prof. C. Piguet, both University of Geneva, for their generous support. This work was financed continuously by the Swiss National Foundation. Dr. H. Goesmann, University of Karlsruhe, is thanked for collecting the X-ray data.

Received: February 7, 2003

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