A Logical Concept of Structure Prediction Derived from Supramolecular Polymers of Alkaline Earth Metal Halides Formed by Hydrogen Bonding and Complexation of the Metal Ion

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Abstract: Several different dimensional polymers derived from alkaline earth metal iodides are obtained as a result of supramolecular noncovalent bonding modes of the metal ion, namely complexation and hydrogen bonding. These polymers consist of complex cations linked to the halide ions by hydrogen bonds of the water ligands coordinated to the metal. They are built up in a logical way, depending on the ratio of complexing ligands to complexing and hydrogen-bonding ligands so that their dimensionality and, to a certain extent, their structure can be predicted.

Keywords: alkaline earth metals · coordination complexes · hydrogen bonds · structure elucidation · structure prediction

Introduction

Supramolecular chemistry provides ways and means to design and generate organized equilibrium architectures of nanoscopic dimensions with novel structural and functional properties.[1, 2] The final supramolecular entity (or a collection of such) evolves through a sequence of spontaneous but directed recognition, growth, and termination steps of suitably instructed components and specified interaction schemes. Noncovalent interactions, such as hydrogen bonding, metal-ion coordination, and electrostatic and hydrophobic forces, permit the precise positioning of molecular components in a well-defined supramolecular architecture.[1, 2]

The implementation of the underlying principles of noncovalent interactions in molecular-based materials allows the generation of spatially confined and macroscopically ordered ensembles. Long-range correlation of positions or orientations of the active constituents will be of paramount importance to fully explore the potential of supramolecular materials and functional devices derived from them. The improvement of existing methods and the development of novel procedures to generate organized supramolecular assemblies represents a central objective and requires the availability of structurally reliable, functional synthons to engineer periodic, three-dimensional architectures that have specific structural characteristics.

Such is the case for networks of different dimensionalities. These materials are in the focus of materials research because, in particular, they are highly anisotropic.[3] The challenges presented by the production of a well-defined dimensionality, and the formation of chiral and chemically functionalizable pores has recently stimulated the application of self-assembly principles that originate from supramolecular chemistry[1, 2] and which are based on hydrogen bonding and metal-ion coordination.[1, 2, 4]

Metal-ion-containing devices are of particular interest as active components in functional materials because they possess a wide range of well-defined coordination geometries and diverse properties that are relevant to electronic, optical, magnetic, and catalytic applications.[5] Self-assembly of the metallosupramolecular architecture is effected through ligands with suitable binding sites in a proper spatial arrangement.[1, 2] On the other hand, hydrogen bonding is probably the most widely spread interaction motif in biological systems.[4] Therefore, it is of interest to explore both interactions in order to pursue the goal of constructing different dimensional architectures that contain functional components.[6]

In our group, we are especially interested in alkaline earth compounds as their application might be found in the wide area of, for example, high-temperature superconductors and thin film oxides.[7] Various methods are available for the deposition of thin films on a substrate, for example, MO-CVD (metal–organic chemical vapor deposition), dipping, spraying, or spinning.[8] In this context, we decided to focus on the dimensionality of the polymers formed by alkaline earth metal halides with both i) a complexing, but otherwise innocent, polyether oxygen donor ligand, and ii) a complexing as well as hydrogen-bonding H_2O ligand. Depending on the ratio of "complexing-only" ligands to "complexing-and-H-bonding" ligands, the overall dimensionality of the compound can be controlled and, therefore, predicted.

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Results

We were able to obtain a number of adducts between halides of alkaline earth metals (calcium and barium) and oxygen donor ligands. These adducts display structures of all dimensionalities as a result of hydrogen bonding. From these results, it seems that the number of water molecules strongly influences the dimensionality of the network formed (Table 1).

Table 1. Overview of the structures formed and their corresponding dimensionality.

Compound	No. H-bonding H_2O	Dimensionality
$\{[Ba(triglyme)_2(H_2O)]I_2\}_{0/\infty}$ (**1**)	1	0
$\{[Ca(diglyme)_2(H_2O)_2]I_2\}_{1/\infty}$ (**2**)	2	1
$\{[Ba(diglyme)_2(H_2O)_3]I_2\}_{2/\infty}$ (**3**)	3	2
$\{[Ca(triglyme)(H_2O)_4]I_2\}_{3/\infty}$ (**4**)	4	3

The reaction of BaI_2 with triglyme (triglyme = triethylene glycol dimethyl ether) that contains 1‰ of water, gave $\{[Ba(triglyme)_2(H_2O)]I_2\}_{0/\infty}$ (**1**). This compound contains a single water molecule that acts as both a complexing and a hydrogen-bonding ligand. Compound **1** is obtained as colorless rod-like single crystals from the mother liquor in a yield of 42%. X-ray structural analysis shows that it crystallizes in the orthorhombic space group *Pbca* and has one molecule per asymmetric unit (Figure 1).[9] The barium cation is coordinated by nine oxygen atoms provided by two triglyme ligands and one water molecule. The coordination geometry can best be described as a distorted trigonal prism formed by O3, O5, O6, and O1, O4, O8. The rectangular faces are capped by one oxygen each (O2, O7, O9). The Ba1–O(triglyme) bond lengths vary between 2.832(3) and 2.939(4) Å, whereas the water molecule is bonded more tightly (Ba1–O9 2.730(4) Å) as a terminal ligand. The O-Ba1-O angles of vicinal oxygens of the triglyme ligands are all in the same order of magnitude (56.39(11)–59.49(11)°) so that the summation of these angles only is very similar for both ligands. However, the angles found between the first oxygen and last oxygens of the ligand vary dramatically from O1-Ba1-O4 (70.78(11)°) to O5-Ba1-O8 (152.08(10)°). This gives a total angle sum for the first triglyme ligand of 244.44° and 326.50° for the second; the oxygen atoms O5–O8 and Ba1 are almost planar. The four oxygen atoms of each triglyme ligand each lie approximately in one plane, and the two planes, O1–O4 and O5–O8, are inclined to each other by ≈15.5°. The oxygen atom of the water molecule is almost 1 Å below the plane of O5–O8, and points away from the O1–O4 plane.

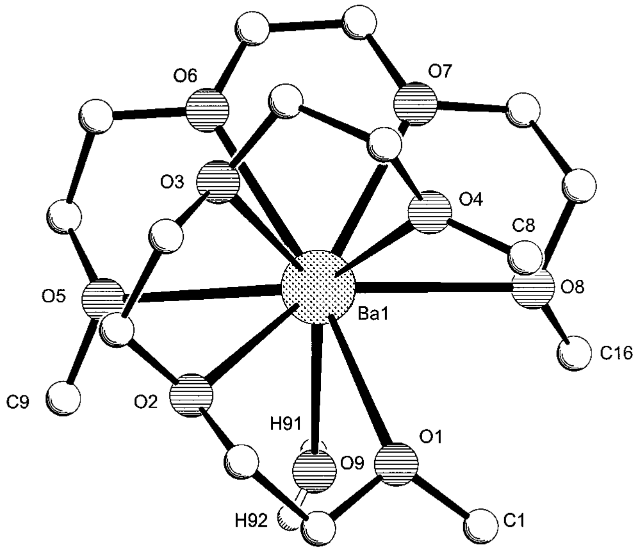


Figure 1. Structure of the $[Ba(triglyme)_2(H_2O)]^{2+}$ cation in **1**; H atoms of the polyether ligands have been omitted for clarity.

In the crystal, the $[Ba(triglyme)_2(H_2O)]^{2+}$ cations form hydrogen bonds to the iodides I1 and I2 through the hydrogen atoms of the water molecule (Figure 2). Thus, the O9(H92)–I1 bond is 3.529(5) Å (2.86(7) Å) and the O9(H91)–I2 bond is 3.432(6) Å (2.72(6) Å); this indicates quite a strong hydrogen-bonding interaction. The iodides act as terminal ligands and each hydrogen of the water ligand binds to one iodide. Therefore, the overall structure of the compound is zero-dimensional with discrete molecules of **1** and no closer interactions between the molecular units. There may be a slight intramolecular contact between I2 and Ba1 as the

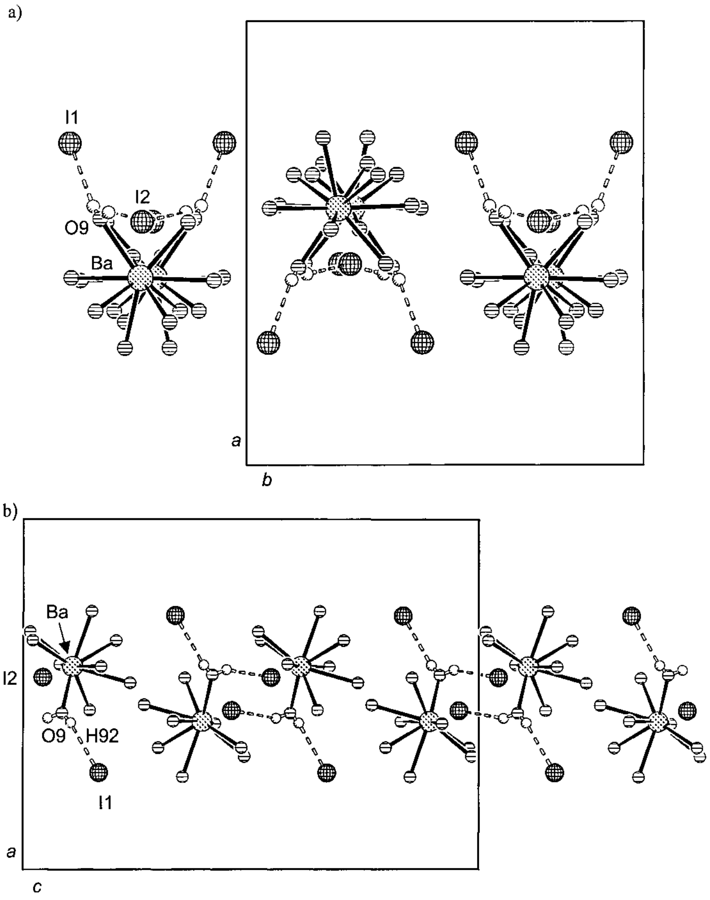


Figure 2. View onto a) the *ab* plane of **1** and b) the *ac* plane of **1**. C atoms and the corresponding H atoms have been omitted for clarity.

coordination sphere of Ba shows a large unoccupied space on the side occupied by the water ligand. In fact, the hydrogen-bonded iodide I2 is at a distance of 3.9549(8) Å from Ba1; this is too far away for a chemical bond, but might allow for weak electrostatic interactions between the two ions. In addition, the O9-H91-I2 angle of 151.18(12)° is much steeper than the O9-H92-I1 angle of 168.38(10)°. This supports the hypothesis of weak interactions between I2 and the barium cation. The water molecule in **1** can be classified as a class 1′, type J,[10, 11] as the oxygen is coordinated by one lone pair to one divalent cation; the other lone pair shows no or little interaction with the cation. The barium atom possesses a valence bond sum of 2.27 and thus shows sufficient coordination by its ligands.[12]

The second example is of a compound with two hydrogen-bonding water ligands $\{[Ca(diglyme)_2(H_2O)_2]I_2\}_{1/\infty}$ (**2**). It was obtained from a solution of dried CaI_2 in a mixture of diglyme and water (1 %) in a yield of 24 %. Compound **2** crystallizes in the monoclinic space group *Cc* with one complex cation $[Ca(diglyme)_2(H_2O)_2]^{2+}$ and two iodides, linked by hydrogen bonds to the cation, per asymmetric unit.[9] The alkaline earth cation has a distorted square-antiprismatic coordination geometry with the oxygen atoms of one diglyme ligand and of one water molecule in each square of the antiprism (Figure 3). The two square planes, O1-O3-O4-O5 and O2-O6-O7-O8, are almost parallel to each other with an angle of 4.9°. The calcium atom lies almost in the geometric center, 1.395(2) Å above the first and 1.382(2) Å below the second plane. The average Ca–O(diglyme) bond lengths of 2.441(4) Å are shorter than the Ca–O(H_2O) bonds of 2.489(4) Å. The oxygen atoms of the water molecules are situated on neighboring sites of the square antiprism and form an O1-Ca-O2 angle of 65.0(2)°. They can best be classified as class 1, type D for O2 and as class 1′, type J for O1, as the water molecule O2 is almost coplanar with the alkaline earth metal cation.[10, 11] The two water molecules are linked to each other by hydrogen bonding to I1 with H11–I1 2.898(4) and H21–I1 2.999(4) Å. Iodide I1 acts as an intramolecular μ_2-bridging ligand. The angle at I1 is very acute with H11-I1-H21 = 53.94(9)°. The so-formed cationic units $\{[Ca(diglyme)_2(H_2O)_2]I\}^+$ are linked together by another hydrogen-bonding system, which involves the remaining hydrogen atoms of the water ligands and I2 in order to build a one-dimensional chain. The H–I2 bond lengths (2.555(4) and 2.588(4) Å) are shorter than the H–I1 bond lengths by more than 0.3 Å. This indicates a stronger intermolecular than intramolecular hydrogen bonding. The H-I2-H angle is almost linear (173.5(1)°). The so-formed infinite strands run parallel to each other within planes parallel to the *ab* plane of the unit cell. The propagation vectors of the chains are oriented by ≈120° to each other and vary from one plane to the next (Figure 4). Considering the positions of the iodide within one chain, a weak dipole moment is induced not along the chain propagation vector but perpendicular to it in its width, as the I1 ions are all oriented to the same side (above) of the strands and the I2 ions all lie above the gravicenter of the pure complex cation (Figure 3). There are no further contacts between the chains to compensate for such a dipole moment. Whether this fact of being polar has an influence or not on the physical properties of compound **2** is under current investigation.

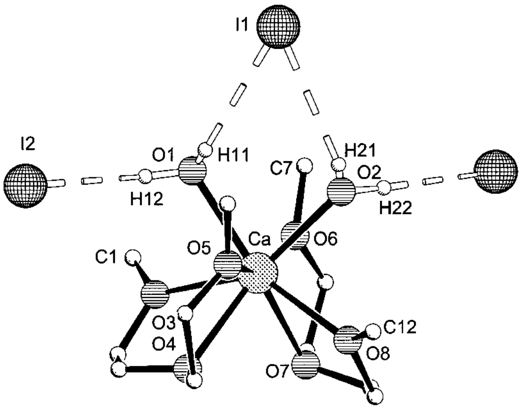


Figure 3. Hydrogen bonding in **2**; H atoms of the polyether ligand have been omitted for clarity.

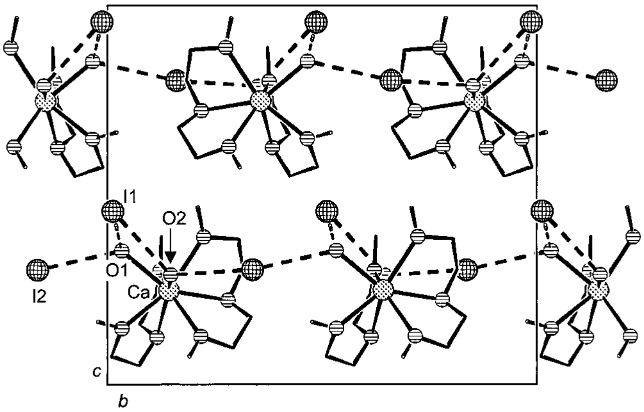


Figure 4. View along the *a* axis onto the *bc* plane of **2**, with chains oriented 120° to each other; H atoms have been omitted for clarity.

While the calcium atom is satisfied with a coordination number of eight and a valence bond sum of 2.23 in **2**,[12] the barium ion allows the coordination of a third water molecule in addition to the two diglyme and two water ligands under the same reaction conditions. This gives a coordination number of nine in $\{[Ba(diglyme)_2(H_2O)_3]I_2\}_{2/\infty}$ (**3**). The two-dimensional compound **3** crystallizes in the orthorhombic space group *Pbca* with two independent molecules of $[Ba(diglyme)_2(H_2O)_3]I_2$ in the asymmetric unit.[9] The coordination geometry around the barium ions can best be described as a distorted tricapped trigonal prism of oxygen atoms (Figure 5). The cationic units $[Ba(diglyme)_2(H_2O)_3]^{2+}$ of Ba1 and Ba2 are linked together by I2 and I4 through the water ligands O01, O02, O04, and O06 of the two independent complexes. The μ_3-ligand I2 bridges O01, O04, and O06 with the bond lengths of 3.529(4), 3.491(4), and 3.510(4) Å, respectively. The I4 anion binds to O01, O02, and O06 with 3.664(4), 3.670(4), and 3.576(4) Å. I2 and I4 also act as delimiting ligands in a similar manner to two of the terminal CH_3 groups of the diglyme ligands; this separates the layers in the crystal structure (Figures 6 and 7). There are no close contacts between the I2 or I4 and any aliphatic hydrogen.

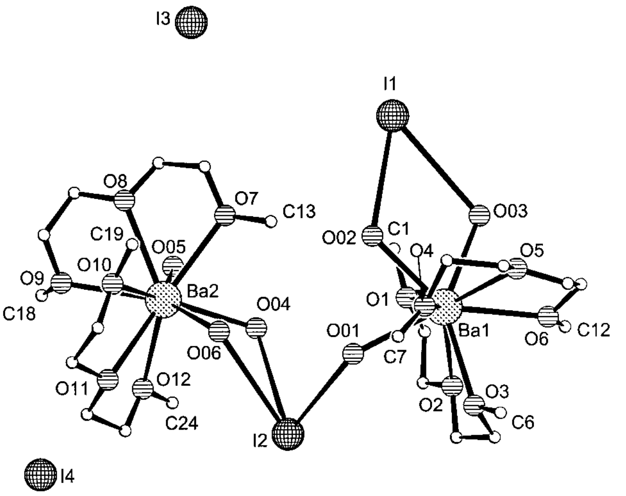


Figure 5. Coordination and hydrogen bonding in the asymmetric unit of **3**; H atoms have been omitted for clarity.

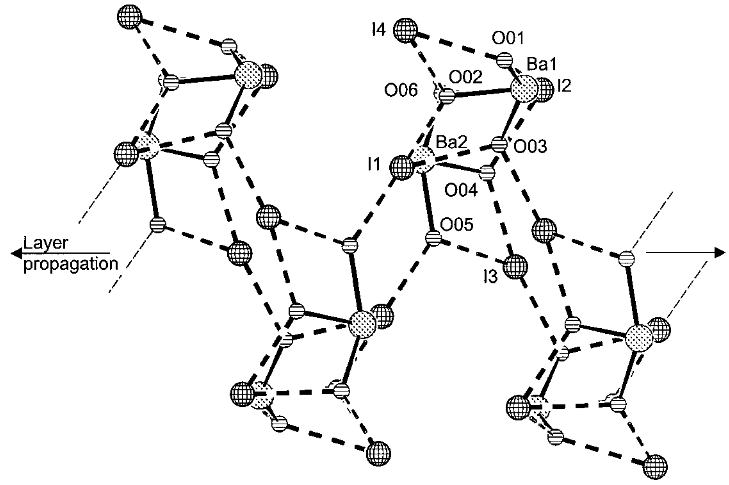


Figure 6. Hydrogen-bonding system in a layer of **3**; C atoms and the corresponding H atoms have been omitted for clarity.

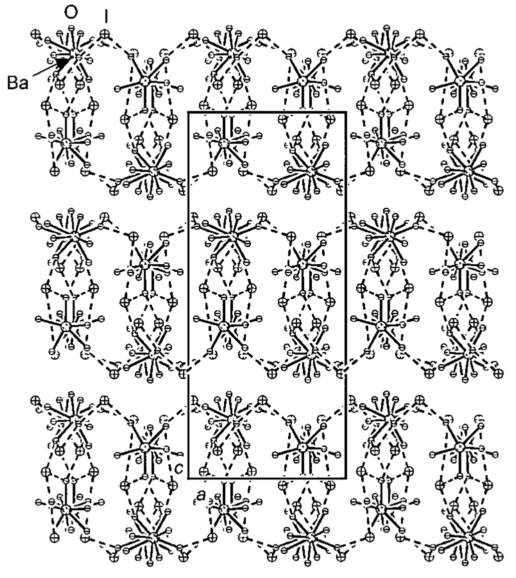


Figure 7. View onto the *ac* plane of **3**; C atoms and the corresponding H atoms have been omitted for clarity.

Their angle sum is thus rather small (200.58(7)° for I4 and 207.40(7)° for I2) relative to those of I1 and I3 as well as other μ_3-bridging iodides.[13] Thus, I1 and I3 are the μ_3-bridging ligands that connect the Ba1 and Ba2 cation pairs together to form a double layer. I1 is connected by hydrogen bonding to O02, O03, and O05 (3.466(4), 3.540(4), and 3.553(4) Å, respectively) with an angle sum of 318.95(8)°, whereas I3 holds the network together through O03, O04, and O05 (3.538(4), 3.469(4), and 3.602(5) Å, respectively) and an angle sum of 325.69(9)°. A cation formed by Ba1 is thus always bonded to iodides and to three cations of Ba2 by hydrogen bonds and vice versa, but is never directly linked to a cation of its own kind (Figure 6). The water molecules in **3** cannot be classified with certainty because the positions of the hydrogen atoms could not be determined in the crystal structure. The barium atoms in **3** have a very high valence bond sum compared with those in **1** (2.38 for Ba1 and 2.44 for Ba2) which means a better and tighter complexation by the diglyme ligands and the three water molecules in **3** than that of the two triglyme ligands and one water molecule in **1**.[12]

The structure of **3** can, to some extent, be compared with that of **2**. In **2**, there is a intramolecularly bonding I1 with a acute angle at the iodide, and an intermolecularly bridging I2 with an almost linear configuration. In **3**, I1 can be considered as the intramolecular bridging iodide for the cation formed by Ba1 with a acute angle; however, at the same time, it can also be considered as an intermolecular linker to the cation of Ba2. In the same way, I3 is intramolecularly hydrogen-bonded to cation Ba2 and represents the intermolecular bridge to the cationic unit of Ba1. In fact, the acute angles of O-I-O in **2** and **3** are comparable (≈53° and 55–56°, respectively). For I2 and I4, angles between 51° and 88° are observed.

The last example of a hydrogen-bonded polymeric compound in this series, $\{[Ca(triglyme)(H_2O)_4]I_2\}_{3/\infty}$ (**4**), was obtained from a solution of CaI_2 in triglyme as colorless blocks. It crystallizes in the monoclinic space group *C*2/*c* (No. 15).[9] The structure has already been published in a different context; however, the most important structural features are repeated here as they are helpful in the following interpretations.[14] In the cationic part of the structure, the calcium atom lies on a crystallographic twofold axis, which also passes through the geometrical center of the triglyme ligand (0, *y*, ¼(e)) (Figure 8).

The metal ion has a coordination number of eight and has the coordination geometry of a distorted square-antiprism, so that it is similar to compound **2**. The two water molecules and two oxygen atoms of the triglyme are in one square plane, the other two oxygens and two water molecules in the other plane of the prism. Both planes are inclined by 8.6(1)° with respect to each other. The calcium ion lies in between at a distance of 1.278 Å from each plane. All water molecules are involved in hydrogen bonding; each of them are linked to two iodides. Two of the oxygens, O1 and O2, of one square face of the antiprism and an iodide thus build up a ribbonlike structure in one direction. A second strand is formed by the other two water molecules, O1′ and O2′, of the second square face and their hydrogen bonding to I′, which features a direction vector of the ribbon almost perpendicular to the first (Figure 9). The corresponding O(H)–I distances are between 3.514(5) and

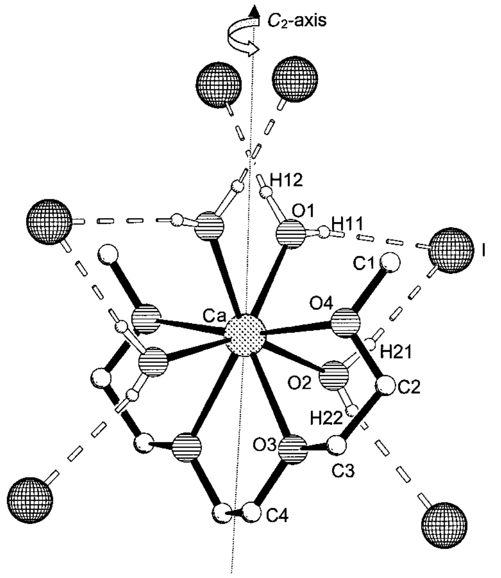


Figure 8. Complex cation of **4** and hydrogen bonding; H atoms of the polyether ligand have been omitted for clarity.

3.579(5) Å. A three-dimensional network with channels along the *c* axes with a diameter of ≈5 Å (Figure 9b) is formed. Each anion is a μ_4-bridge between three cationic [Ca(triglyme)$(H_2O)_4$]$^{2+}$ units and has contacts with two water molecules of one cationic unit and one water ligand of a second and a third unit. Crystallographic inversion centers are found in the geometric center of each O*n*-I*m*-O*n*′-I*m*′ rhombus (*m* = 1, *n* = 1; *m* = 1, *n* = 2) . The hydrogen bonds maintained by O1 and O1′ are class 1, type D, whereas O2 and O2′ are class 1′, type J.[10, 11] The valence bond sum of **4** is 2.24, which is the same as that of **2**. This indicates that the diglyme and triglyme ligands together with the corresponding water molecules are complexed to the alkaline earth metal ion with about the same strength. This is confirmed by very similar Ca–O bond lengths in **2** and **4**. A quasi-identical overall network as in **4** is obtained when the one triglyme ligand is formally substituted by two DME (DME = dimethoxyethane) ligands to yield [Ca(dme)$(H_2O)_4$]I_2, which is another example of a complex that contains four water molecules and innocent polyether ligands.[14] It also confirms the rules that can be derived from the above examples for the determination of the dimensionality from the number of water ligands involved in hydrogen bonding.

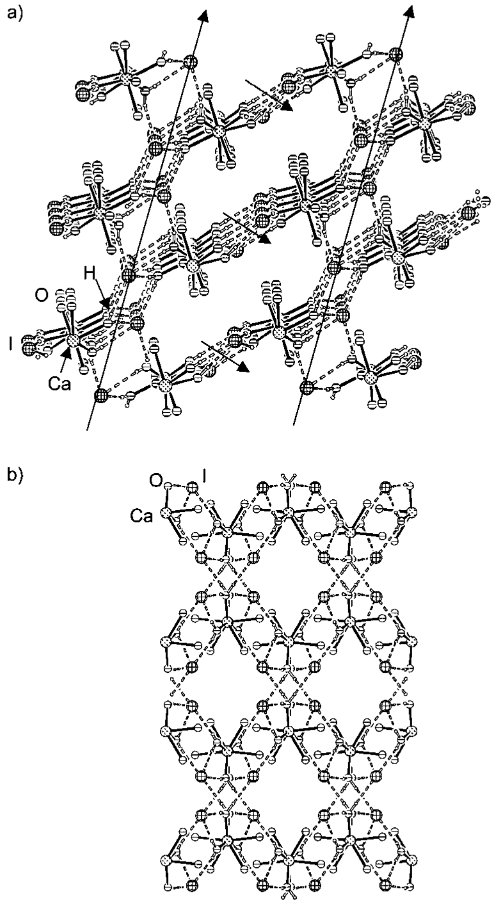


Figure 9. Views of **4** a) along the *b* axis onto the *ac* plane showing the orientation of the bands formed by hydrogen bonding; b) along the *c* axis onto the *ab* plane; C and the corresponding H atoms have been omitted for clarity.

Discussion

Comparisons: A comparison of the most important crystal structure data as well as the bond lengths and angles of all four compounds is given in Tables 2 and 3. The two barium compounds both possess the coordination number of nine at the metal center, whereas the smaller radius of the calcium cation allows only the fixation of eight oxygen atoms. In **1**, the Ba–O(triglyme) bond lengths are in average longer than the Ba–O(diglyme) bonds in **3**; this is compensated by a shorter Ba–O(H_2O) bond in **1** than those in **3**. The Ba–O(diglyme) bonds in **3** are 0.05 Å shorter than those of the known compound [Ba_2(thd)$_4$(diglyme)$_2$(μ-H_2O)][15] (Hthd = 2,2,6,6-tetramethyl-3,5-heptanedione), even though the coordination number of **3** is higher by one in this compound. This explains the extremely high valence bond sum for barium in **3** through such a tight bonding of ligands. More generally, the Ba–O-(polyether) bond lengths as well as the corresponding O-Ba-O angles are within the same order of magnitude as those found in the literature for other polyether ligands, such as tetraglyme or polyether (2.617(4)–2.995(7) Å and 55.4(4)–59.75(14)°, respectively).[16, 17, 18] The shorter Ba–O(H_2O) bond in **1** compares well to the value of 2.726(3) Å given in the literature,[17, 19] while those in **3** are ≈0.05 Å longer. However, they are still shorter than those found in a barium cryptate with the same coordination number for barium, [Ba($C_{18}H_{36}N_2O_6$)$(NCS)_2$(H_2O)][20] with 2.86 Å, or the barium compound with two water ligands involved in hydrogen bonding, [$BaL_2(H_2O)_2$]I_2[21] (L = $H_2NC_2H_4OC_2H_4OC_2H_4ONH_2$), with 2.813(5) Å, in which the barium atom has a coordination number of ten. The hydrogen-bonding system of this reported compound compares well with our calcium compound **2**: a one-dimensional polymeric structure that involves only the water molecules and the counter ions. However, the ligand L is not an innocent ligand with regards to H bonding; its NH_2 groups are also involved and thus yield an overall three-dimensional network.[21] For the two calcium compounds, all Ca–O bond lengths are in the same order of magnitude for

Table 2. Crystal data of **1**, **2**, **3**, and **4**.

	1	**2**	**3**	**4**
formula	$C_{16}H_{38}BaI_2O_9$	$C_{12}H_{32}CaI_2O_8$	$C_{12}H_{34}BaI_2O_9$	$C_8H_{26}CaI_2O_8$
M_R	765.6	598.26	713.53	544.17
T [K]	200	200	200	200
crystal size [mm]	0.2 × 0.25 × 0.48	0.32 × 0.38 × 0.46	0.21 × 0.32 × 0.42	0.07 × 0.07 × 0.58
space group	*Pbca*	*Cc*	*Pbca*	*C2/c*
crystal system	tetragonal	monoclinic	tetragonal	monoclinic
a [Å]	21.766(3)	9.470(2)	15.004(3)	9.572(2)
b [Å]	16.649(3)	16.701(3)	19.508(4)	16.306(3)
c [Å]	14.938(4)	14.880(3)	34.650(7)	12.981(3)
α [°]	90	90	90	90
β [°]	90	98.64(3)	90	105.32(3)
γ [°]	90	90	90	90
V [Å^3]	5448.2(2)	2326.7(8)	10142(4)	1954.1(7)
Z	8	4	8	4
ρ_{calcd} [g cm^{-3}]	1.867	1.708	1.869	1.850
$\mu(Mo_{K\alpha})$ [mm^{-1}]	3.761	2.951	4.033	3.504
$F(000)$	2944	1176	5440	1056
θ range	2.45–27.97	2.44–27.00	1.80–26.02	2.50–27.01
reflections collected	6151	2401	9214	1774
independent reflections	6151	2401	9214	1774
parameters	265	228	441	104
final R indices $R1/wR2$ [$I > 2\sigma(I)$][a]	0.0277/0.0614	0.0245/0.0641	0.0619/0.1425	0.0396/0.0872
R indices (all data) $R1/wR2$	0.0335/0.0540	0.0246/0.0643	0.1106/0.1760	0.0603/0.1022
GOOF[b]	0.679	1.116	1.029	1.147

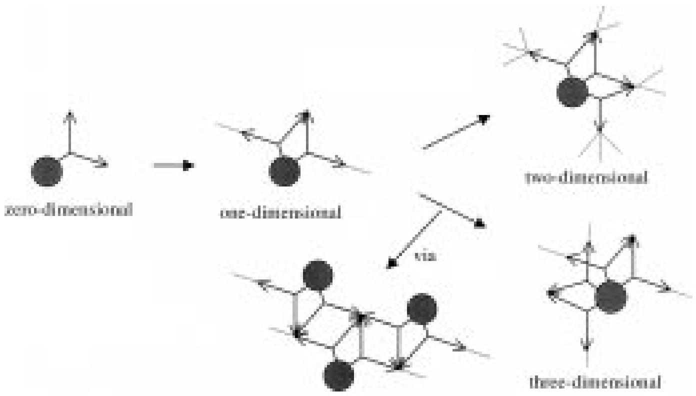
[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]\}^{1/2}$. [b] $\text{GOOF} = S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$; n = no. of reflections, p = no. of parameters. Weighting scheme: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ in which $P = [2F_c^2 + \text{Max}(F_o^2,0)]/3$.

Table 3. A comparison of the most important structural features of **1**, **2**, **3**, and **4**.

	1	**2**	**3**	**4**
number of H_2O	1	2	3	4
dimensionality	0	1	2	3
coordination number	9	8	9	8
M^{2+}–O(glyme) [Å]	2.832(3)–2.939(4)	2.433(4)–2.492(4)	2.785(10)–2.884(10)	2.487(5)–2.506(4)
M^{2+}–O(H_2O) [Å]	2.730(4)	2.384(5), 2.390(5)	2.742(10)–2.792(9)	2.392(4), 2.424(5)
O(H)–I [Å]	3.432(6), 3.529(5)	3.476(6)–3.528(6)	3.466(8)–3.670(9)	3.514(5)–3.579(5)
O(H)-I-O(H) [°]	–	53.94(2), 173.5(3)	51.28(8)–153.64(12)	50.77(6)–82.55(7)
I-O-I [°]	128.58(8)	105.80(7)–115.75(7)	105.51(9)–129.96(12)	99.09(5)
O-M^{2+}-O(glyme) [°]	56.3(1)–59.4(1)	65.1(1)–66.8(1)	57.5(4)–60.2(3)	62.3(2)–65.1(2)
O-M^{2+}-O(H_2O) [°]	–	79.4(2)	70.3(3)–73.3(3)	70.0(3), 71.4(10)

compounds **2** and **4**. In **2** the water ligands are bonded slightly more tightly than in **4**, whereas in **4**, the polyether ligand is bonded, on average, closer to the cation. All the Ca–O(polyether) bond lengths of **2** and **4** lie within the range found for other diglyme or polyether carboxylate adducts of calcium (2.430(2)–2.625(4) Å), and so do the O-Ca-O angles (62.5(3)–65.99(14)).[22, 23] The Ca–O(H_2O) bond lengths in **2** and **4** are ≤0.1 Å longer than those found in the literature for complexes that have the same coordination number at the metal atom,[24] and ≤0.05 Å shorter than the Ca–O(H_2O) bond in the seven-coordinated compound [Ca($C_{18}H_{24}O_7$)(NCS)$_2$(H_2O)].[25] Extremely long Ca–O(H_2O) bond lengths are observed in [Ca([18]crown-6)(H_2O)$_2$]Cl_2 · 2 H_2O, in which the calcium has a coordination number of eight; however, the two water molecules in *trans* positions of a hexagonal bipyramid are bonded at 2.555(8) Å.[26] The O(H)–I hydrogen bond lengths become longer in average when going from **1** to **4**, while those in **3** and **4** are the same, within standard deviations. This might be explained by the difference in the functionality of the iodide, which varies from a terminal ligand in **1** to μ_2-bridging in **2**, μ_3-bridging in **3**, to μ_4-bridging in **4**. The bite angles in the triglyme ligands of **1** are 3–9° smaller than those in **4**. The same order of magnitude of difference is observed when the bite angles of the diglyme ligands in **3** are compared to those of **2**. This is probably the result of the different cationic radii of Ca^{2+} and Ba^{2+} as well as the resulting difference in the coordination numbers. The O-I-O angles are become smaller as the iodide bridges more and more water molecules (from **2** to **4**). On average, the O-M^{2+}-O angles between adjacent water ligands become smaller as the number of water molecules complexed to the metal cation is increased.

Structural relationships: As there are rules for the construction of different dimensional networks, the structures should also be related to each other by some constant structural features (Scheme 1). In fact, several similarities can be observed for the two barium compounds. Thus, compound **3** can be derived from compound **1** when one terminal oxygen atom of each triglyme ligand in **1**, that is O1 and O5 in vicinal positions to the water ligand O9, is formally replaced by one water molecule and the triglyme ligands are exchanged by diglyme molecules to give the same coordination number of barium in both structures. The relationship between the two calcium structures is even more fascinating. It can be explained by the strand structure of **2**: taking two such strands, so that the intramolecularly bridging iodides point upwards in one and downwards in the other, these are sheared by half an asymmetric unit in direction of the chains and then fused together to form ribbons in one direction of the structure of **4**. In order to obtain a three-dimensional network, two more water molecules have to be introduced on each of the calcium atoms of each cationic unit, formally exchanging the two diglyme ligands by one tetraglyme and two water ligands, so that all water ligands are vicinal and in approximately one plane.



Scheme 1. Schematic representation of the structural evolution from **1** to **4** via **2** and **3**. Gray spheres: $[M(L)_n]^{2+}$ (M = Ca, Ba; L = polyether ligand; $n = 1$ or 2); lines emerging from the spheres = bond to H_2O; arrows = hydrogen bond from H_2O (base) to I^- (tip).

Hydrogen bonding and dimensionality: The dimensionality changes from zero to three in compounds **1** to **4**. How can this be accounted for? The following conditions are the same for all four compounds: i) the cations are all complexes with a charge of +2, ii) the counterions, two iodides per cation for all cases, have a charge of −1 and are the only H-bond acceptors, iii) the M^{2+} cations are complexed by two types of neutral ligands, namely polyethers and water; the latter are arranged in vicinal positions, iv) only the water molecules are involved in hydrogen bonding, and v) each hydrogen of all water molecules forms a single hydrogen bond to iodide, and that two hydrogen atoms of the same water molecule do not bind to the same iodide. Therefore, the only variable is the bridging functionality of iodide and the number of water ligands per complex cation. Iodide is a very versatile ligand with regard to the number of hydrogen bonds that it can accept: up to 10 as reported for $[Ca_2Al(OH)_6]I \cdot 2H_2O$.[27]

In compound **1**, two hydrogen atoms that are potential hydrogen donors come from a single water molecule. To account for the charge of the complex cation, the two iodides can either be linked by hydrogen bonding or included in the structure as free counterions. As the number of iodides equals the number of hydrogens, they will act as terminal ligands on the hydrogen atoms, saturating the latter, and the structure will not be polymerized by further hydrogen bonding. In compound **2**, the number of water molecules, and thus the number of hydrogen donors, is double that of **1**, whereas the number of iodides remains constant at two. Because the iodide can accept more than one hydrogen donor and there are four H-bond donors and only two acceptors, each iodide will act as a μ_2-bridging ligand to give an overall one-dimensional chain structure with one intramolecular bridge between two water molecules of the same cation and one intermolecular bridge between two water molecules of neighboring cations. Compound **3** possesses three water molecules in the coordination sphere of barium. Therefore there are six hydrogen donors compared to two iodide anions as H-bond acceptors. In this case, the iodides act as μ_3-bridging ligands: all anions link two water molecules of the same cation to a water molecule of a neighboring complex. The overall structure obtained in this way is two-dimensional. In compound **4**, there are four times as many hydrogen donors as acceptors present in the structure. Each iodide acts as a μ_4-bridging ligand to four different water molecules, two of them belonging to one and the same cation, the other two to two different cations. This leads to the formation of a three-dimensional network.

Conclusion

It can be seen that the number of hydrogen bonds formed and the bridging functionality of the anions plays a crucial role in the determination of the overall dimensionality of a compound. From the examples given in this paper, certain rules might be derived which seem to be valid under the conditions given above. When the number of H acceptors is the same as the number of hydrogens, a zero-dimensional compound should be expected. Doubling the number of H atoms in relation to the H acceptors will give a one-dimensional structure, whereas a 3:1 ratio of hydrogen atoms to H acceptors implements the formation of two-dimensional networks. Increasing the ratio of H atoms to H acceptor anions to >3:1, further networking becomes necessary in order to saturate all hydrogen atoms, and this takes place through the μ_n-bridging, $n \geq 4$, of the anions, leading to more complicated three-dimensional H-bonded structures. These rules are summarized in the Table 4.

It can thus be seen that the concept of predicting the overall dimensionality and, to some extent, the structure is feasible if the possibilities of hydrogen bonding that are available between the ligands on the cation and the anions are carefully considered. In our case, we decided to choose simple systems in order to exclude interference from different types of hydrogen bonding. Now that these rules have been verified, we plan to investigate more complicated systems in order to obtain more insight into the possibilities of structure prediction.

Table 4. Summary of the general rules of how the different dimensional structures can be predicted.

No. H_2O in the molecule	Ratio H:I	Possible role of iodide	Overall structure
1	1:1	no further contacts	discrete molecules
2	2:1	μ_2-bridging ligand linking 2 H of the same or of neighboring cationic units	chains
3	3:1	μ_3-bridging ligand	sheets
4	4:1	$\geq\mu_3$-bridging ligand	3D network

Experimental Section

All reactions were carried out on a vacuum line by Schlenk techniques, with nitrogen as the inert gas. BaI_2 and CaI_2 were purchased from Merck and Aldrich, respectively, and dried under vacuum at 300 °C before use, except for **4**. IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrometer on KBr plates and in dried Nujol.

$\{[Ba(triglyme)_2(H_2O)]I_2\}_{0/\infty}$ (1): BaI_2 (0.3 g, 0.77 mmol) was treated with triglyme (25 mL, dried over a molecular sieve (4 Å) and freshly distilled before use) containing 1‰ water, and the mixture heated to reflux for 10 min and filtered while hot. Colorless single crystals of **1** were obtained on cooling the mixture to room temperature over 24 h. Rodlike single crystals were collected in a yield of 12% with respect to Ba. A higher yield was obtained when the mother liquor was concentrated; this gave **1** as a white powder. The crystals were washed rapidly with cold *n*-pentane and used for elemental and IR analyses. IR: $\tilde{\nu} = 3394$ (m, sh), 2917 (Nujol), 2747 (w), 2065 (w), 1937 (w), 1595 (m), 1455 (Nujol), 1403 (m), 1369 (s), 1352 (Nujol), 1304 (s), 1276 (m), 1247 (m), 1200 (m), 1114 (s, sh), 1024 (m), 983 (m), 944 (m), 933 (m), 854 (m), 840 (m), 823 (m, sh), 722 (Nujol), 666 (w), 529 (m, sh), 353 (w), 291 (w), 233 cm^{-1} (w); elemental analysis calcd (%) for $C_{16}H_{38}BaI_2O_9$: C 25.10, H 5.00, Ba 17.94; found: C 21.98, H 4.6, Ba 17.23. The percentage of carbon is too low. This is probably caused by the formation of very stable carbonates during combustion.

$\{[Ca(diglyme)_2(H_2O)_2]I_2\}_{1/\infty}$ (2): CaI_2 (0.42 g, 1.43 mmol) was dissolved by heating in freshly distilled diglyme (50 mL) that contained 1% H_2O. The mixture was filtered while hot. On slow cooling to room temperature, rodlike single crystals of **2** were obtained in a yield of 36% with respect to Ca. IR: $\tilde{\nu} = 3385$ (s), 3015 (m), 2933 (Nujol), 2248 (w), 2075 (w), 1609 (s), 1456 (Nujol), 1377 (m), 1356 (Nujol), 1292 (m), 1244 (m), 1202 (m), 1092 (s, sh), 1011 (m, sh), 935 (m), 863 (m), 836 (m), 807 (w), 721 (Nujol), 583 (m, sh), 364 (w), 301 (w), 227 cm^{-1} (w); elemental analysis calcd (%) for $C_{12}H_{32}CaI_2O_8$: C 20.20, H 4.80, Ca 6.70; found C 16.12, H 4.41, Ca 6.5.

$\{[Ba(diglyme)_2(H_2O)_3]I_2\}_{2/\infty}$ (3): The same procedure was used as for **2** but with BaI_2 (0.51 g, 1.3 mmol) and freshly distilled diglyme (50 mL). Yield: 31% with respect to Ba. Because of the strongly hygroscopic reaction of **3** when in contact with the atmosphere, it was not possible to obtain a correct elemental analysis. IR: $\tilde{\nu} = 3373$ (s), 2924 (Nujol), 2031 (w), 1571 (s), 1460 (Nujol), 1376 (Nujol), 1304 (m), 1154 (m),1077 (m), 966 (m, sh), 891 (m), 769 (m), 722 (Nujol), 667 (w), 355 (w), 246 (w), 233 (w) cm^{-1}.

$\{[Ca(triglyme)(H_2O)_4]I_2\}_{3/\infty}$ (4): $CaI_2 \cdot 5H_2O$ (0.46 g, 1.23 mmol) was dissolved in triglyme (50 mL). The light yellow solution was layered with *n*-hexane and left to diffuse at room temperature. Colorless single crystals of **4** were obtained after three days in a yield of 23% with respect to Ca. The compound is very stable at air and room temperature. IR: $\tilde{\nu} = 3381$ (m), 3182 (m), 2929 (Nujol), 1958 (w), 1603 (s), 1456 (Nujol), 1350 (Nujol), 1285 (m), 1247 (s), 1199 (vs), 1110 (vs), 1028 (sh), 982 (m), 943 (s), 848 (vs, sh), 723 (Nujol), 540 (s, sh), 389 (w), 347 (m), 238 cm^{-1} (m); elemental analysis calcd (%) for $C_8H_{26}CaI_2O_8$: C 17.66, H 4.82, Ca 7.37; found C 17.52, H 4.68, Ca 7.48.

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[9] Crystals of **1**, **2**, **3**, and **4** were measured on a STOE IPDS diffractometer with monchrimated graohite $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å. The structures were solved with direct methods and refined by full-matrix least-squares on F^2 with the SHELX-97 package.[28] All heavy atoms could be refined anisotropically. The positions of the water hydrogen atoms could be located except for **3**, the positions of the hydrogen of the polyether ligands were calculated with a riding model. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-152924 for **1**, CCDC-152925 for **2**, CCDC-152926 for **3** and CCDC-141688 for **4**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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