Recent Advances in the Chemistry of "Clusters" and Coordination Polymers of Alkali, Alkaline Earth Metal and Group 11 Compounds

6 AUTHORS, INCLUDING:

Katharina M. Fromm
Université de Fribourg
131 PUBLICATIONS **3,216** CITATIONS

SEE PROFILE

Adeline Y Robin
The Walter and Eliza Hall Institute of Medic…
29 PUBLICATIONS **1,477** CITATIONS

SEE PROFILE

William Maudez
3D-Oxides
11 PUBLICATIONS **193** CITATIONS

SEE PROFILE

Jorge Sague
Robert Mathys Stiftung Foundation
15 PUBLICATIONS **271** CITATIONS

SEE PROFILE

Forschungsbericht − Research Report

Recent Advances in the Chemistry of "Clusters" and Coordination Polymers of Alkali, Alkaline Earth Metal and Group 11 Compounds

Katharina M. Fromm*, Estelle D. Gueneau, Adeline Y. Robin, William Maudez, Jorge Sague, and Rémi Bergougnant

Basel/Switzerland, University, Department of Chemistry

Abstract. This contribution gives an overview on the different subjects treated in our group. One of our fundamental interests lies in the synthesis and study of low-dimensional polymer and molecular solid state structures. We have chosen several synthetic approaches in order to obtain such compounds.

Firstly, the concept of cutting out structural fragments from a solid state structure of a binary compound will be explained on behalf of BaI_2. Oxygen donor ligands, used as chemical scissors on BaI_2, allow obtaining three-, two-, one- and zero-dimensional derived compounds depending on their size and concentration. Thus, a structural genealogy tree for BaI_2 can be established. This method, transferred to alkali halides using crown ethers and calix[n]arenes as delimiting ligands, leads us to the subject of one-dimensional ionic channels.

A second chapter deals with the supramolecular approach for the synthesis of different dimensional polymer structures derived from alkaline earth metal iodides, and based on the combination of metal ion coordination with hydrogen bonding between the cationic complexes and their anions. Under certain circumstances, rules can be established for the prediction of the dimensionality of a given compound, thus contributing to the fundamental problem of structure prediction in crystal engineering.

A third part describes a fundamentally new synthetic pathway for generating pure alkaline earth metal cage compounds as well as alkali and alkaline earth mixed metal clusters. In a first step, different molecular precursors, such as solvated alkaline earth metal halides are investigated as a function of the ligand size and reactivity. They are then reacted with some alkali metal compound in order to partially eliminate alkali halide and to form the clusters. The so obtained unique structures of ligand stabilized metal halide, hydroxide and/or alkoxide and aryloxide aggregates are of interest as potential precursors for oxide materials. Approaches to two synthetic methods of the latter, sol-gel and (MO)-CVD, are investigated with our compounds.

In order to generate single source precursors for oxide materials, we started to investigate transition metal ions, especially Cu and Ag, using multitopic ligands. This has led us into the fundamental problematic of "crystal engineering" and solid state structure prediction and we found ourselves confronted to numerous interesting cases of polymorphism and pseudo-polymorphism. Weak interactions, such as π-stacking, H-bonding and metal-metal interactions, and solvent, counter ion and concentration effects seem to play important roles in the construction of such low-dimensional structures.

Finally, the physical properties of some of our compounds are described qualitatively in order to show the wide spectrum of possibilities and potential applications for the chemistry in this field.

Keywords: Alkali metals; Alkaline earth metals; Coordination polymers; Clusters; Cage compounds; Structural investigations; Structure prediction

Introduction

We got interested in the non-aqueous chemistry of alkali and alkaline earth metal elements for several reasons: i) the chemistry of alkali and alkaline earth metal compounds in water can best be described as ionic whereas not much was known about their behaviour in organic solvents; ii) alkali and alkaline earth metal clusters − in the sense of aggregates or cage compounds − were observed as by-products in metallation reactions in organic chemistry which encouraged us to make such compounds on purpose; iii) we wanted to know whether there is an analogy in the clusters of group 1 and 2, and transition metal clusters, i. e. of group 11; iv) concerning the "covalent" polymers, the principle of cutting out structural fragments from a solid state structure with chemical scissors was to be tested; v) single source precursors for the chemical vapour deposition or sol-gel technique in the synthesis of oxide materials are scarce; and vi) we wanted to contribute to the problem of structure prediction in the case of supramolecular coordination polymers. Applications for such alkali and alkaline earth metal compounds can be found in many fields, such as metallation reactions and superbases in organic chemistry, biomineralization and biomimetics as far as biology is con-

* Prof. Dr. K. M. Fromm
University of Basel
Department of Chemistry
Spitalstrasse 31
CH-4056 Basel
Tel. : +41 61 267 1004
Fax: +41 61 267 1021
E-mail: katharina.fromm@unibas.ch
www.unibas.ch

Curriculum vitae of the principal author

Katharina M. Fromm, born in Germany and raised in France, Germany and USA, studied chemistry at the University of Karlsruhe, Germany, and the EHICS (Ecole des Hautes Etudes des Industries Chimiques de Strasbourg) in Strasbourg, France, with an Erasmus stipend. Back at the University of Karlsruhe, she started her thesis, supported by a Landesgraduierten-grant, in the group of Prof. Dr. E. Hey-Hawkins (currently at the University of Leipzig). In 1994, she received her Ph.D. from the University of Karlsruhe with a preparative work on the "Synthesis of new mono-cyclopentadienyl substituted Phosphido-Complexes of Mo, Nb and Ta". A postdoctoral stipend from the Deutsche Forschungsgemeinschaft (DFG) allowed her to start her own independent research on alkaline earth metal halides in the group of Prof. Dr. J. Strähle at the University of Tübingen. During a postdoctoral stay in the group of Prof. Dr. J.-M. Lehn at the University of Strasbourg, France, she got introduced to supramolecular chemistry. Postdocs in the groups of Prof. Dr. D. Fenske and Prof. Dr. R. Ahlrichs in Karlsruhe completed her training in cluster and theoretical chemistry, before she moved to the University of Geneva, Switzerland, where she started her habilitation in the group of Prof. Dr. A. F. Williams in 1998. Her research interests focused on alkali and alkaline earth metal compounds in non-aqueous solvents. After her habilitation in 2002, she was offered an Emmy-Noether-Programm, Phase II, by the DFG, a C3-position at the University of Erlangen, Germany, and a research professorship (Förderprofessur) from the Swiss National Science Foundation at the University of Basel, Switzerland, which she accepted in May 2003. Since then, her group is steadily growing, maintaining research interests in group 1 and 2 chemistry, and, furthermore, in ion transport channels, and group 11 coordination networks.

cerned, or precursors for superconductors or other oxide materials required for physical applications. For the latter, thin films of such materials are currently in the focus of research, and therefore we aimed at the synthesis of precursors for thin film synthesis methods such as the sol-gel or chemical vapour deposition (CVD) technique.

This article will review the different research subjects in our group, starting with the inorganic "covalent" polymers, the approach of alkali metal ions with crown ethers and calix[n]arenes to build channels, followed by the supramolecular coordination polymers of alkaline earth metal ions, a survey of our cluster compounds, and ending with Cu^I, and Ag^I coordination polymers before concluding about the properties and some potential applications.

Results and Discussion

1 Inorganic "covalent" polymers

The aim of this part of the project consists in the principle of cutting out structural fragments from a three-dimensional compound, using chemical scissors and by maintaining parts of the initial structure [1, 2]. In order to make a choice on which "bonds" to "cut", these bonds need to be different for instance in strength, and the most obvious parameter to look at is thus the bond lengths. A good starting material is for instance BaI_2, which possesses a $PbCl_2$-type structure in the solid state, with the alkaline earth metal ion surrounded by nine iodide ions in form of a distorted, tri-capped trigonal prism (Fig. 1a). This leads to very different Ba−I distances, seven of which are comprised between 3.3 and 3.6 Å, and the other two are approximately 4.1 Å long. The idea is to use chemical scissors in order to "cut" along the longest bonds in the structure and to, successively, cut out structural fragments. Indeed, with H_2O acting as chemical scissor on BaI_2, the three-dimensional compound $[BaI_2(\mu_2\text{-}H_2O)_2]$ (**1**) can be isolated (Fig. 1b). Compared to BaI_2, the longest Ba−I-contacts are cut, the trigonal prism of iodide around the cation is maintained, whereas the three capping anions are replaced by four μ_2-bridging water molecules. The remaining Ba−I contacts are six of the shorter ones and are found between 3.3 and 3.6 Å. Upon substitution of one of the two bridging water molecules by a sterically more demanding oxygen donor ligand like acetone $(CH_3)_2CO$ to yield $[BaI_2(\mu_2\text{-}H_2O)\{(CH_3)_2CO\}]$ (**2**), a two-dimensional structure is obtained with the acetone ligand in a terminal position (Fig. 1c). In fact, the bulky CH_3-groups allow separation of the layers from each other. Still, the trigonal prismatic arrangement of the six iodide ions around barium is maintained [1].

Using a sterically even more demanding donor ligand like THF, two derivatives of BaI_2 can be obtained depending on the quantity of "chemical scissors" used. With three THF-molecules per BaI_2 unit, a one-dimensional polymer $[BaI_2(thf)_3]$ (**3**), is obtained, in which only four Ba−I bonds are maintained to yield a zig-zag chain motif (Fig. 1d). The

remaining coordination sites on the cation are filled with the bulky THF-ligands to lead to the coordination number of seven for barium. Two more Ba—I bonds can be cut by adding more THF to yield the zero-dimensional [BaI$_2$(thf)$_5$] (**4**), in form of a pentagonal bipyramid with the anions in axial positions (Fig. 1e). The Ba—I bonds become shorter as their number per cation as well as its coordination number decreases to reach 3.374 Å, which is consistent if not shorter than the sum of ionic Shannon radii [1 and therein].

Figure 2 Excerpt of the one-dimensional structure of **5**

Figure 1 Structural genealogy tree for compounds derived from BaI$_2$

It was thus possible to establish a structural genealogy tree for BaI$_2$ which could also be transferred to SrI$_2$ and Ba(OTf)$_2$ (OTf = CF$_3$SO$_3$$^-$) [3]. Whereas the structures for the corresponding SrI$_2$-derivatives are similar to the presented BaI$_2$-adducts, other structures are obtained for barium triflate. Using THF as scissor on this starting material leads to the resulting compound which is a one-dimensional THF-adduct of Ba(OTf)$_2$, [{[Ba(OTf)$_2$(thf)$_3$]$_2$[Ba(OTf)$_2$(thf)$_2$]}$_{1/\infty}$ (**5**). The asymmetric unit is complicated to describe: it consists of two barium atoms Ba1 and Ba2 with a different coordination sphere each, two THF-molecules and six triflate ligands for the former, three THF-ligands and five triflate anions for the latter. The coordination sphere of Ba1 is filled by eight oxygen atoms in form of a square antiprism. It is coordinated by six triflate anions, of which four are μ$_3$- and two are μ$_2$-bridging ligands, as well as two terminal THF-molecules (Fig. 2). For Ba2, the coordination sphere is different with five triflate anions, four of them μ$_3$-bridging and one μ$_2$-bridging, and three terminal THF-ligands. The coordination sphere is quasi the same as for Ba1, a distorted square antiprism [3].
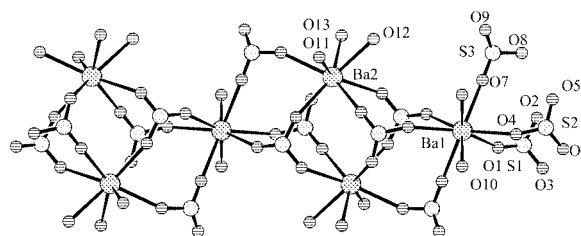
The crystal structure of Ba(OTf)$_2$ has not been investigated yet to our knowledge, but the IR-spectra seem to indicate tridentate triflate ligands corresponding to a similar structure of the compound as for other M(OTf)$_2$ compounds, M = Ni, Co, Zn, Cd [4]. Many of such triflates have a layered structure and thus a two-dimensional array. The one-dimensional compound **5** can therefore be considered as excerpt of such a structure. Furthermore, the literature known complex [{Ba(OTf)$_2$}$_4$(py)$_{14}$].py [5] can be considered as an excerpt from the crystal structure of **5**, regarding the structural part containing barium cations and triflate anions. [3] Pyridine seems to be a stronger chemical scissor than THF in this context.

We are now investigating other binary compounds, also of transition metals and lanthanides, in which very different bond lengths are observed to proceed similarly. This is insofar of interest as such low-dimensional compounds possess an intrinsic anisotropy, which can be fundamental for the expression of their physical properties.

As alkali metal iodides present the same M—I bonds in all directions, crown ethers were used to apply our strategy of cutting out fragments from a solid state structure. So far, this lead to the isolation of molecular species [Na⊂(DB18C6)I(L)], L = THF, (**6**), 1, 3-dioxolane, (**7**), in which the sodium cations are coordinated in an asymmetric fashion (Fig. 3a and 3b) [6].

Using larger crown ethers such as DB24C8 yields [Na⊂(DB24C8)]I (**8**), in which the cation is completely wrapped up by the ligand, leading to charge separation, and the iodide is no longer coordinated to the cation (Fig. 3c). Channels containing for instance one-dimensional NaI in DB18C8 could not be isolated so far. However, using protons as pseudo-alkali metal ion, and working with HI, I$_2$ and DB18C6 in THF and water as solvent mixture, a high yield of dark red needle-like single crystals of the composition [(H$_3$O)⊂(DB18C6)(H$_2$O)][(H$_2$O)⊂(DB18C6)(H$_2$O)]I$_3$ (**9**), (Fig. 4) is obtained [7, 8]. Its structure consists of almost perfectly stacked crown ether ligands, each coordinating to oxygen atoms in their centre. These central oxygen atoms are linked to each other via other bridging oxygen atoms. Hydrogen atoms could not be located in the solid state structure. However, the ligands in one of the two channels are more distorted than in the other, forming the less well packed channel. Attributing this distortion to a strong influence such as provoked by a positive charge, we concluded that this channel carried the positive charges
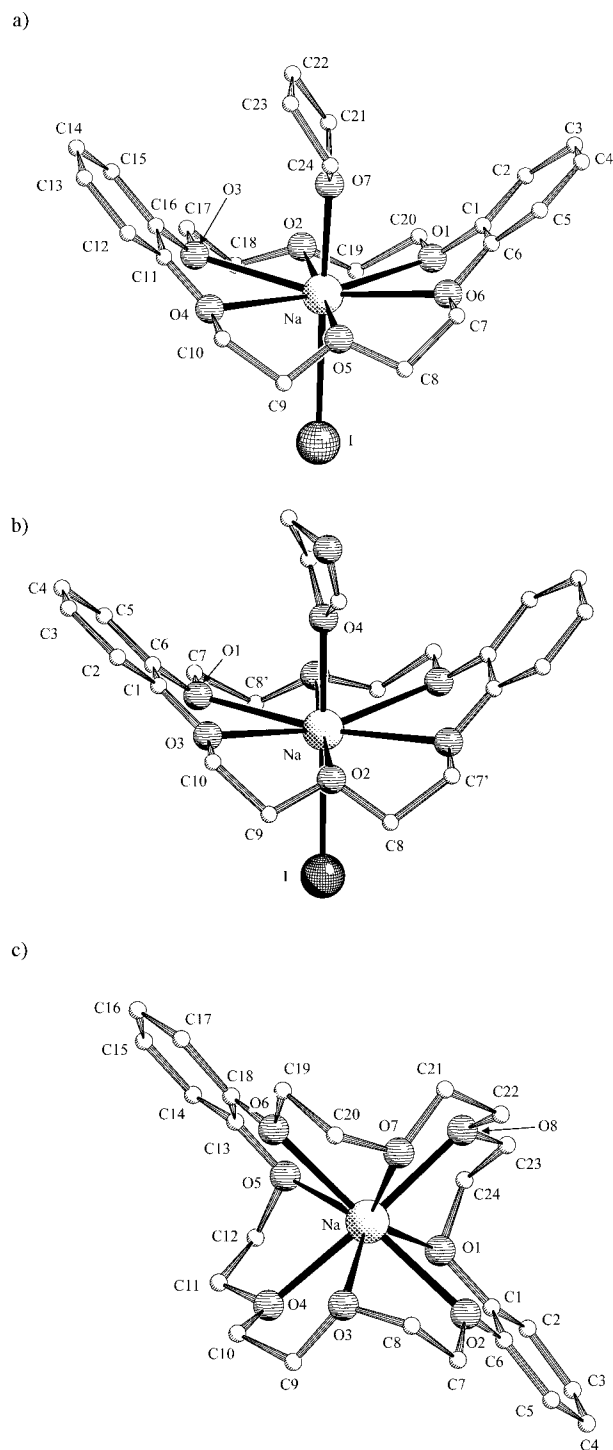
a)

b)

c)

Figure 3 Molecular structure in the solid state of **6** (a), **7** (b) and **8** (c)

Figure 4 Side-view of the one-dimensional strands formed in **9**

and could therefore be considered as the $[(H_3O) \subset (DB18C6)(H_2O)]$ part of the structure. It is only the second solid state structure known in literature in which the di-benzo crown ether molecules are stacked in such a fashion [9], and it is the first time to have one-dimensional water and acid isolated in such channels [7].
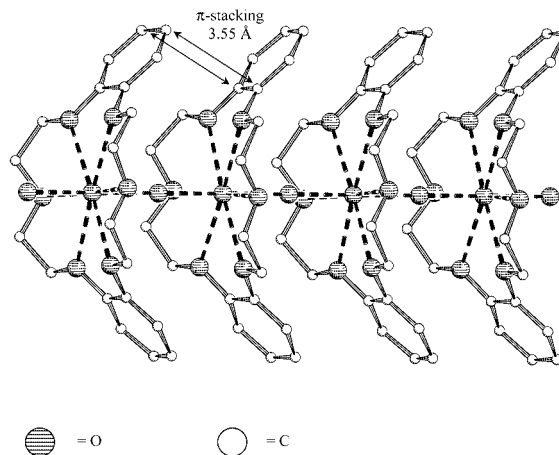
Other potential channel-formers are calix[n]arenes, which have been presented in earlier research reports in the context with transition metals [10]. We are interested in the alkali metallated species of these calix[n]arenes, as they are often used as intermediates in solution for the generation of transition metal derivatives. Little is known about the structures of such intermediate species, and the very few examples that have been isolated to date show interesting structural motifs. The low number of examples in the literature is probably due to the fact that these compounds do not easily crystallize, they are fragile towards hydrolysis, and their structure seems to be very much dependent on the presence, size and quantity of further donor ligands, stabilising the lithiated or otherwise metalated compound [11]. Single crystal structures containing these ligands are always a challenge insofar as calix[n]arenes can have different conformations. While working with tert-butyl-calix[4]arenes, we always observed the cone structure in the solid state so far. In a first step, complete metallation of the latter was achieved with each, LiO^tBu and KO^tBu in THF.

When calix[4]arene is treated with LiO^tBu in THF at room temperature, colourless single crystals of $[Li_8(calix[4]arene-4H)_2(thf)_8] \cdot 6THF$ (**10**) are obtained [11]. The molecular unit of **10** consists of two face-sharing Li_4O_4-heterocubanes with an inversion centre in the geometrical middle of the central $Li2-O3-Li2'-O3'$-ring (Fig. 5a). Half of the oxygen atoms O2, O3 and O4 stem from the first calixarene, the other three O2′, O3′ and O4′ from the second calixarene ligand. Four lithium atoms, Li1, Li2 and their symmetry equivalents, lie between the two calixarene molecules, whereas Li3 points into the cavity of the deprotonated ligand and is bonded *endo*. It finds its tetrahedral coordination sphere completed by the oxygen atom O5 of a THF molecule fitting into the cavity of the calixarene, introducing itself from the larger side of the conical ligand featuring the *tert*-butyl groups. Li4 is bonded *exo* to only one oxygen atom of a calixarene ligand, and is further coordinated by three terminally bonded THF molecules linked via O6, O7 and O8. Two oxygen atoms of the calixarene ligand, O2 and

O4, act as μ_3-bridging ligands on three lithium atoms of the heterocubane system. One oxygen atom, O3, can be considered as μ_4-bridging donor atom with three short Li−O bonds. This arrangement gives a coordination number of four to all six lithium atoms in the di-heterocubane unit. Weak interactions of Li3 with the carbon atoms at the basis of three aromatic rings, C17, C28 and C39, can additionally be discussed.
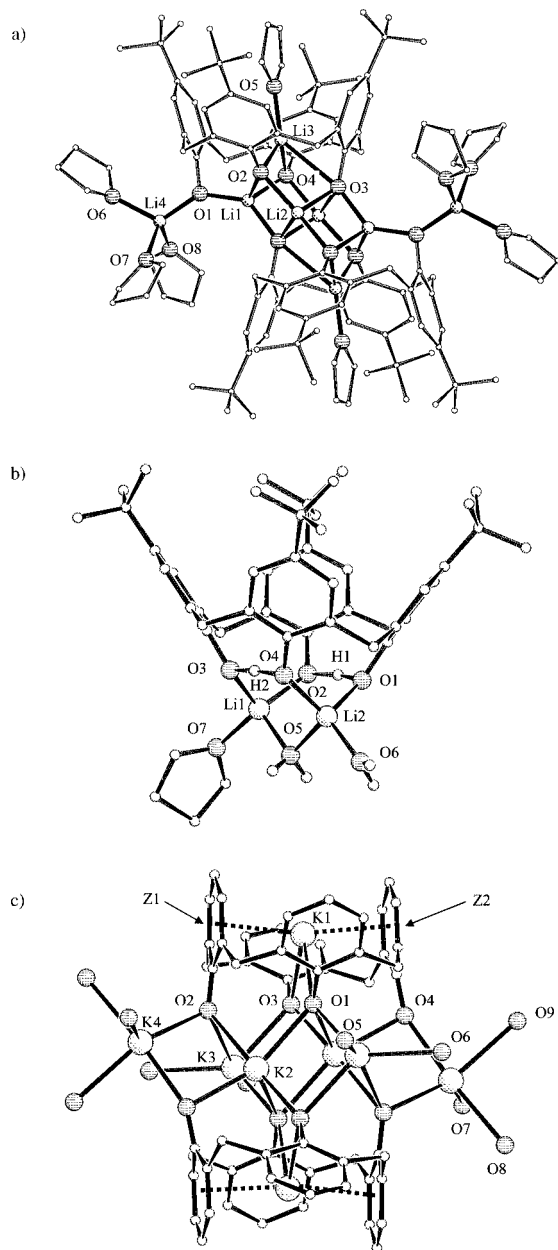

Figure 5 Structures of the cluster molecules of **10** (a), **11** (b), and **12** (c)

The literature known compound $[(L^1)_2Li_8(HMPA)_4]$ (L^1 = *p-tert*-butylcalix[4]arene) forms a fully lithiated calix[4]arene species in which also a dimeric structure is observed [11]. The lithium skeleton of $[(L^1)_2Li_8(HMPA)_4]$ can be described as two edge-sharing square pyramids, one oriented pointing upwards, the other downwards. The apical lithium ions of $[(L^1)_2Li_8(HMPA)_4]$, bonded *endo* to the calixarene, possess only a coordination number of three, as the solvent and ligand HMPA is too large to enter the upper rim cavity of the calixarene. Thus, the size of the ligand, on one hand the smaller THF and on the other the larger HMPA, determines the overall structure of the alkali metal cluster formed by the lithiated calixarene in this case.

Further studies concerning the ability of calix[4]arenes L^1 to form monomeric lithiated derivatives, and the reactivity of **10** towards hydrolysis, lead to the formation of a partially hydrolysed compound identified as the monomeric species $[Li_2(L^1\text{-}2H)(H_2O)(\mu\text{-}H_2O)(thf)]\cdot3THF$ (**11**) [11]. The crystal structure of **11** is quite remarkable because partial hydrolysis of the fully deprotonated and lithiated dimeric compound **10** could also have lead to the formation of dimeric species such as those already known in the literature for the zinc derivative of L^1, $[Zn_2(L^1\text{-}2H)_2]$ [12]. The molecular unit of **11** consists of a twice deprotonated *p-tert*-butylcalix[4]arene (Fig. 5b). Two remaining lithium atoms Li1 and Li2 still bind to the "lower rim" of the calixarene cavity. The coordination sphere of Li1 is completed with the oxygen atom O7 of a THF molecule and the oxygen atom O5 of a water molecule. The latter is a μ_2-bridging ligand and connects also to Li2, whose coordination sphere is completed by the oxygen O6 of a second water molecule in terminal position. This leads to a near-tetrahedral geometry for the lithium ions. In d_8-THF solution, the ^{7}Li spectrum is composed of two broad signals indicating the non-equivalence of both lithium atoms in **11**. The ^{1}H-NMR spectrum of **11** exhibits a pair of doublets in the −CH$_2$ region (δ 3.1 to 4.3 ppm), indicative of the cone conformation for the calixarene in THF solution. In the case of calix[4]arene, this cone-shape is usually retained upon metallation, indicating that the solid state structure is maintained in solution. In the solid state, the two remaining phenolic protons H1 and H2 could be localized in the structure, and form intramolecular hydrogen bonds between O1 and O2, and O3 and O4 respectively.

In order to complete our family of calixarenes complexes with larger alkali metal ions, in a similar synthetic pathway, reaction of *p-tert*-butylcalix[4]arene L^1 with KO^{t}Bu in THF affords colourless single crystals of the new dimeric metallocalixarene specie $[K_4(L^1\text{-}4H)(THF)_5]_2\cdot1THF$ (**12**) [11]. In a similar way to the lithiated compound **10**, molecular units of **12** comprise two fully deprotonated *p-tert*-butylcalix[4]-arene tetraanions fused at the lower rim by six bridging potassium cations arranged in a "sandwich" way between the two calixarenes moieties. The cavity of each calixarene is further filled with a fourth type of potassium ions, as in the previously described dimeric compound **10**, but no THF is *endo* coordinated to the potassium ion (Fig. 5c). Due to the larger ionic radius and the softer character of potassium compared to lithium, compounds **10** and **12** are not isostructural. The cluster core of **10** consists of two fused hetero-cubanes and one lithium ion linked on each side whereas in the potassium compound **12**, the hetero-

cubane structure is not maintained, and the outer cation K4 is linked differently. The potassium ion K1 in **12**, which is bonded *endo* to the calixarene, is much more pushed upward into the calixarene cavity than Li3 in **10**. Thus, the core structure in **12** consists of two fused open hetero-cubanes. The K1 ion is complexed by two oxygen atoms of the calixarene ligand, reaching a valence bond sum of 0.4, indicating that further coordination must exist. Indeed, to complete its coordination sphere, strong π-donation occurs from the two phenyl rings linked to O2 and O4 toward the cation K1 as well as from C1 and C20, basal carbon atoms of the phenyl rings linked to O1 and O3, respectively. The centres of the phenyl rings Z1 (C8-C13), and Z2 (C22-C27), are at distances of 2.799 Å for Z1 and 2.780 Å for Z2 of K1. This is by 0.05 Å shorter than the equivalent distances reported for theoretical calculations of $[K(C_6H_6)_2]^+$ [13]. In the solid state, only longer K^+-Aryl(centroid) (Aryl = aromatic six-ring) distances have been reported. Even in the cyclopentadienyl compound KCp, in which the potassium ion is sandwiched between two Cp-rings of a zigzag-chain-structure and interacts with two more Cp-rings of the neighbour chain, the K−Cp(centroid) distances are still longer than in **12** [11].

The strong interactions of two phenyl rings with the potassium ion K1 in **12**, compared to the weak ones with Li3 in **10**, can be a model for the high selectivity of potassium channels in living organisms. These interactions were shown to belong to cation−π interactions in general, and to be very strong for **12**. In detail, the selectivity of the benzene ring in the gas phase was shown to be highest for Li^+ and lowest for Rb^+, whereas in aqueous media, K^+ is always preferred leading to the formation of a sandwich compound. Similar interactions were attributed to the potassium selective channels of *Drosophila* [11 and therein].

In a next step, we tested larger calixarene ligands in order to have more than one metal ion present in the cavity of the ligand. The larger the calixarene ligand, the more possibilities there are for the formation of different conformers, making these compounds difficult to crystallize. Such compounds can be obtained from a two-phase system, in our case where K_2CO_3 is dissolved in water in the lower phase, and p-tertbutyl-calix[8]arene is suspended in THF in the upper phase. In such systems, the ligand usually arranges itself at the interface with the polar OH-groups towards the polar solvent, whereas the rest of the molecule remains in the apolar phase. Colorless crystals of [K(calix[8]arene-H)(thf)$_4$(H$_2$O)$_7$] (**13**) are formed at the interface of both phases after a period of ca. two days [14]. The asymmetric unit consists of one singly deprotonated calix[8]arene ligand, one potassium cation, and seven water molecules (Fig. 6a). The metal ion is bonded to one side of the calixarene ligand, where it is coordinated by O7 and O8. The coordination sphere of the potassium cation is completed by three oxygen atoms of water molecules, O9, O9′ and O10, as well as by one oxygen atom O11 of a THF molecule to yield a distorted octahedral environment for the cation. The oxygen atom O10 is positioned over the center of the cavity

in the calixarene ligand on the same side of the ligand as the potassium ion. It forms a hydrogen bonding contact through the cavity of the macrocycle, and to the oxygen atom O15 of a water molecule on the opposite side of the organic ligand. The latter is involved in further hydrogen bonding to the water molecules of O16, O17, and O16′. The four water molecules O15, O16, O17 and O18 form, together with their symmetry equivalents, a distorted cubane structure. The *C2*-symmetry of the (H$_2$O)$_8$-cubane however, and its coordination by four THF-ligands to O16, O16′, O18 and O18′ allow only one distribution of the protons. Twelve of the sixteen H-atoms bridge the edges of the cubane, whereas the remaining four are directed towards the THF-ligands. Thus, at least one proton of O10 has to point towards O15 in order to maintain the H-bonding system. To the best of our knowledge, this is the first water cubane structure with *C2*-symmetry isolated in the solid state.
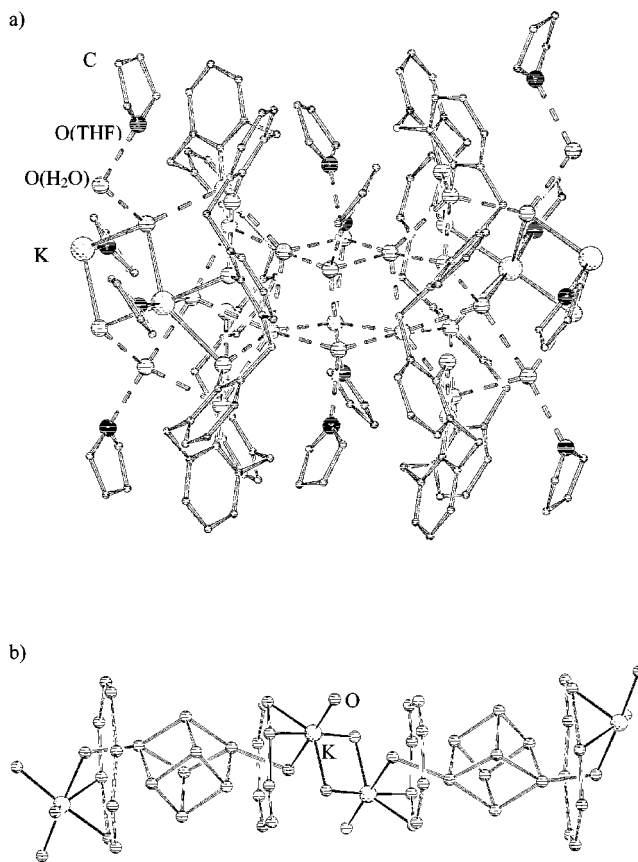

Figure 6 Side-view of the one-dimensional strands formed in **13** (a) and simplified core structure of the channel, C- and H-atoms omitted (b).

All in all, a one-dimensional system is obtained. The calix[8]arene can be considered as rings (or pearls) on a hydrogen-bonding chain between the water cubane cluster and the potassium dimer unit (Fig. 6b). Furthermore, there are three more THF ligands, and one additional water molecule in the asymmetric unit. The water molecule, O21, bridges the two water ligands O9 and O10. Two of the

THF-molecules and their symmetry equivalents are H-bonded to O16 and O18 as well as their symmetry equivalents and thus coordinate around the water cluster; the third one is linked to the bridging water molecule O21, and all of these ligands act as terminal ligands. Thus, the THF ligands and the calix[8]arene ligands form together a channel system with the non-polar part of the molecules pointing outward, the polar oxygen donors pointing inward the channel. The inside of the channel is filled with water molecules and potassium ions. We are now investigating such channels on a larger scale as models for biological ionic channels and try to test their ionic conductivity. Other alkali cations as well as other sizes of calixarenes are currently under investigation in our group.

2 Supramolecular inorganic polymers

This part focuses on the formation of different dimensional polymer structures obtained by the combination of two binding modes: firstly the metal ion coordination, and secondly the hydrogen bonds. The aim of this project is to contribute to the field of structure prediction, or, at least, the prediction of the dimensionality of a compound in the solid state. In the group, we are interested in cationic complexes of alkaline earth metal ions with at least one water molecule in the coordination sphere of the cation, using this water ligand as hydrogen bonding partner for spherical anions such as iodide [15−18]. In collaboration with other groups, we also deal with designed ligands which carry information to coordinate a transition metal on one hand and H-bond acceptors and donors on the other hand, and which are able to build up two-dimensional structures in the solid state, combining metal ion coordination with an H-bonding system [19].

Some first experiments lead to the conclusion, that it is only possible to predict interactions between complex cations, the counter ions and solvent molecules under very restricted conditions. For instance, the compound of the general formula trans-[Ca(L)$_4$(H$_2$O)$_2$]I$_2$ doesn't form similar solid state structures even when ligands L of similar size, and the same donor atoms are used, which are not involved in H-bonding [15]. Thus, the compound in which L = THF, **14**, forms a two-dimensional network via hydrogen bonds, whereas for L = ethyl acetate (CH$_3$COOC$_2$H$_5$), **15**, one-dimensional chains are observed (Fig. 7a and b).

These together with other results [16] lead us to fix several rules under which at least the dimensionality of a compound can be predicted. The following conditions are required in the case of structures of supramolecular polymers of alkaline earth metal iodides: i) the cations form complexes charged 2+ with inert polyether ligands and H-bonding water molecules, ii) the counterions, charged 1-, are the only H-bond acceptors, here two iodide ions per complex cation, iii) the water ligands, if several, are arranged in vicinal positions, iv) only the water molecules are involved in hydrogen bonding, and v) each hydrogen atom of water molecules forms a single hydrogen bond to iodide
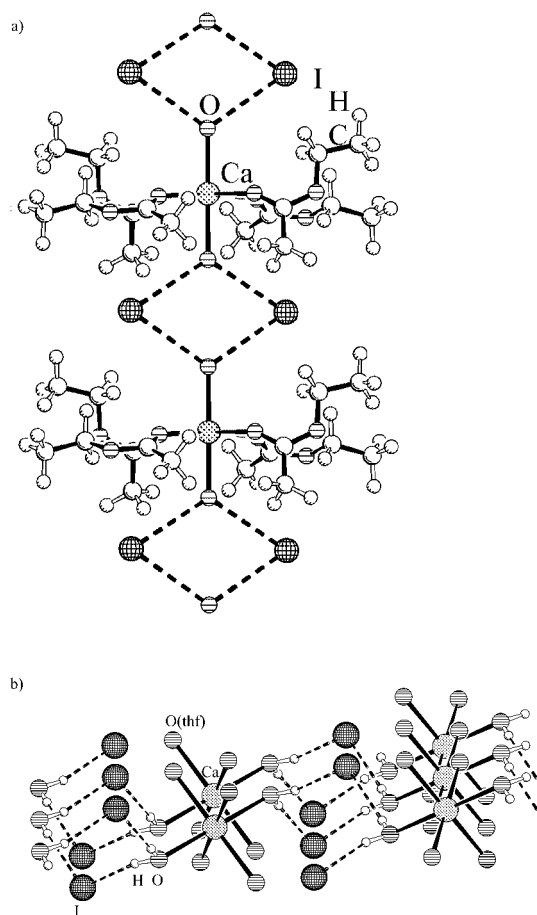

Figure 7 Excerpts of the solid state structures of **14** (a) and **15** (b)

ions, excluding that two hydrogen atoms of the same water molecule bind to the same iodide ion [17]. So, the only variable is the bridging functionality of iodide ion and the number of water ligands per cationic complex. It was found that under these conditions, the number of water molecules coordinated to the alkaline earth metal cation, directs the dimensionality of the final compound. Thus, a compound with one water molecule, like [Ba(triglyme)$_2$(H$_2$O)]I$_2$ (**16**) has a zero-dimensional structure, one with two water molecules forms a one-dimensional chain, i. e. [Ca(diglyme)$_2$-(H$_2$O)$_2$]I$_2$ (**17**), three water molecules present will give a two-dimensional double-layer as in [Ba(diglyme)$_2$(H$_2$O)$_3$]I$_2$ (**18**) and four water molecules bonded to the cation will lead to a three-dimensional compound, i. e. [Ca(triglyme)-(H$_2$O)$_4$]I$_2$ or [Ca(dme)$_2$(H$_2$O)$_4$]I$_2$, (**19**) and (**20**), respectively (Fig. 8 a, b, c and d, for **16**, **17**, **18** and **20** respectively). [17] Isostructural compounds to **17** and **20** have been obtained with Sr instead of Ca. [20]

In the case where four water ligands are bonded to the alkaline earth metal cation, even the compound in which the anions are directly linked to the cation can form such a three-dimensional structure, as has been shown for [Ba(OH)I(H$_2$O)$_4$] (**21**) (Fig. 9) [18].
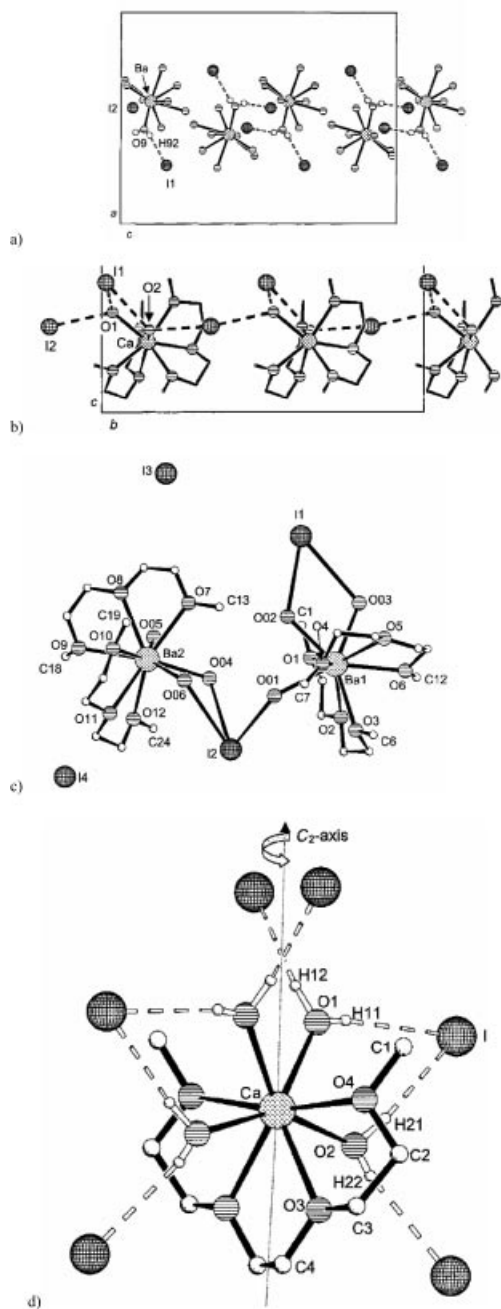
Figure 8 Networks on the solid state structures of **16**(a), **17**(b), **18**(c), **19**(d); for **20**, the triglyme ligand in **19** can be replaced by two DME-molecules

We are now investigating how this concept can be generalized to other metal ions, ligands and anions in order to contribute to this important field of fundamental research.

3 Clusters of alkali and alkaline earth metals

Looking for an analogy to transition metal clusters (in this case, clusters are defined as aggregates without necessarily presenting metal-metal bonds), the following general reaction scheme 1 for obtaining alkaline earth metal clusters was applied:
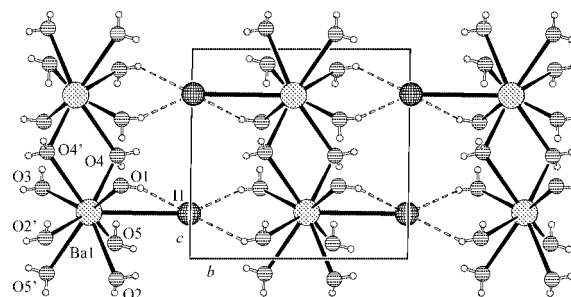
Figure 9 Excerpt of the solid state structure of **21**

$$n\ MX_2\ +\ n\ ^nBuLi\ +\ n\ LiOR\ \xrightarrow[+\ Ligand\ L]{-\{[LiX][^nBuLi]\}_n}\ [(L)_mM_nX_n(OR)_n],$$
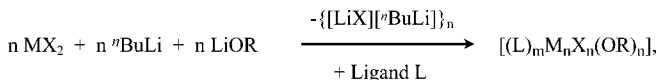
Scheme 1 Reaction scheme 1 for the generation of new alkaline earth metal cluster compounds

with MX_2 being an alkaline earth metal iodide, LiOR being either the hydroxide or LiO^{t}Bu, and L an oxygen donor ligand like THF or some polyether. [21, 22]

In a first step, our interest focuses on the investigation of potential starting compounds of the type $[MI_2(L)_x]$, as such adducts are formed in the cases where L is also used as solvent. In water as solvent, ion separation takes place and a typical ionic behaviour of the alkaline earth halides is observed. In organic solvents such as THF or polyethers (L = DME, diglyme), the M—I contacts remain mostly intact, and the alkaline earth halide is dissolved forming adducts $[MI_2(L)_x]$ where x depends on the size of the cation and the size and flexibility of the ligand L, similar to the ones observed for lanthanide cations, their coordination chemistry being very similar. [23] As described in the first part of this paper, the zero-dimensional structures $[MI_2(thf)_5]$, M = Ba and Sr, **4** and **22** respectively, were found to have a trans arrangement of the anions in a distorted pentagonal bipyramidal arrangement of ligands around the cation, as expected from the VSEPR model, due to maximum repulsion of the negative charges. This is also observed for $[CaI_2(thf)_4]$ (**23**) a literature known compound which we also crystallised, but in a different space group [21, 24]. As the cation is smaller than Sr and Ba, the coordination number is reduced from seven to six (Fig. 10) [21, 25].

When SrI_2 is dissolved and re-crystallized from freshly dried and distilled diglyme ($CH_3OC_2H_4OC_2H_4OCH_3$), only the compound cis-$[SrI_2(diglyme)_2]$ (**24**) is obtained [25–27]. Two independent molecules are found in the asymmetric unit, and both molecules consist of a strontium cation to which two diglyme ligands and two anions are directly linked (Fig. 11). In contrast to **22**, the I—Sr—I angles are with ca. 91.5° much smaller and close to a right angle. Together with the oxygen donor ligands, the coordination sphere of the cation can now be described as severely distorted square antiprismatic. The coordination number of eight for the strontium cation is common. Generally, the
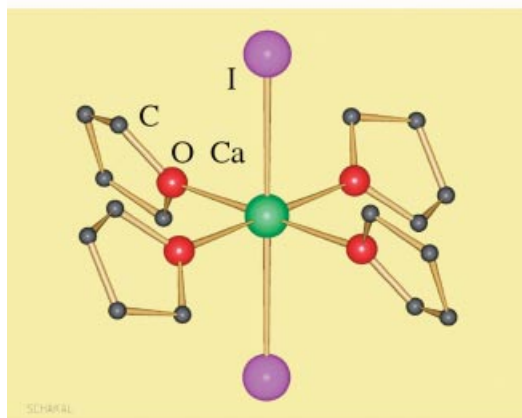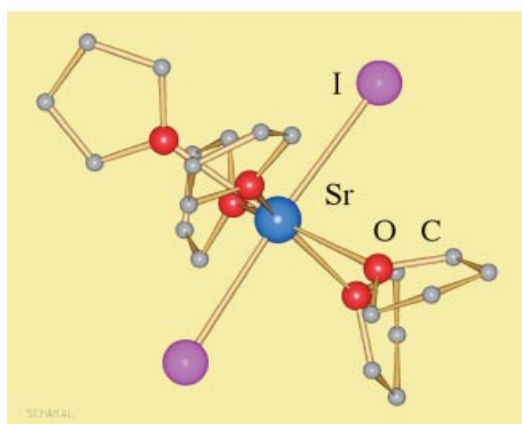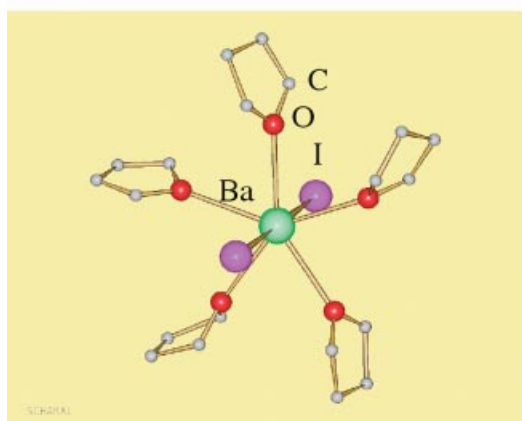
Figure 10 Comparison of the molecular structures of **23** (a), **22** (b) and **4** (c)

strontium cation usually behaves similar to the barium ion rather than calcium as far as coordination numbers are concerned. The most intriguing fact about this structure is that both anions occupy vicinal positions. In general, to obtain

such structures with the anions in cis-position, a sterically important ligand, which shields one side of the cation, such as slightly too small crown ethers, is required. And then, the X−M−X angles are usually much larger, the M−X bonds are longer than in **24**, and the anions are involved in H-bonding to build up a polymer structure. **24** is therefore the first example of a polar molecular alkaline earth metal iodide precursor. The strongly bent I−Sr−I feature in this structure reminds of the alkaline earth metal halides, especially the heavier ones with strontium, barium and iodide as counter ions, in the gas phase. Indeed, experimental as well as theoretical data show bent structures for the molecules in the gas phase [21, 28]. So, **24** could be compared to a gas phase species stabilized by oxygen donor ligands. The bent structure reminds also of the cyclopentadienyl derivatives of the alkaline earth metals. They have bent structures as well. However, in the solid state, they form polymers via contacts to neighbouring units [27].
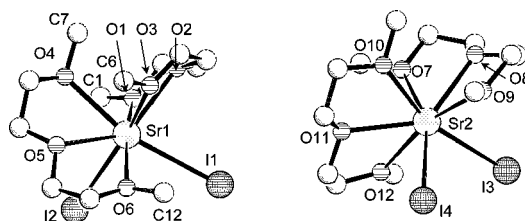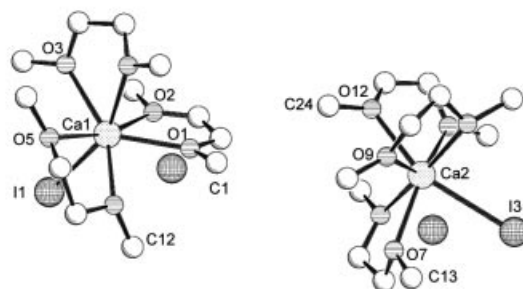

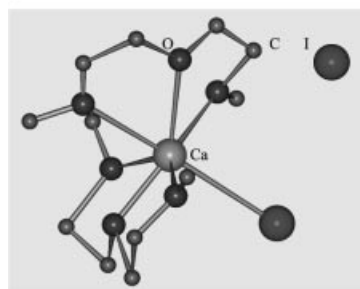**Figure 11** The two independent molecules in **24**

Figure 12 Independent molecules of **25** (a), and molecular structure of **26**, when three DME molecules of **25** are replaced by two diglyme ligands (b)

The second compound, [CaI(dme)$_3$]I(**25**), presented here, was obtained when crystallizing CaI$_2$ from freshly dried and distilled DME [27]. **25** is built up from two independent cationic molecules A and B per asymmetric unit, each consisting of a calcium cation, Ca1 and Ca2, to which one iodide ion and three DME-ligands are bonded terminally, respectively via both oxygen atoms each, and two separate iodides as counter ions (Fig. 12a). Thus, the cation reaches coordination number of seven. The coordination can roughly be described as a distorted pentagonal bipyramid with one iodide ion and an oxygen atom in axial positions. A similar compound can be obtained replacing the three DME-ligands of **2** by two, larger diglyme molecules. The number of oxygen atoms then remains identical, and so does their arrangement around the cation. The compound which is then obtained can be written as [CaI(diglyme)$_2$]I (**26**) (Fig. 12b). We have shown before (compounds **19** and **20**) that small polyether molecules (such as DME) can easily be replaced by larger ones (diglyme or triglyme for instance) as long as the number of oxygen atoms remains constant, without significant changes in the structure. The cations [CaI(dme)$_3$]$^+$ and [CaI(diglyme)$_2$]$^+$ of **25** and **26** possess a strong dipole moment along the Ca$-$I bond vector, as can be seen from figure 12. Such polar species are scarce: in the literature, only one example with calcium and iodide was described so far to our knowledge, [CaI(thf)$_5$]$^+$, in which the cation possesses coordination number of six, the counter ion being an extremely bulky phosphonium diylide [29].

In order to determine the space needed for different ethereal ligands, other adducts with differently sized polyethers as well as mixtures of ligands are currently under investigation. Among the presented starting materials, the THF-adducts were used so far in order to obtain cluster compounds as described in the reaction scheme 1. The results are presented in the next paragraphs [20, 30].

Using CaI$_2$ under the conditions given in reaction scheme 1, we were able to isolate the largest Ca-cluster so far, Li[Ca$_7$I$_6$(μ_3-OH)$_8$(thf)$_{12}$]$_2$(μ_2-I)(THF)$_n$ (**27**) with a unique structure of two double-hetero-cubanes linked together via hydrogen bonds to a central iodide ion, yielding a dumb-bell-shaped cluster of fourteen calcium ions (Fig. 13a) [30]. The cluster is made up of OH-bridged Ca$_3$-triangles, put together to build tetrahedra which are fused via one Ca-cation. This central cation has a coordination sphere of six OH-groups in a nearly octahedral environment. Two THF-ligands and one iodide ion are terminally bonded to the other six Ca-cations, which have their quasi octahedral coordination sphere completed by three OH-groups. One of these OH-groups binds to an iodide ion in order to bridge to the second Ca$_7$-cluster unit, build up in a mirror fashion to the first. One counter cation is needed and can be found as a Li-ion, coordinated by four THF-ligands.

When SrI$_2$ is used as starting material in a reaction scheme 1, [Sr$_3$I$_3$(μ_3-OH)$_2$(thf)$_9$]I (**28**) is obtained (Fig. 13b) [21]. Here, three metal ions are arranged in a perfect tri-

angle, its edges being bridged by iodide. The three cations are also "glued" by two μ_3-bridging OH-groups, one above, the second below the plane spanned by the cations. Each Sr-cation carries furthermore three THF-ligands to complete its coordination sphere to a distorted pentagonal bipyramid. It is interesting how the I$-$Sr$-$I angle varies from [SrI$_2$(thf)$_5$], (**22**), with ca. 176° to 172° in **28**. This triangular arrangement seems to be a fundamental unit for the construction of higher aggregates, since most of the alkaline earth metal clusters form polyhedra or sheet structures in which triangles of alkaline earth metal ions are fused together.
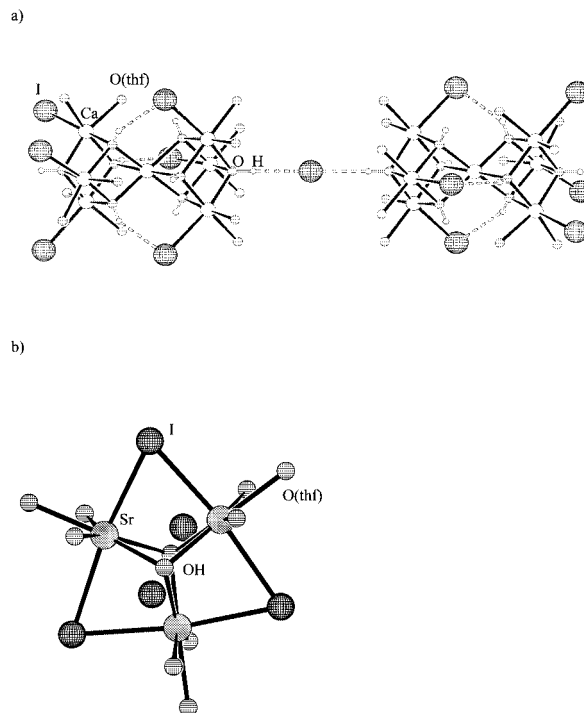

Figure 13 Cluster molecules of **27** (a) and **28** (b)

These two purely alkaline earth metal clusters **27** and **28** are not volatile, and can thus not be used as CVD (Chemical Vapor Deposition) precursors. However, they form extremely stable sols in THF upon hydrolysis with, in the case of the calcium compound, a particle size of ca. 1000 nm and a particle composition of Ca(OH)$_2$(H$_2$O)$_n$ which can be used to synthesize thin films of halide-free CaO. [21]

In order to introduce volatility, we aimed to replace LiOH by LiO^{t}Bu which is for itself volatile. To our surprise, the solid state structure of LiO^{t}Bu was unknown when we got interested in the compound, even though that other analytical methods and some single crystal data of bad quality were pointing to a hexameric structure. We were able, simultaneously but independently to another research group, [21, 31], to crystallize LiO^{t}Bu in order to obtain a satisfactory structure. The compound [LiO^{t}Bu]$_6$ (**29**) forms in principle hexamers, two independent molecules being found in the unit cell. The oxygen atoms are arranged in a distorted octahedral arrangement, with eight triangular

faces to be capped by six lithium cations. Due to this fact, the cations are disordered over all possible places which made structure solution quite difficult as the molecules are also highly symmetric. Nevertheless, the most probable structure can be described as a hexagonal anti-prism of O and Li atoms (Fig. 14a), confirming the literature discussion. [21, 32, 33]
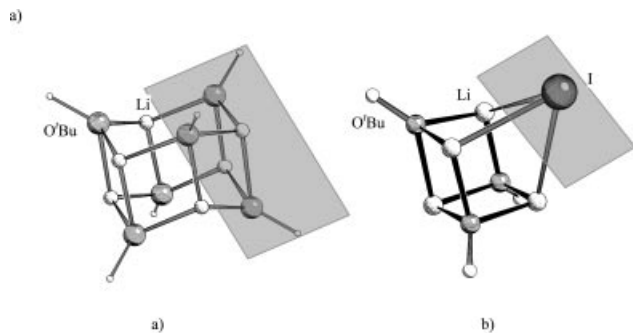

Figure 14 Structural relationship between the molecular structures of **29** (a) and **30** (b)

Under the above reaction conditions (scheme 1) and with CaI_2 as starting material, a pure lithium cluster $[Li_4(\mu_3\text{-}O^tBu)_3(thf)_4I]$ (**30**) with a distorted hetero-cubane structure was obtained (Fig. 14b). [32] Structurally, it can be related to the starting material **29** as shown in figure 14, replacing formally a $[Li_2(O^tBu)_3]^-$ unit by I^-. With this compound, we were for the first time able to isolate and structurally characterize the lithium compound produced along the reaction as secondary product. As can be seen from its composition, the iodide ion has been partially stripped off the alkaline earth starting product, and so there must also be a new calcium compound to be discovered. Recently, it was possible to characterize the latter. Instead of yielding a pure Ca-compound, a mixed metal cluster is obtained. The compound $[ICa(O^tBu)_4(Li\{thf\})_4(OH)]$ (**31**) consists of a calcium cation to which an iodide ion and four O^tBu-groups are bonded, the former in a terminal fashion (Fig. 15 a). [34] Four lithium cations are linked to the O^tBu-groups as well, the oxygen and lithium atoms forming a distorted square anti-prism. The open square face formed by the alkali metal ions is bridged by an OH-group. In order to complete the tetrahedral coordination sphere around each lithium cation, each is terminally coordinated by one THF ligand. The whole cluster has thus a spherical overall shape with mainly organic, apolar ligands pointing to the outside and shielding the cluster core. This is in principle a favourable structure for volatile compounds as intermolecular forces are expected to be weak. In analogy, the compounds $[IM(O^tBu)_4\{Li(thf)\}_4(OH)]$, M = Sr (**32**), [21], Ba (**33**), [35], were isolated (Fig. 15 b and c).

Comparing the structures of the three related compounds **31**, **32**, **33**, it can be seen that the cluster core is more and more flattened the smaller the cation, and, vice versa, the M−OH bond gets longer with increasing cation size. For compound **33**, solution and solid state analysis
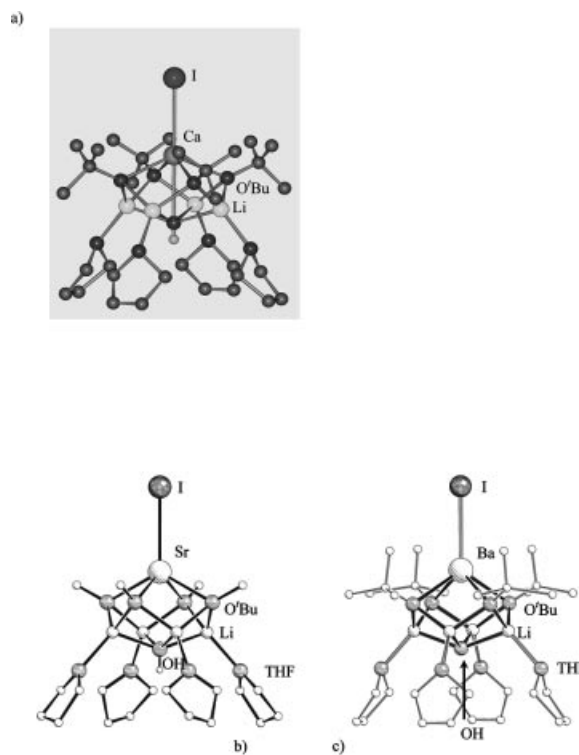

Figure 15 Comparison of the cluster structures of **31** (a), **32** (b) and **33** (c)

were found to be congruent as far as ^6Li and ^{13}C NMR is concerned. The ^1H-NMR of a solution of **33** in d_8-THF shows a temperature dependency of the signal for the OH-proton, indicating interactions of H-bonding nature in the cavity formed by the THF-molecules of the cluster (Fig. 16). It also turns out to be volatile, and therefore, deposition tests were carried out. Partially crystalline product was deposited on $SrTiO_3$, and after thermal treatment at 600 °C, halide-free BaO is formed on the surface, as identified by Auger electron spectroscopy. As an ingredient for high temperature superconductors, compounds **31**, **32** and **33** could possibly be a new solution in the generation of halide free, quantitatively deposited oxides.
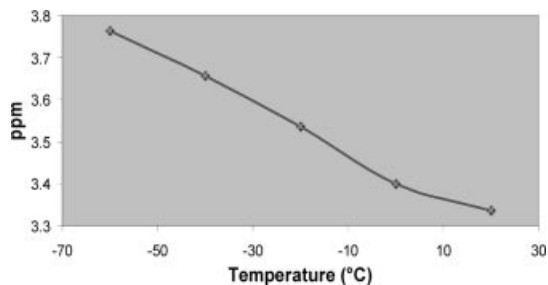

Figure 16 Temperature dependency of the OH-proton shift in ^1H-NMR of **33**

With the aim to make single source precursors for oxide materials, containing several metal ions within one compound, we started to investigate multitopic ligands and

their ability to coordinate to group 11 and group 1 or 2 metal ions. While studying group 11 metal ions, Cu^I, Cu^{II} and Ag^I, the problem of polymorphism and pseudo-polymorphism with such compounds came into the focus of our interest. Some of the results obtained in this context will be presented in the next chapter.

4 Coordination polymers and supramolecular structures of group 11 metal ions

In a first step, a ditopic ligand was chosen, built from pyridine and glycol units, thus being able to coordinate a "soft" cation via the nitrogen atoms, and a hard cation via the oxygen atoms. The chosen ligand is shown in scheme 2, and it has the advantages of being easily accessible, and of being easily modified in the position of the nitrogen atoms as well as in the middle part by choosing longer spacers such as diethylene glycol derivatives [36].
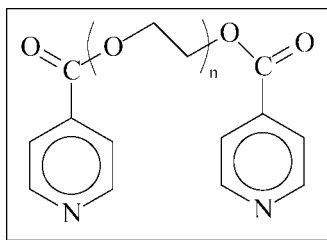
Scheme 2 Representation of the ligand family used in our coordination chemistry, for n = 1 → L = **34**

This ligand L, **34**, has a flexible backbone and might thus lead to coordination polymers with different conformations of ligand. The ligand alone crystallizes in its anti conformation, stacking the molecules parallel to each other and with hydrogen bonds stabilizing the network (Fig. 17). This can be represented as an S-shape, whereas the gauche conformation, the second stable structure of the ligand, is furthermore represented as U-shape. Their energies differ weakly by 0.8 kcal/mol [36].
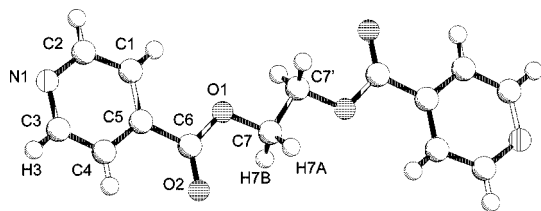

Figure 17 Molecular structure of the ligand L, **34**, showing its anti conformation

When **34** is reacted with CuCl in a mixture of solvents THF/CH$_3$CN, red single crystals of the composition [CuCl(L)](THF)$_{0.5}$ (**35**) are obtained [36]. A one-dimensional compound is found by repeating units of copper atoms which are, two by two, alternatingly bridged by two chloride anions and two ligands in gauche conformation, respectively (Figure 18a). Each copper cation is therefore

coordinated by two N-atoms of two different ligand molecules and two chloride ions. The Cu−Cl bonds are very asymmetric with 2.3255(9) and 2.546(1) Å, indicating that the Cu(μ-Cl)$_2$Cu unit could be interpreted as a dimer of two Cu−Cl fragments. The so-formed chains are stacked on top of each other so that the cavities in the centre of the Cu(μ-L)$_2$Cu rings form channels in which the disordered solvent molecules are located. The THF molecules are not in the same plane as the copper atoms and the two ligand molecules, but are placed in between the chains. Apparently, the presence of the THF molecules keeps the chains apart from each other, and prevents π-stacking in **35**.
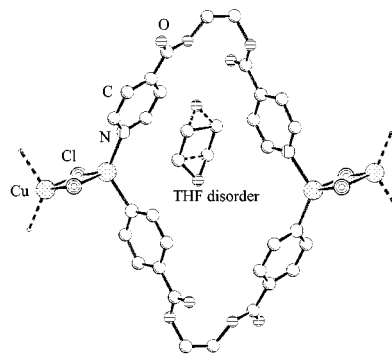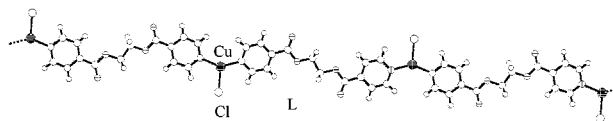

Figure 18 One-dimensional structures of **35** (a) and **36** (b)

After several days in the mother liquor, the crystals of **35** transform into yellow species of which single crystals were measured to be [CuCl(L)] (**36**) [36]. In contrast to **35**, compound **36** forms one-dimensional chains of copper atoms linked via the ligand, the latter coordinating through the nitrogen donor atoms (Fig. 18b). The copper ion, having a trigonal planar arrangement of ligands (angle sum = 360°), is coordinated by two nitrogen atoms of two different ligands and a chloride ion. The conformation of the ligand in **36** is anti and thus the same as in the free ligand **34**. **36** can be directly obtained when the reaction is carried out in pure CH$_3$CN as solvent.

Apparently, the presence of THF as solvent in the structure also influences on the conformation of the ligand. **35** slowly transforms into **36** when the crystals remain in the mother liquor, giving rise to the assumption that **36** is the thermodynamic more stable product obtained by diffusion of THF out of the structure and following reorganisation. Even though the transformation relies on severe rearrange-

ments in solution, one can propose a possible mechanism for it. Structurally speaking, one has to formally cut the longer Cu−L bond first (Scheme 3). The ligand would then bend over to the other side and displace a chloride ion at the next copper atom in order to adopt a stretched out anti conformation. One Cu−Cl bond at each copper atom is thus formally cut, and the structure of **35** could be transformed into compound **36**.
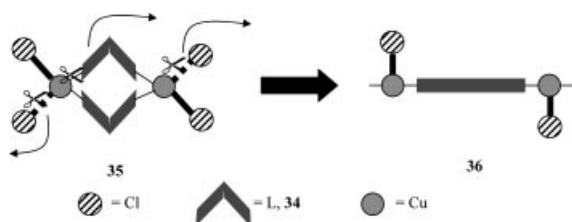
Scheme 3   Possible mechanism of transformation of **35** to **36**

Pseudo-polymorphs and real polymorphs can also be observed when L, **34**, is reacted with AgNO$_3$. Single crystals of the Ag-compounds are obtained in H-formed tubes, dissolving the silver salt in a polar solvent in one compartment, dissolving the ligand L in THF in the other compartment, and layering both with a mixture of solvents in order to bring both compartments into contact. Slow diffusion leads then to reaction and the formation of crystalline material. Only the results obtained when the silver salt is dissolved in H$_2$O will be reported here, but other results are numerous and currently under final investigation in our group [37].

When AgNO$_3$ is dissolved in water and mixed with a solution of L in THF, colourless single crystals of {[Ag(L)](NO$_3$)} (**37**) are obtained [37]. The structure consists firstly of one-dimensional chains of undulating Ag-L-Ag-L-motifs, the pyridine rings coordinating to the metal ions via the nitrogen atoms (Fig. 19a), and the ligand adopts the anti conformation. Each metal ion reaches a coordination number of five, with two nitrogen atoms in axial and three oxygen atoms of two nitrate anions in equatorial positions of a distorted trigonal bipyramid. Apart from the anions which act as bridging ligands between two silver ions of adjacent chains, other forces hold the chains parallel to each other: hydrogen bonding occurs as well as π-stacking.

Under similar conditions, the second compound {[Ag(L)](NO$_3$)(H$_2$O)} (**38**) is obtained via the diffusion technique [37]. The asymmetric unit is formed of one silver atom, one ligand molecule, a nitrate counter ion and one water molecule. Again, one-dimensional chains are formed by coordination of the pyridine rings of the ligand L to two different metal ions (Figure 19b). In contrast to **37**, the ligand L now adopts a gauche conformation, giving the strands an undulating zig-zag structure. The coordination number of the silver ion by O- and N-atoms has decreased from five in **37** to four in **38**. The second reason is the Ag-Ag interaction observed in **38**, with a Ag−Ag distance of 3.136(1) Å, leading to pairs of almost perfectly parallel chains. The metal-metal contacts in **38** are the shortest dis-
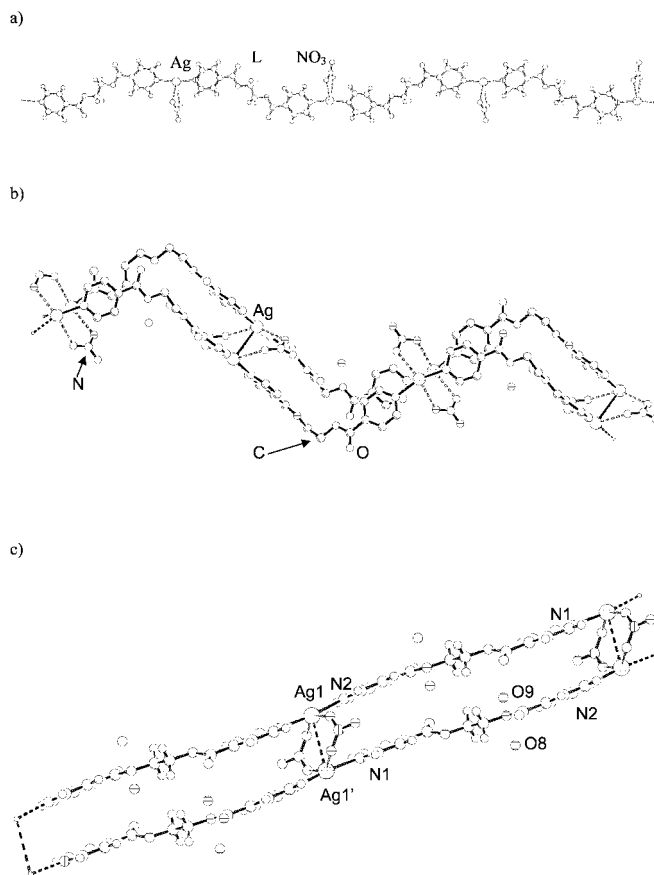

Figure 19   Solid state structures of **37** (a), **38** (b) and **39** (c)

tances between two parallel chains. Other forces contribute furthermore to the double chain formation: π-π interactions and two bridging NO^{3-} anions which coordinate only via two oxygen atoms as compared to **37**.

Under the same reaction conditions, colourless single crystals of {[Ag(L)](NO$_3$)(H$_2$O)$_2$} (**39**) are obtained in low yield only [37]. Again, a one-dimensional chain structure, alternating Ag-ions and ligand molecules, is obtained (Fig. 19c), in which the ligand molecules coordinate to two metal cations via the nitrogen atoms of the pyridine rings and possess anti conformation. Two chains form pairs by parallel arrangement via an inversion centre, allowing three different interactions between the chains (Fig. 19c). Firstly, weak π-stacking can be observed. Secondly, as in **38**, metal-metal interactions are present. Again, the Ag−Ag distance is the shortest contact between the two chains with 3.408(6) Å, which is however by 0.3 Å longer than in **38**. An inversion centre is found in the geometric middle of the metal-metal contact. Thirdly, as mentioned above, weak anion coordination is observed. In fact, the two silver cations are held together by two bridging NO$_3^-$ anions, acting as bidentate ligands.

Between the pairs of chains in **39**, a new kind of interaction is observed, which is not present in **37** or **38**: Ag-π-interactions with distances of 3.477 Å between the metal ion of one pair and the centre of the pyridine ring of a next pair, leading to a layer structure of chains. The remaining

space between such layers is filled with four water molecules per double-chain unit. These water molecules are linked via the nitrate anions in order to build ribbons of H-bonds running parallel to the layers.

The three compounds **37**, **38** and **39** have in principal one general structural feature in common, that is the presence of one-dimensional coordination polymer chains made of Ag^+ and L. The presence and the different number of water molecules in **38** and **39** lead to severe changes in the arrangement of the chains with respect to each other compared to **37**, as well as in the ligand conformation as far as **38** is concerned. Thus, compounds **38** and **39** also feature metal-metal contacts, leading to pairs of chains. Weak interactions are, in their sum, responsible for their formation. Aromatic π-π-stacking is observed in all three compounds. However, two major facts can be found which are responsible for the formation of different solid state structures. One is evidenced in the ligand conformation. In **39**, it adopts anti conformation, whereas in **38**, gauche arrangement is observed. The second point is the presence of different amounts of water molecules per asymmetric unit. Thus, the factor influencing the overall arrangement of the double-chains to each other in the crystal seems to be the number of water molecules and the resulting number of possible hydrogen bonds. The H-bonds also influence the fact that the chains run parallel in **39**, or cross each other in **38**, and that the ligand adopts two different conformations in **38** and **39**. Very probably, the Ag-π contacts in **39** are also responsible for inducing the parallel packing of the chains in this structure. Energies of such stacking interactions may be similar to coordinate bond energies for some heavy metals such as Tl^+, Ag^+ and Pb^{2+} and have roughly been estimated to up to 40 kJ/mol [37−39]. From Cu^I coordination compounds **35** and **36** with the same ligand L, it can be concluded that the H-bonds toward solvent molecules such as THF of H_2O may induce deformation of the ligand L, whereas in absence of solvent molecules, the ligand has so far always adopted the anti conformation as in the free ligand. The here observed coordination polymers for Cu and Ag are schematically represented in Scheme 4.

Representative examples of other coordination networks in which weak interactions also play a role and a survey of π-π-interactions in crystal engineering can be found in the literature as well [40, 41].

Many other coordination polymers are possible with our ligand, varying the reaction conditions such as counter ions, solvents, concentrations and also the size of the ligand along the spacer and the position of the nitrogen atom in the aromatic ring. Currently under investigation, these results will give rise to more publications in the field of crystal engineering before continuing the initial idea of combining such polymers via a second metal ion coordinated to the oxygen donor part of the ligand.
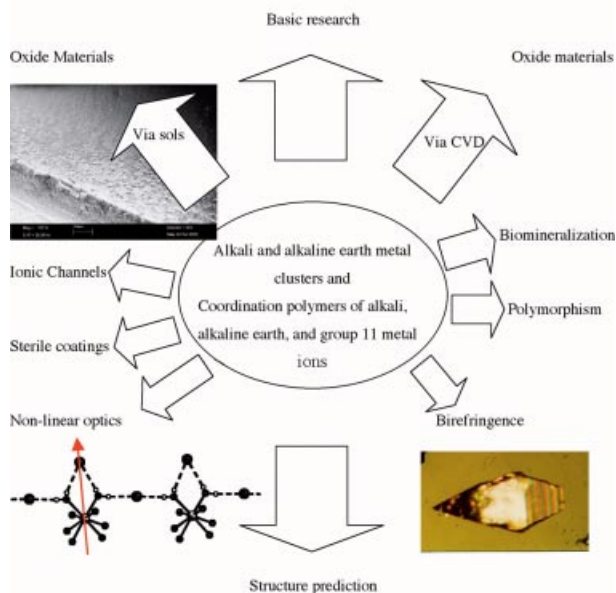
5 Applications

Among the above results, some were found to exhibit interesting properties. Thus, the one-dimensional [Ca(diglyme)$_2$-
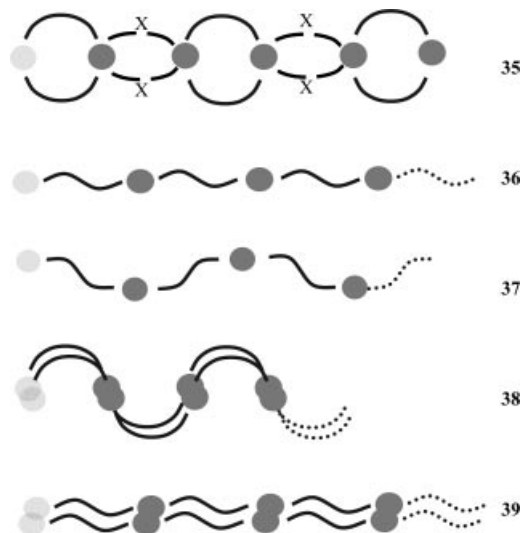
Scheme 4 Schematic representation of the here observed coordination polymers.

Scheme 5 Overview on possible application of our chemistry

($H_2O)_2$]I_2 (**17**) crystallizes in the polar space group Cc, leading to the physical properties of i. e. non-linear optics (NLO) and piezoelectronics. For this compound, we were able to show that it is capable to produce second harmonics when irradiated with the fundamental wave length of a laser. The effect is weaker than in the classically used KH_2PO_4, however, good materials for NLO based on inorganic coordination compounds with a long-time resistance against heat and light are in the focus of actual research for certain applications. The compounds [Na⊂(DB18C6)I(L)], **6** and **7**, crystallize in acentric space groups as well, and the

crystals are observed to be birefringent under the polarizing microscope.

[IBa(O^{t}Bu)$_4${Li(thf)}$_4(\mu_4$-OH)] (=„BaLi$_4$") (**33**), being volatile, it seemed to us a suitable precursor for barium oxide. Solution studies of the cluster, especially by NMR, revealed that the cluster retains its structure in solution, except for a fast exchange of THF ligands in d$_8$-THF. We then brought **33** onto a substrate of SrTiO$_3$ via a dip-coating method consisting of slowly withdrawing the substrate from the solution and let the solvent evaporate. At room temperature, the partially crystalline material was shown to be indeed the cluster of **33**. After thermal treatment as used in the synthesis of superconductors, only BaO was shown to be left on the surface, thus proving the possibility to use **33** as precursor for CVD of metal oxides. The two pure alkaline earth metal clusters, **27** and **28**, were not only shown to form sols on hydrolysis, but also the corresponding carbonates upon reaction with air. We now investigate the formation of CaCO$_3$ in the context of biomineralization.

Among the coordination polymers, we are interested in the disinfectant properties of silver compounds. As known from literature, they could be used as coating for catheters and other biocompatible materials in order to avoid bacteria to develop on such surfaces. Our compounds are currently being tested for such applications [37].

Conclusion

For alkali and alkaline earth metal compounds, we are able to present results in different contexts concerning low dimensional polymer, based on direct metal−halide contacts as well as on a supramolecular approach. For the latter, we continue our investigations with the goal of further contributions to crystal engineering and structure prediction. A new access to alkali and alkaline earth metal clusters is established and still leads to new results in this field. A recent review article deals with the importance of such oxygen donor based alkali and alkaline earth compounds [42]. Our results have shown that alkali and alkaline earth metal chemistry is not restrained to the ionic behaviour in water as solvent, but that substitution reactions and coordination chemistry similar to transition metals is possible.

Recently, we got involved in group 11 chemistry, and especially the coordination polymers of Cu$^{I/II}$ and Ag^I. This has led us into the field of polymorphism and gives also a contribution to crystal engineering and structure prediction. Some of our results present interesting physical properties, which we are investigating together with cooperation partners from physics, biology and medicine.

References

[1] K. M. Fromm, *Angew. Chem.* **1997**, *109*, 24, 2876−2878, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2799−2801.

[2] K. M. Fromm, *Cryst. Eng. Comm.* **2002**, *4(57)*, 318−322.

[3] K. M. Fromm, G. Bernardinelli, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1626−1630.

[4] K. Boumizane, M. H. Herzog-Cance, D. J. Jones, J. L. Pascal, J. Potier, J. Roziere, *Polyhedron* **1991**, *10*, 2757−2769.

[5] A. D. Frankland, P. B. Hitchcock, M. F. Lappert, G. A. Lawless, *J. Chem. Soc., Chem. Commun.* **1994**, 2435−2436.

[6] K. M. Fromm, E. D. Gueneau, J.-P. Rivera, G. Bernardinelli, H. Goesmann, *Z. Anorg. Allg. Chem.* **2002**, *628*, 171−178.

[7] K. M. Fromm, E. D. Gueneau, H. Goesmann, C. Bochet, *Z. Anorg. Allg. Chem.* **2003**, *629*, 597−600.

[8] M. Dulak, R. Bergougnant, K. M. Fromm, H. R. Hagemann, A. Y. Robin, T. A. Wesolowski, submitted.

[9] S. Rashid, S. S. Turner, P. Day, M. E. Light, M. B. Hursthouse, S. Firth, R. J. H. Clark, *Chem. Commun.* **2001**, 1462−1463.

[10] U. Radius, *Z. Anorg. Allg. Chem.* **2004**, *630*, 848−857.

[11] E. D. Gueneau, K. M. Fromm, H. Goesmann, *Chem. Eur. J.* **2003**, *9*, 509−514.

[12] J. L. Atwood, P. C. Junk, S. M. Lawrence, C. L. Raston, *Supramol. Chem.* **1996**, *7*, 15−17.

[13] J. Amicangelo, P. B. Armentrout, *J. Phys. Chem. A* **2000**, *104*, 11420−11432.

[14] R. Bergougnant, A. Y. Robin, K. M. Fromm, submitted.

[15] K. M. Fromm, G. Bernardinelli, H. Goesmann, M.-J. Mayor-Lopez, J. Weber, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1685−1691.

[16] K. M. Fromm, G. Bernardinelli, H. Goesmann, *Polyhedron* **2000**, *19*, 1783−1789.

[17] K. M. Fromm, *Chem. Eur. J.* **2001**, *7*, 2236−2244.

[18] K. M. Fromm, H. Goesmann, *Acta Crystallogr.* **2000**, *C56*, 1179−1180.

[19] D. G. Kurth, K. M. Fromm, J.-M. Lehn, *Eur. J. Inorg. Chem.* **2001**, 1523−1526.

[20] K. M. Fromm, W. Maudez, to be published.

[21] K. M. Fromm, E. D. Gueneau, G. Bernardinelli, H. Goesmann, J. Weber, M.-J. Mayor-López, P. Boulet, H. Chermette, *J. Am. Chem. Soc.* **2003**, *125*, 3593−3604 and therein.

[22] K. M. Fromm, *Chimia* **2002**, *56*, 676−680.

[23] Z. Xie, K. Chiu, B. Wu, T. C. W. Mak, *Inorg. Chem.* **1996**, *35*, 5957−5958; W. J. Evans, T. S. Gummersheimer, J. W. Ziller, *J. Am. Chem. Soc.* **1995**, *117*, 8999−9002; G. Heckmann, M. Niemeyer, *J. Am. Chem. Soc.* **2000**, *122*, 4227−4228; L. Huebner, A. Kornienko, T. J. Emge, J. G. Brennan, *Inorg. Chem.* **2004**, *43*, 5659−5664; M. Niemeyer, *Acta Crystallogr. Sect. E: Struct. Rep. Online* **2001**, *E57*, m363−m364.

[24] K. F. Tesh, D. J. Burkey, T. P. Hanusa, *J. Am. Chem. Soc.* **1994**, *116*, 2409−2417.

[25] K. M. Fromm, *Chimia* **2003**, *57*, 175−178.

[26] K. M. Fromm, *Cryst. Eng. Comm.* **2002**, *4*, 318−322.

[27] K. M. Fromm, W. Maudez, *Eur. J. Inorg. Chem.* **2003**, *18*, 3440−3444.

[28] R. J. Gillespie, E. A. Robinson, *Angew. Chem.* **1996**, *108*, 539−560; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 495−514.

[29] E. D. Brady, T. P. Hanusa, M. Pink, V. G. Young, Jr., *Inorg. Chem.* **2000**, *39*, 6028−6037.

[30] K. M. Fromm, *Chem. Comm.* **1999**, *17*, 1659−1660.

[31] H. Nekola, F. Olbrich, U. Behrens, *Z. Anorg. Allg. Chem.* **2002**, *628*, 2067−2070.

[32] E. D. Gueneau, K. M. Fromm, unpublished results.

[33] R. D. Thomas, S. G. Bott, P. W. Gravelle, H. D. Nguyen, Book of Abstracts, 215th ACS National Meeting, Dallas, March 29th-April 2nd (1998).

[34] W. Maudez, K. M. Fromm, to be published.

[35] K. M. Fromm, E. D. Gueneau, H. Goesmann, *Chem. Comm.* **2000**, 2187−2188

[36] A. Y. Robin, K. M. Fromm, H. Goesmann, G. Bernardinelli, *Cryst. Eng. Comm.* **2003**, *5*, 405−410.

[37] A. Y. Robin, M. Meuwly, K. M. Fromm, H. Goesmann, G. Bernardinelli, *Cryst. Eng. Comm.* **2004**, *6*, 336−343.

[38] J. M. Harrowfield, B. J. Peachey, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1995**, *48*, 1349−1356.

[39] L. Troxler, G. Wipff, J. M. Harrowfield, *J. Phys. Chem.* **1998**, *A102*, 6821−6830.

[40] Some examples: A. P. Cote, G. K. H. Shimizu, *Inorg. Chem.* **2004**, *43*, 6663−6673; Q. Chu, L. MacGillivray, Abstracts of Papers, 228th ACS National Meeting, Philadelphia, PA, United States, August 22−26, 2004 (2004), INOR-724; P. I. Richards, A. Steiner, *Inorg. Chem.* **2004**, *43*, 2810−2817; H. W. Roesky, M. Andruh, *Coord. Chem. Rev.* **2003**, *236*, 91−119; A. J. Blake, N. R. Champness, A. N. Khlobystov, D. A. Lemenovskii, W.-S. Li, M. Schroder, *Chem. Commun.* **1997**, *15*, 1339−1340.

[41] C. G. Claessens, J. F. Stoddart, *J. Phys. Org. Chem.* **1997**, *10*, 254−272.

[42] K. M. Fromm, E. D. Gueneau, *Polyhedron* **2004**, *23*, 1479−1504.