

Coordination polymer networks with s-block metal ions

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Abstract

Alkali and alkaline earth metal cations form the s-block elements of the periodic table where they belong to the groups 1 and 2, respectively. They play an important role in nature, for instance alkali cations Li^+ , Na^+ and K^+ have very specific functions such as the regulation of the ionic equilibrium of living cells in our body. Alkaline earth cations also have a contribution in our body, for instance calcium is the most important constituent of our organism. They above all, and always, find applications in man-made materials in a wide range of fields: catalysts, ferroelectrics, metallic conductors and superconductor materials.

They are known for their mainly ionic chemistry in aqueous medium, and a varying coordination number, depending on the size of the binding partners as well as on electrostatic interactions between the ligands and the metal ions. This makes the strategic synthesis of coordination polymer

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networks with these metal ions a challenge and explains why few systematic results in the generation of metal–organic frameworks (MOFs) are found in the literature. This review highlights the recent results in the field, bringing together the systematic approaches with results obtained by serendipity, to give an overview on current and future possibilities.

Keywords: Alkali metal ions; Alkaline earth metal ions; Coordination polymer networks; Metal–organic frameworks; s-Block metal coordination compounds

1. Introduction

The coordination chemistry of groups 1 and 2 metal compounds with organic ligands in the widest sense has been, until relatively recently, largely unknown compared to transition metal coordination networks. This is true despite the fact that many s-block metal–organic compounds are already of commercial importance. Thus, pharmaceuticals, dyes, and pigments typically use alkali and/or alkaline earth metal cations in preference to transition or lanthanide metal ions because most of them have the advantage of being non-toxic, cheap and soluble in aqueous media. Indeed, s-block cations should not be ignored as simple “spectator” ions when it comes to properties which depend on the solid-state structure and the intermolecular interactions. This is especially relevant in pharmaceutical industry where one salt might be preferred over others for practical as well as commercial purposes. Therefore, understanding the changes of material properties caused by changing the s-block metal ion is based on consideration of the fundamental properties such as charge, size, and electronegativity of these cations and their influence on the nature of the resultant solid-state structure. Furthermore, the chemistry of group 1/2 metal ions is not limited to the classical ionic behavior as known from aqueous media, but may exhibit a more covalent character similar to transition metal compounds when polar organic solvents are used.

With the aid of modern X-ray diffraction techniques, a variety of molecular and polymeric structures can be elucidated. Coordination polymer networks are made mainly from neutral or anionic ligands (linkers) with at least two donor sites which coordinate to metal ions or aggregates (nodes) also with at least two acceptor sites, so that at least a one-dimensional arrangement is possible. Depending on the number of donor atoms and their orientation in the linker, and on the coordination number of the node, different one (1D)-, two (2D)- and three (3D)-dimensional constructs are accessible. While systematic studies to construct transition metal–organic frameworks (MOFs) are frequent in the current literature, due to the often well-defined coordination numbers of the metal ions, they are still sparse for s-block elements. Due to the span of coordination numbers possible for alkali and alkaline earth metal ions, control over the final structure is a challenge, and many results are obtained by serendipity. In this review, the current literature is highlighted, classified for the group 1 metal ions, then group 2 metal compounds, as well as for donor atoms in the organic ligands, mainly focusing on the classical O-, N, and S-donors, but also including aromatic rings as donor ligands. Thus, a first chapter will be dedicated to alkali metal compounds with polymeric structures, starting with organic O-donor ligands, followed by examples with N-donor, C-donor, and S-donor ligands. The same systematic will be used for group 2 metal ions.

2. Group 1 metal compounds

2.1. Neutral oxygen donor ligands

Ethers in general (THF, Et₂O, etc.) are among the most frequently used solvents for alkali metal compounds. They are usually polar enough to dissolve group 1 compounds with ionic character because they are able to coordinate to the metal ions. By acting as “chemical scissors” on alkali metal salts, they are able to stabilize structural fragments of these compounds by acting as neutral donor ligands where coordination is needed. Such solvent adducts are frequent at the molecular level, but not always identified when of polymer character due to the poorer solubility of the latter. One example is LiBH₄, forming different one-dimensional ether adducts which can be isolated and characterized as 1D structures in the solid state (Fig. 1), i.e. LiBH₄(OEt₂) and LiBH₄(OMeBu) [1].

Instead of monodentate ethers, cyclic polyethers can also be used to stabilize low-dimensional structures of alkali metal salts. Since the pioneering discovery of crown ethers and cryptands by Pedersen, Cram and Lehn, coordination compounds based on these ligands have been studied in considerable detail. Crown ethers with four to six oxygen atoms are in principle predestined for building one-dimensional channel structures. Much effort has been made to obtain such structures for ion conductivity. However, most syntheses lead to structures in which the alkali metal ions are (i) coordinated by the crown ether and (ii) bridged by water molecules to yield a one-dimensional (1D) zig-zag structure without alignment of the crown ether molecules. Only few examples are known from the literature, in which the crown ether ligands are also perfectly stacked to form a channel system. One of these is [Na ⊂ (DB18C6)(μ-OH)][Na ⊂ (DB18C6)(μ-H₂O)]₃ (Fig. 2) [2]. These systems do show transport properties for ions as well as water molecules [2], and could therefore be interesting for solid-state batteries.

Another way of stabilizing one-dimensional structures is by using crown ether molecules, which are too small to accommodate the cation in their centre. In this case, coordination of the crown ether towards a metal ion would take place in a side-on fashion, as exemplified in Cs(18C6)(N₃)(H₂O)(MeOH) (Fig. 3) [3]. For the smaller alkali homologue compounds, molecular mono- or dimeric entities are observed.

Going from molecular ligands such as these crown ethers to 1D polyethers such as PEO (polyethylene oxide), polymer electrolytes of group 1 metal ions are obtained, finding applications in ion rechargeable (lithium ion for instance) batteries. Their exact solid-state structure is not well known, but some studies on lithium, sodium and potassium reveal the coordination of the PEO ligand to the metal ions. Almost independently from the anions, the polyether oxygen atoms wrap around the

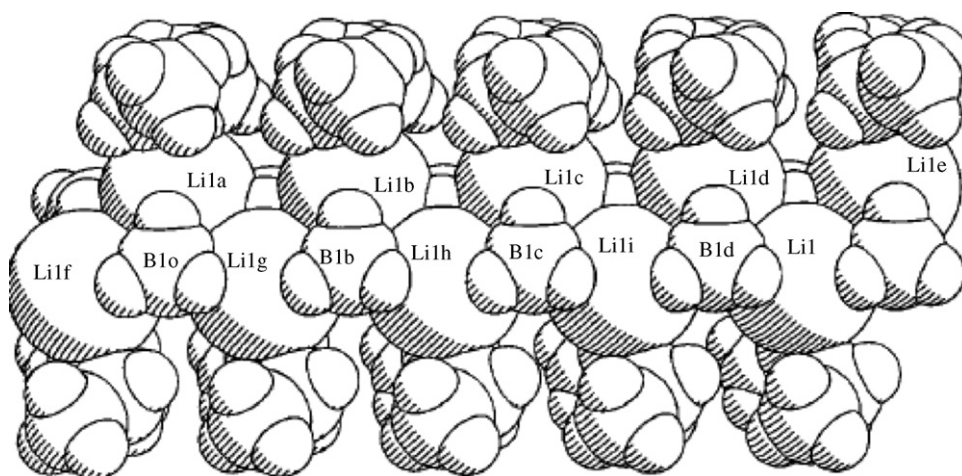


Fig. 1. Ether stabilized 1D structure of $\text{LiBH}_4(\text{OEt}_2)$; with permission from [1].

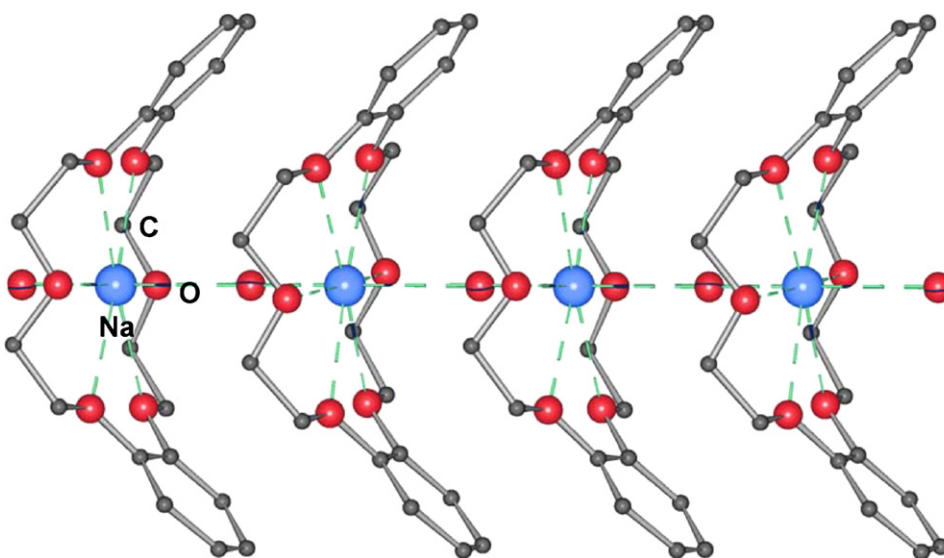


Fig. 2. 1D structure obtained within crown ether ligands [2].

alkali cations to form single or double helical structures with the metal ions in the center of a channel-like feature [4]. The mobility of lithium ions was studied by molecular dynamics simulations, where experimental and calculated X-ray diffractograms are compared for a good fit [5]. Other polyelectrolytes derived from PEO, such as polyether poly(urethane)urea have been studied in a similar context [6].

Derived crown ether ligands such as the dithia[16.3.3](1,2,6)-cyclophane also yield coordination polymer structures, such as a 1D zig-zag chain of KClO_4 stabilized by side-on coordination of the cyclophanes (Fig. 4) [7], whereas the sodium analogue turns out to be a 0D dimer.

Certain functionally (phenolic) substituted azacrown ethers such as N,N' -bis(4-hydroxy-3,5-dimethylbenzyl)-1,4,10,13-

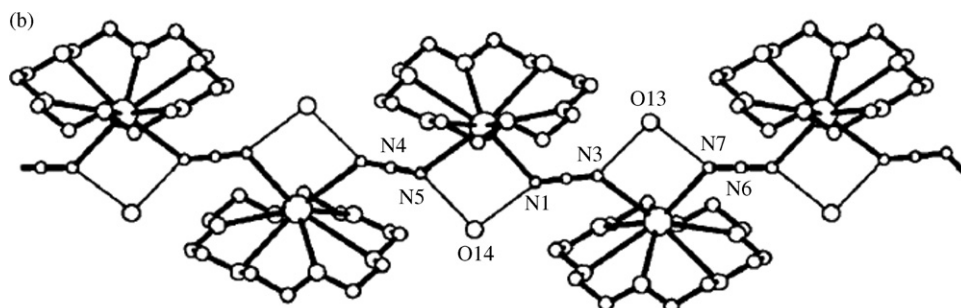


Fig. 3. 1D structure obtained by side-on coordination of crown ether ligands; with permission from [3].

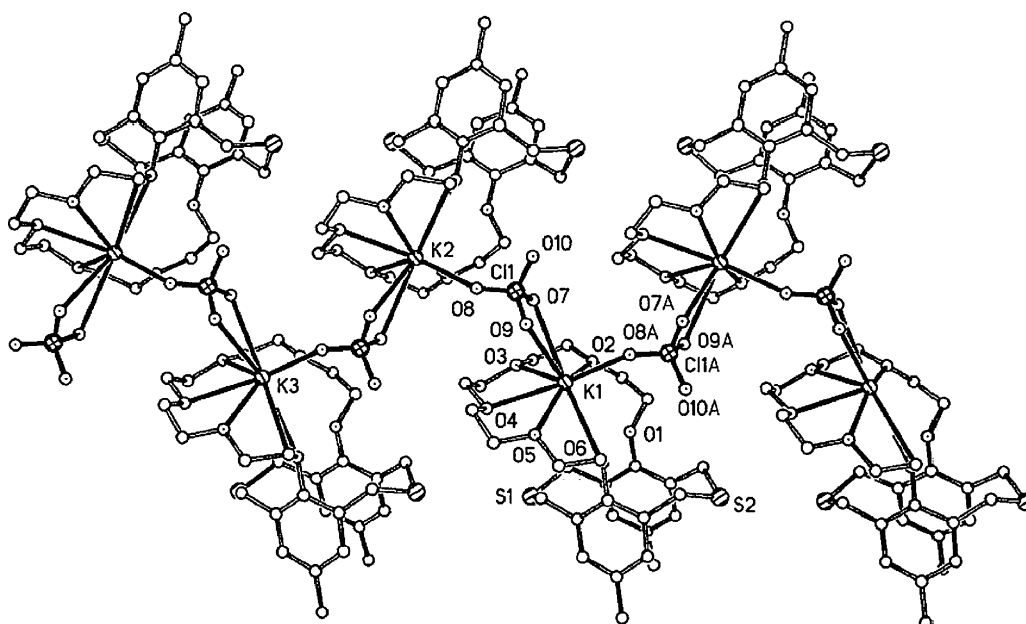


Fig. 4. 1D coordination polymer obtained by the coordination of dithia[16.3.3](1,2,6)cyclophane to KClO_4 ; adapted from [7].

tetraoxa-7,16-diazacyclooctadecane can act as bridging ligands to build polymer compounds in which they play the role of linker, whereas so far we have seen the ether ligands as coordinating, but not as bridging entity [8]. Sodium and potassium thiocyanate complexes are formed, in which the phenolic OH group in the side arm of the crown ether coordinates to the cation incorporated in the crown moiety of another molecule (Scheme 1).

Fourier-transform IR spectra of such compounds show that the O–H stretching band of the phenolic OH group in the polymer-like complexes shifts to lower frequency by ca. $210\text{--}290\text{ cm}^{-1}$ compared with those of the corresponding host compounds. ^{13}C NMR titration experiments indicate that these polymeric structures are however not maintained in solution.

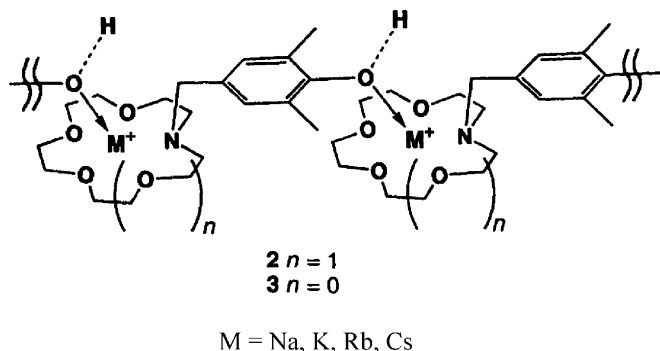
An emerging approach in the rational assembly of networks is through the use of secondary building units (SBUs), which are most commonly metal-containing aggregates that dictate the direction of polymer extension. The use of SBUs is attractive

in part because of their steric requirements and rigidity, which dramatically reduce the number of possible network topologies arising for a given node/linker combination. Application of the SBU concept has mainly focused on inorganic solid-state chemistry and also on covalently linked transition metal cage complexes.

If this construction method is used together with a template anionic building block such as a carbaborane, the neutral oxygen donor ligand cyclotrimeratrylene (CTV) may build low-dimensional structures, for instance connecting $[\text{Na}_2(\text{H}_2\text{O})_2(\text{dmf})_2(\mu\text{-dmf})_2]^{2+}$ -clusters into a distorted hexagonal coordination polymer (Fig. 5)[9].

Using the simpler 1,4-dioxane as polyether ligand, it can act as terminal and/or connecting unit between metal ion clusters, leading to different dimensional polymer structures, as exemplified by the 1D-chains, 2D-sheets and 3D diamondoid network of, respectively, $[\{(\text{ROLi})_4(\text{dioxane})_x\}]$, $\text{R} = \text{Ph}$, $x = 3$; $\text{R} = 4\text{-Et-C}_6\text{H}_4$, $x = 2.5$; and $\text{R} = 1\text{-naphth}$, $x = 2$ (Fig. 6) [10a]. Other tetrahedral nodes to generate a diamondoid network with 1,4-dioxane are based on the smaller Li_2O_2 -ring dimers formed from (4-Br-2,6-Me $_2\text{C}_6\text{H}_2\text{OLi}$) [10b].

This example of the literature is reminiscent of transition metal coordination polymer structures and leads over to the following compounds in which anionic oxygen donor ligands play important roles in the formation of coordination polymer networks. However, if the supposedly bridging bidentate donor ligand is not “strong” enough to displace anions, respectively to coordinate in the expected bridging fashion, or has the wrong orientation, molecular entities are obtained, such as in $[\text{Na} \subset (\text{DB18C6})\text{I}(1,3\text{-dioxolane})]$, where 1,3-dioxolane is a potential bridging ligand, but with a poor orientation and interfering with the crown ether ligand [11]. If such steric factor is eliminated, 1,3-dioxolane can act as ligand on tetrahedral nodes to yield a diamondoid structure [10b].



Scheme 1. Scorpionate-type crown ether ligands for the construction of 1D alkali metal polymer chains; by permission of the Royal Society of Chemistry from [8].

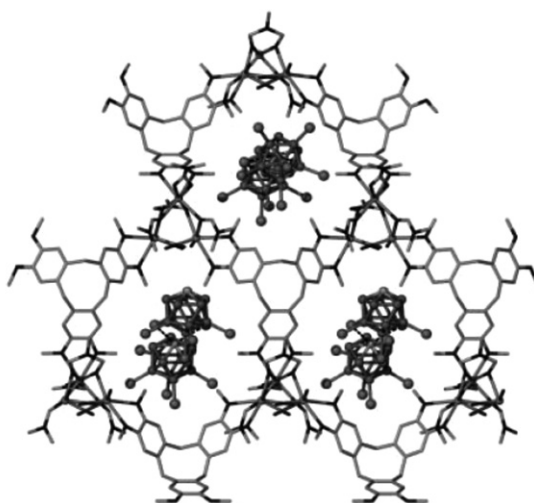
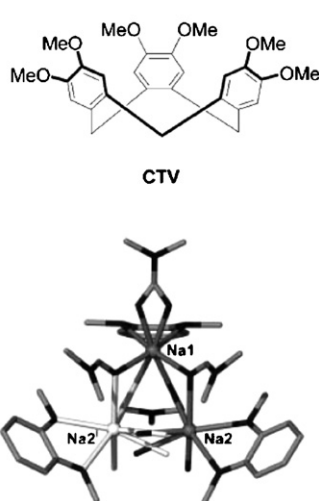


Fig. 5. Structural details of $[\text{Na}_2(\text{dmf})_4(\text{H}_2\text{O})_2(\text{ctv})][(\text{dmf})_{0.5}(\text{ctv})][\text{CB}_{11}\text{H}_6\text{Br}_6]_2$, with permission from [9].

2.2. Anionic oxygen donor ligands

So far, we have looked at inorganic salts or clusters of alkali metal ions to which neutral oxygen donor ligands are coordinated, and which possess 1D, 2D or 3D structures. This chapter will now deal with organic, anionic ligands with a negative charge on the oxygen atom. The first examples to cite here are alkoxides, aryloxides and carboxylates.

2.2.1. Alkoxides and aryloxides

One of the best known polymers of alkali alk- and aryloxides, MOR, are of course the methoxides and simple phenoxides which form insoluble compounds based on chain or sheet structures [12–18]. Structures can be tuned as a function of the steric demand of R, and thus, the larger R, the more aggregates (0-dimensional) are obtained [19].

Aryloxides can form coordination polymer compounds as well, and, additionally to the metal–oxygen interaction, the aromatic group can participate in the coordination to the metal ion. This is especially the case for the heavier and thus softer alkali metals, such as Rb or Cs (Fig. 7) [20].

Alkali metal salts of organic acids are numerous, and very often not well characterized in the solid state. The presence of two oxygen atoms in the acid function leads to a stronger bridging function than for alkoxides, resulting more typically in the formation of layered structures [21–24].

The use of cyclic polyphenols, like calixarenes, allows isolating one-dimensional coordination polymer compounds in which the cations can even be mobile similar to biological ion channels. One such example is given in $[\text{K}(\text{calix}[8]\text{arene-H})(\text{THF})_4(\text{H}_2\text{O})_7]$ (Fig. 8) [25].

2.2.2. Carboxylates

One other interesting example is the synthesis of ferromagnetic 2D-coordination polymer compounds from nitroxyl free-radical carboxylic acids (4-carboxy-TEMPO and 3-carboxy-PROXYL, see Scheme 2) and sodium or potassium ions (Fig. 9) [26].

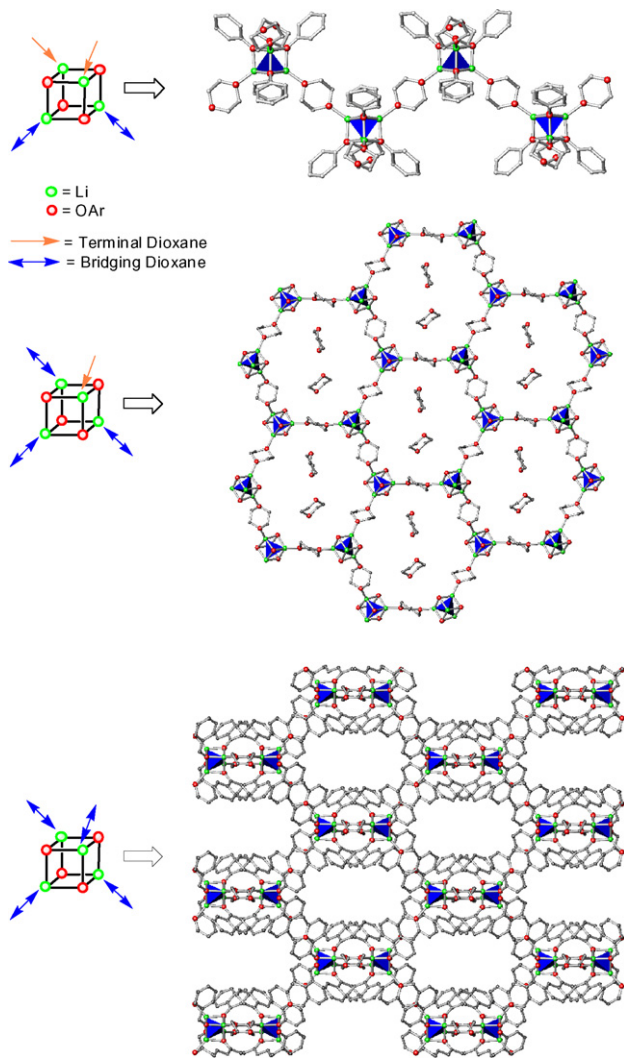


Fig. 6. Different dimensional polymeric structures depending on the number of bridging dioxane ligands; by permission of the Royal Society of Chemistry from [10].

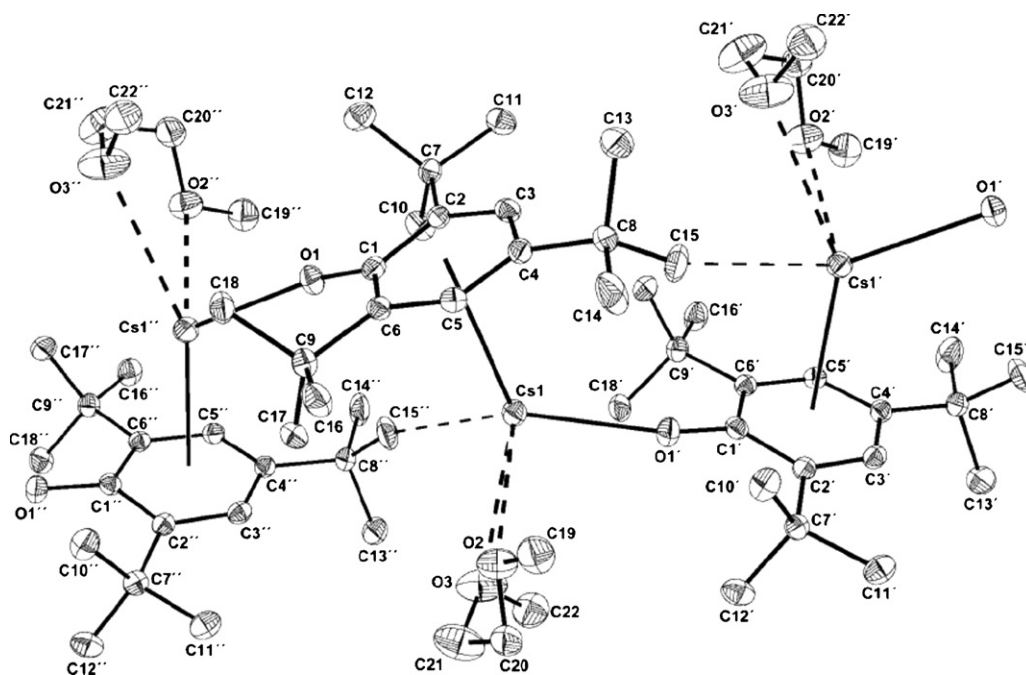


Fig. 7. 1D structure of $[\text{Cs}(2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2\text{O})(\text{DME})]$; with permission from [20].

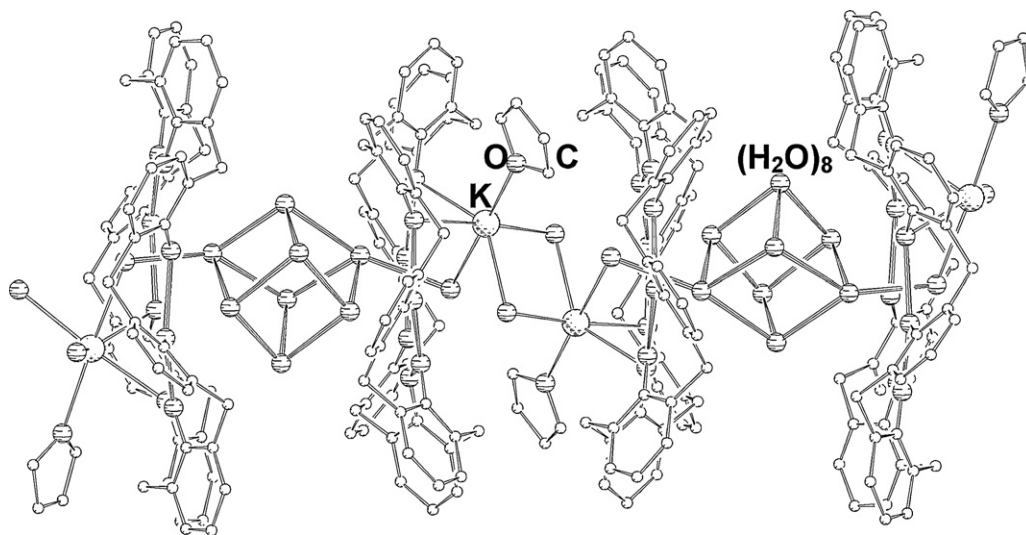
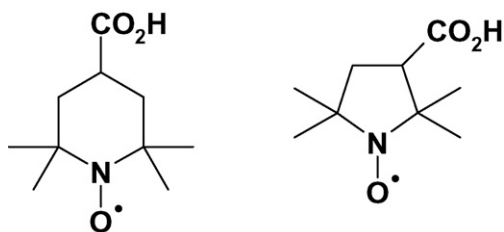


Fig. 8. Part of the 1D structure of $[\text{K}(\text{calix}[8]\text{arene-H})(\text{THF})_4(\text{H}_2\text{O})_7]$ [25].

Combining the anionic carboxylate groups with neutral N-donor sites within one ligand, such as the 3,5-pyridinedicarboxylate (3,5-pdc), the dimensionality of such polymers can be increased into a 3D-network, as exemplified



Scheme 2. 4-Carboxy-TEMPO (left) and 3-carboxy-PROXYL (right); by permission of the Royal Society of Chemistry from [26].

in $[\text{Na}_2(3,5\text{-pdc})(\text{H}_2\text{O})_4]$, in which additional H-bonding occurs [27].

Upon addition of a further coordinating anion, the layers of Na-acetate for instance can be cross-linked into a three-dimensional porous network with channels in which the solvent molecules can be found (Fig. 10) [28].

2.2.3. Sulfonates and nitro-derivatives

Apart from aryl-, alkoxides and acid derivatives, sulfonates are an important class of oxygen donor ligands to alkali metal ions. A ligand combining sulfonate groups and aryloxy groups is Orange G, a synthetic azo dye used in histology in many staining formulations. One difficulty in examining sulfonated dyes is that they exhibit generally poor crystal growth properties, mak-

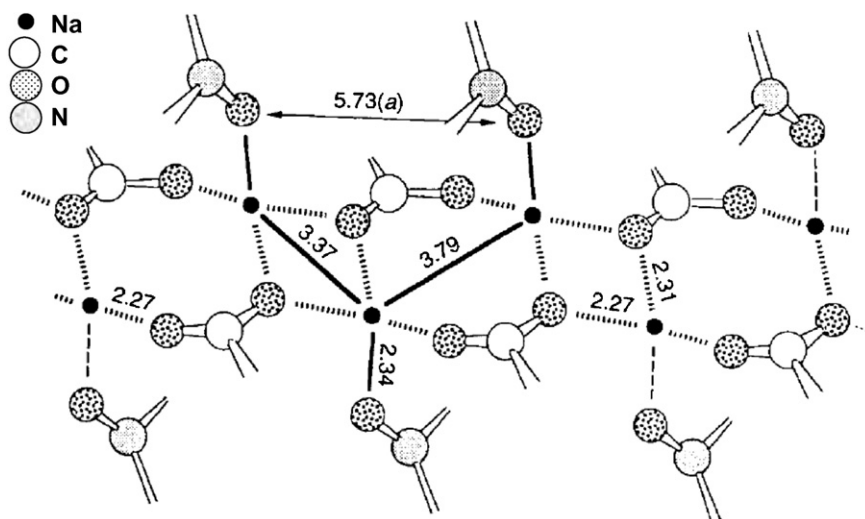


Fig. 9. Ferromagnetic 2D coordination polymer of 4-carboxy-TEMPO with Na; by permission of the Royal Society of Chemistry from [26].

ing single-crystal diffraction studies difficult. An exception is the disulfonated naphthalene-based dye Orange G, 7-hydroxy-8-(phenylazo)-1,3-naphthalenedisulfonic acid, the salts of which are found to grow as robust crystals [29]. The s-block metal salts of the Orange G dianion (Og) can be categorized into three structural classes related to those previously proposed for simple monosulfonated azo dyes. All of the structures feature alternate organic/inorganic layering, but whereas the Mg, Ca, and Li complexes are solvent-separated ion-pair species, the Sr and Ba complexes form simple discrete molecules based on metal sulfonate binding bonding, and the heavy alkali metal complexes utilize a variety of MO interactions to form two- and three-dimensional coordination networks. These structural differences

are rationalized in terms of simple properties of the metals (charge, size, and electronegativity) and the steric demands of the arylsulfonate groups. This is summarised by saying that the most electronegative metals favor M-OH₂ bond formation and hence solvent-separated ion-pair structures, whereas the most electropositive metals form higher-connectivity complexes with more M-O₃S bond formation. Thus, the sodium derivative forms a two-dimensional extended structure, involving the sulfonate groups as well as the keto O-atom in the coordination of the metal ions as well as bridging water molecules (Fig. 11).

Another application of sulfonates in combination with other donor groups is found in high-energy materials. It is well known that the nitration products of phloroglucinol (PG)

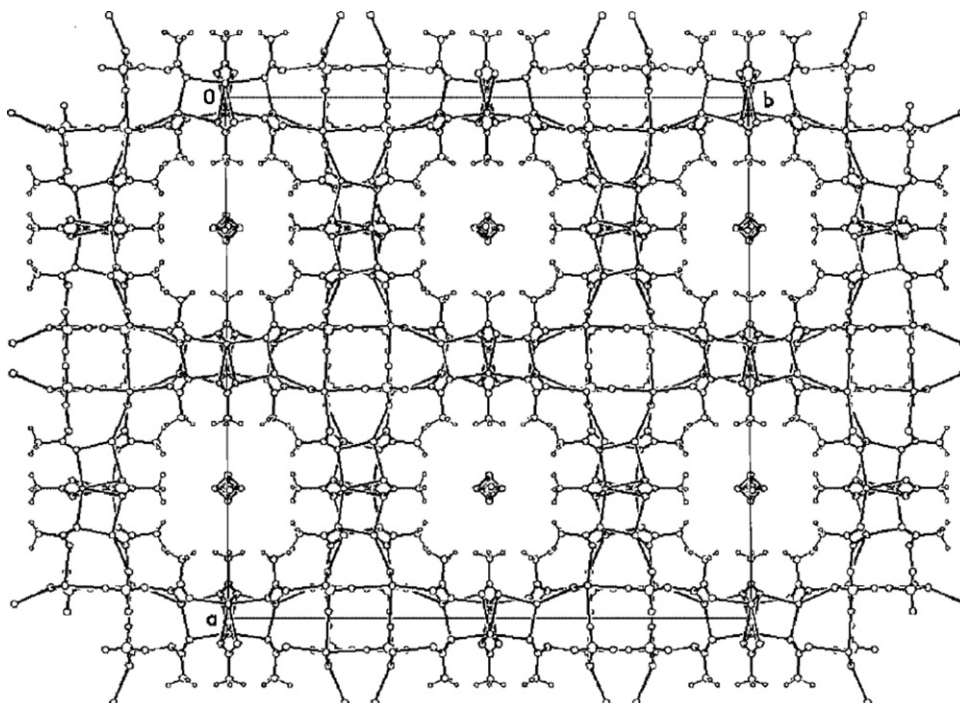


Fig. 10. The Na₄(OAc)₃(ClO₄)·0.25(MeOH) structure viewed down the *c* axis; with permission from [28].

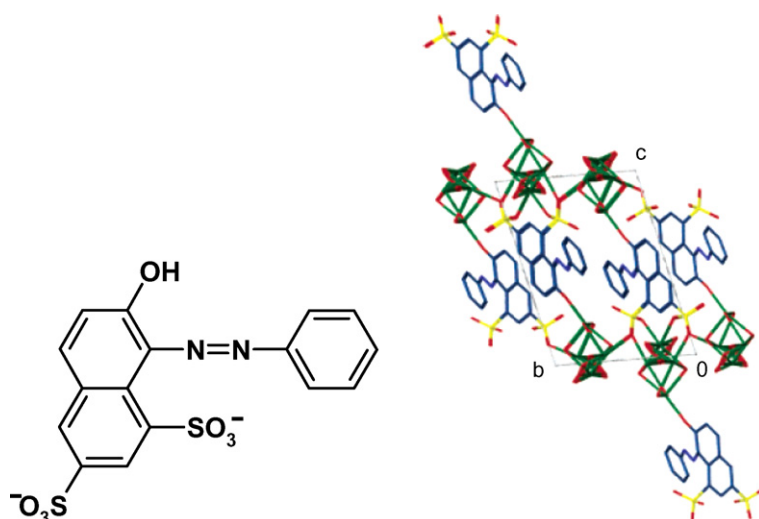


Fig. 11. Structure of the dianion of Orange G (left), and structure of the Na-derivative (right); with permission from [29].

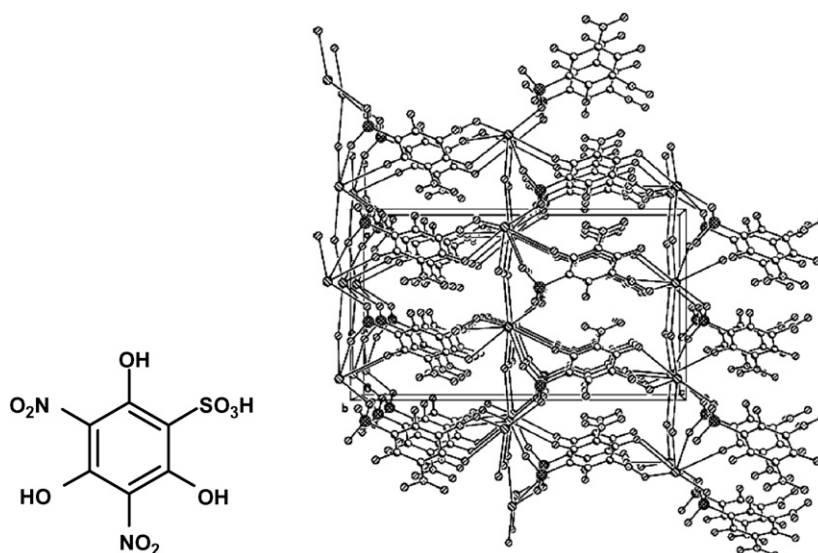
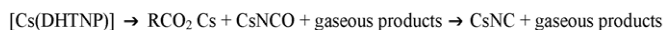


Fig. 12. Structure of DNPGSH (left) and 3D structure of $[K(DNPGS)(H_2O)]$; with permission of Springer from [30].

are important intermediates in chemical industry and can be used as such high-energetic materials. Additionally, in recent years, potassium energetic coordination compounds have received extensive attention due to their potential properties such as low toxicity and minimal pollution. A novel coordination polymer, potassium 3,5-dinitrophenylglucinosulfonate monohydrate $[K(DNPGS)(H_2O)]$, was synthesized by the reaction of 3,5-dinitrophenylglucinosulfonic acid (DNPGS) with potassium hydroxide in aqueous solution, yielding a three-dimensional (3D) network with the participation of the sulfonate, the phenolic and the nitro groups of the ligand, as well as coordinating, bridging water molecules (Fig. 12) [30].

Along these lines, the cesium derivative of 3,5-dihydroxy-2,4,6-trinitrophenolate is relevant [31]. In this compound, each Cs is coordinated to 12 oxygen atoms from eight different 3,5-dihydroxy-2,4,6-trinitrophenolate (DHTNP) anions, and each DHTNP-anion is coordinated with eight Cs cations. The oxygen atoms of the phenolic hydroxyl group and from all of the

nitro groups of the DHTNP-anion simultaneously bind to neighboring Cs ions. These DHTNP molecular chains are interlaced, with the cesium atoms acting as knots, to create an infinite three-dimensional network structure. The molecules are linked by electrostatic interactions and weak van der Waals forces and also display intramolecular hydrogen bonding, which all enhance the thermal stability of this compound, which undergoes two highly exothermic decomposition reaction processes from 166 to 300 °C under the condition of a linear heating rate. The experimental sensitivity results indicate that $[Cs(DHTNP)]$ is quite sensitive to impact and friction (Fig. 13). Its properties resemble those of other trinitrophenylglucinosulfonate salts of alkali metals, which can be used as components of ecologically clean initiating compositions (Scheme 3).



Scheme 3. Proposed thermal decomposition of $[Cs(DHTNP)]$ [31].

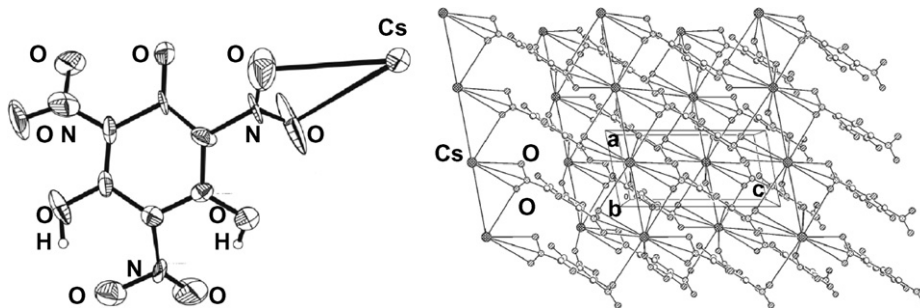


Fig. 13. The coordination of Cs (left) and the packing arrangement of [Cs(DHTNP)]; adapted from [31].

2.2.4. Amino acids

Surprisingly little is known about the structures of alkali metal derivatives of amino acids, which would combine the acid donor group with the amine function. Derivatives, such as the total-kill herbicide glyphosate [*N*-(phosphonomethyl)glycine = H_3L], possess low mammalian toxicity, are relatively quickly degraded in the soil and are usually dealt with in form of alkali metal salts. For the sodium salts, three different solvates of the monosodium compounds have been isolated, namely $\text{Na}(\text{H}_2\text{L}) \cdot 0.5\text{H}_2\text{O}$, sodium glyphosate monohydrate $\text{Na}(\text{H}_2\text{L}) \cdot \text{H}_2\text{O}$, sodium glyphosate dihydrate $\text{Na}(\text{H}_2\text{L}) \cdot 2\text{H}_2\text{O}$, together with a disodium glyphosate nonahydrate $\text{Na}_2(\text{HL}) \cdot 9\text{H}_2\text{O}$ [32]. The first two compounds are both polymeric and based on dimeric repeating units with six coordinate sodium ions, while the disodium salt is based on both discrete octahedral $[\text{Na}(\text{HL})(\text{H}_2\text{O})_5]^-$ anionic complex units with the unidentate glyphosate ligand bonded *via* a carboxylate oxygen, together with a cationic $[\text{Na}_2(\text{H}_2\text{O})_8]^+$ -ribbon polymer (Scheme 4).

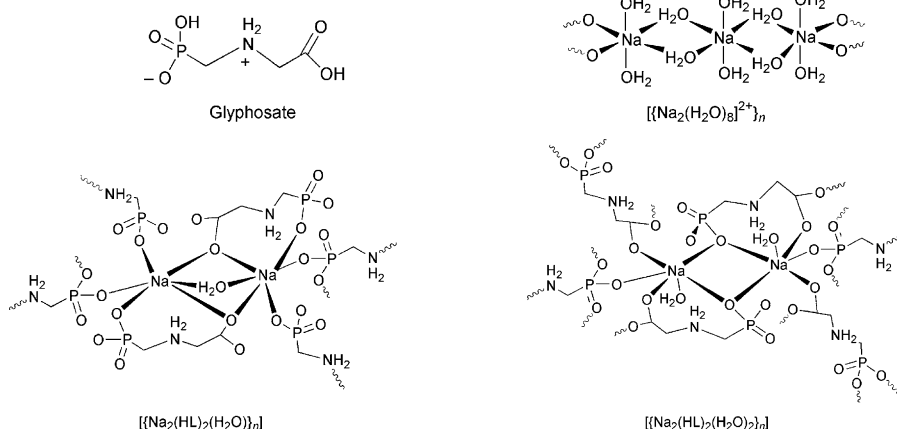
Even though this glycine derivate possesses three potential donor groups for alkali metal ions, i.e. the phosphonate, the carboxylate and the NH-group, the latter does not coordinate to the metal ions in any of the observed structures. This is also observed in the coordination mode of uracil-5-carboxylic acid toward alkali metal ions Na–Cs, for which mainly 1D structures (chains, tapes) are obtained [33].

In sulfonylamines, the donor groups, O- and N-atoms, are now both charged negatively, and participate in metal ion coordination. The donor groups are relatively close together within one ligand molecule, and thus, bridging coordination is preferred over chelating action. This leads to the linear coordination polymer which consists of discrete square tubes based upon Na–O and Na–N interactions (Fig. 14) [34].

For the larger cations potassium and rubidium of the alkali metal series, the same ligand is used, but with an increased coordination number of seven to yield water-free three-dimensional compounds with a more regular structure than the sodium compound (Fig. 15) [35]. In contrast, the Cs-compound features anion monolayers that intercalate planar zig-zag chains of cations ($\text{Cs} \cdots \text{Cs}$ alternately 422.5 and 487.5 pm, $\text{Cs} \cdots \text{Cs} \cdots \text{Cs}$ 135.7°), whereby each chain is surrounded and coordinated by four anion stacks and each anion stack connects two cation chains. All structures exhibit close C–H \cdots A interanion contacts consistent with weak hydrogen bonding [35].

2.2.5. Mixed O- and N-donors

Polydentate ligands with anionic O-donors and neutral N-donors can be obtained by integration of a cyano-function in an appropriate position into anionic O-donors. Thus, 4-cyano-substituted aryloxides, such as (4-NC-2,6-*t*Bu₂-C₆H₂OLi), lead to the formation of 1D chains *via* single metal ions stabi-



Scheme 4. Glyphosate and different derived polymer structures with Na-ions [32].

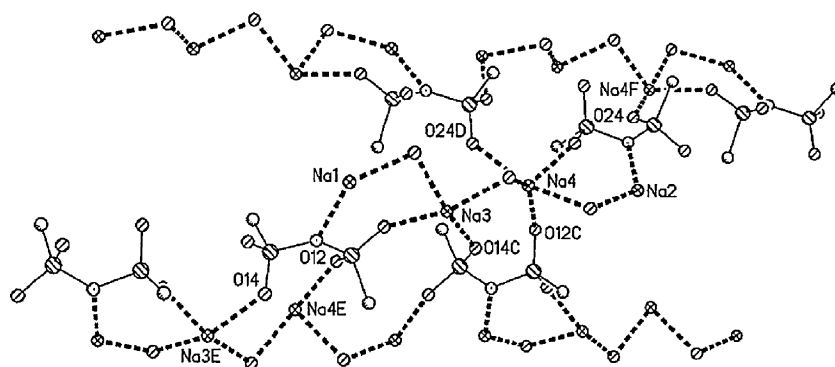


Fig. 14. Chain interactions in $\text{Na}_4[(\text{MeSO}_2)_2\text{N}]_4 \cdot 3 \text{H}_2\text{O}$; with permission from [34].

lized by THF or pyridine ligands (Fig. 17) [36]. Instead of using single metal ions as nodes, small cluster or aggregate units can also be interconnected into chains, sheets or three-dimensional motifs. As an example, lithium derivatives with α -cyanophosphonates, $[(\text{RO})_2\text{P}(\text{O})\text{CHCNLi}]$ ($\text{R} = \text{Et}, i\text{Pr}$), and (organo)sulfonyl-acetonitriles, $(\text{RSO}_2\text{CHCNLi})$, as quasi linear bidentate ligands, tend to form 2D-layered structures by linking Li_2O_2 -units, respectively eight-membered ring dimers $(\text{SO}_2\text{Li})_2$, into sheets (Fig. 16) [37].

2.3. N-donor ligands

Given the fact that alkali metal ions are generally considered as rather hard cations, they interact preferably with oxygen donor atoms rather than nitrogen atoms. However, when oxygen donors are not available in sufficient quantity to satisfy the coordination of the metal ions, nitrogen atoms are also involved in metal ion coordination. This is the case in the tripodal, pyridyl-substituted

tris(pyrazolyl)borate ligands [38]. Whereas the water-rich potassium derivative of this ligand type yields a dimeric structure, the compound with only one water molecule in the potassium coordination sphere leads to a one-dimensional coordination polymer network, in which two of the three arms of the tripodal ligand act as bridging ligands towards two neighbor metal ions (Fig. 17).

Pure nitrogen donation is rare, as shown in the example of the toluene-soluble potassium salt of the $[(2,6-i\text{Pr}_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})\text{C}(\text{H})\text{C}(\text{Me})\text{N}(2,6-i\text{Pr}_2\text{C}_6\text{H}_3)]^-$ -ion, in which the aromatic rings complete the coordination sphere of the potassium ion by metal–aromatic interactions. This kind of interaction is finally responsible for the 1D-extension of the structure in the solid state (Fig. 18) [39].

Similarly, cyano-cyclopentadienyl (CpCN) anions are ideal to combine nitrogen and aromatic ring interactions with alkali metal ions, such as in CpCNM , $\text{M} = \text{K}, \text{Cs}$ (Fig. 19) [40].

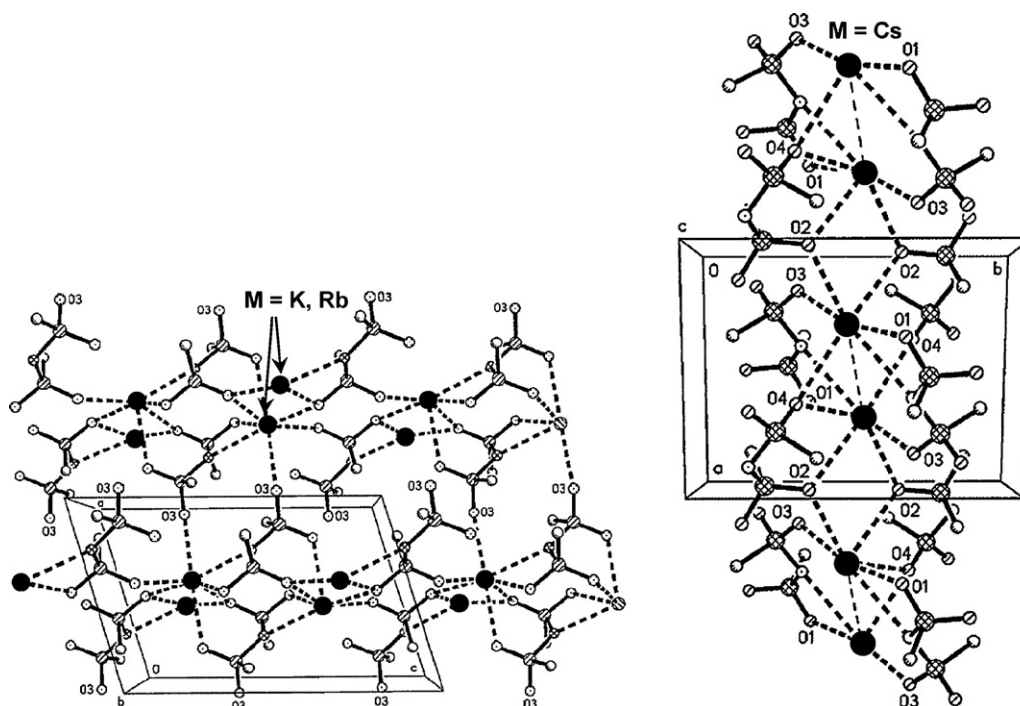


Fig. 15. Isostructural structure for $\text{MN}(\text{SO}_2\text{Me})_2$ ($\text{M} = \text{K}, \text{Rb}$; left), and the Cs-compound (right), adapted from [35].

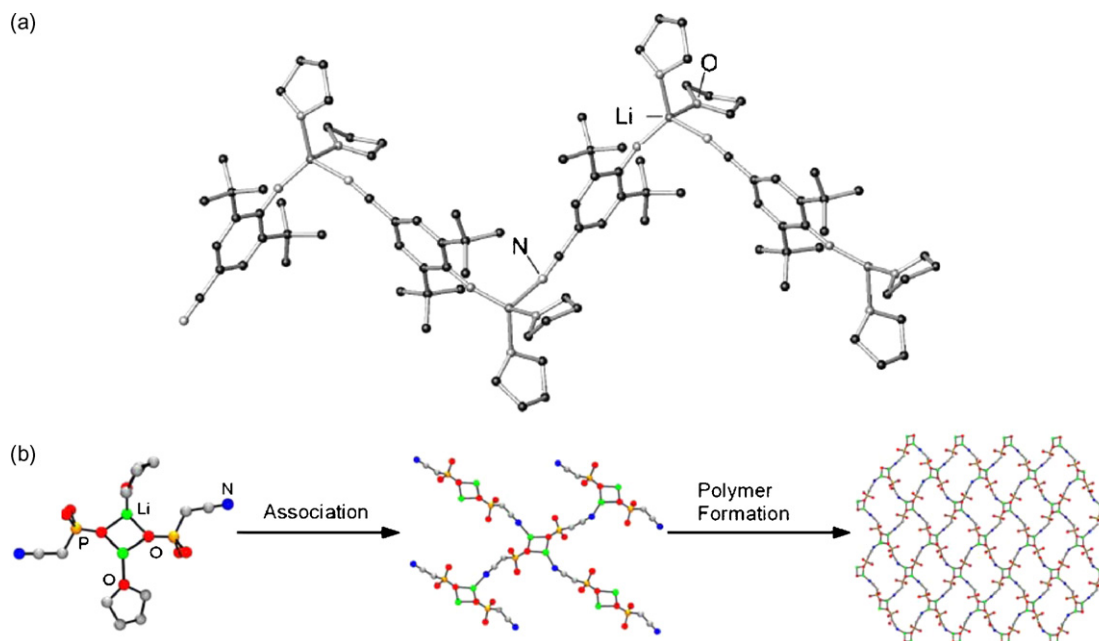


Fig. 16. (a) Cyano-aryloxide as 1D-bridging ligand towards single Li-ions, adapted from [36]; (b) Assembly process of lithiated α -cyanophosphonates by linking Li_2O_2 dimers; adapted from [37].

This leads us to the coordination compounds of alkali metal ions with carbon donors, of which phenyl groups and cyclopentadienyl (Cp)-ligands are the most representative in the formation of extended structures.

2.4. Carbon donor ligands

The larger alkali metal ions are softer than the smaller ones, and accept more easily aromatic coordination. This has been shown in the zig-zag-arranged structures of the solid-state structures of CpM-compounds for the heavier alkali metal ions [41,42]. Substituted phenyl rings with small and non-coordinating side-groups maintain such a chain-structure in the solid state (Fig. 20) [43]. The derived calcium compound is a THF adduct and by the way a monomer.

In combination with phosphor donor atoms which are linked to a cyclopentadienyl-ligand and additional THF, a new 1D struc-

ture can be stabilized, as for instance in the solid-state compound $[(\text{THF})\text{K}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2)]$ (Fig. 21) [44].

Solvent adducts of CpM- and indenyl-M-compounds with diethyl ether or polydentate amines lead either to molecular structures or also polymeric zig-zag chains, as in the case of $\text{CpK}(\text{OEt}_2)$ (multidecker structure), $[\text{K}(\text{indenyl})(\text{L})]$ ($\text{L} = \text{TMEDA}$ (N,N,N',N' -tetramethylethylenediamine) or PMDTA (N,N,N',N'',N'' -pentamethyldiethylenetriamine) [45]. Such different coordination modes are the combined result of electrostatic and steric effects.

Single metal-carbon bonds with more σ -character can be enforced with carbanions carrying large substituents like

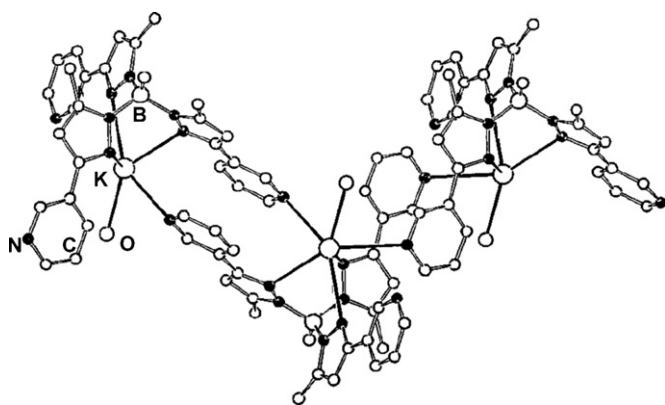


Fig. 17. Solid-state structure of the potassium tripod coordination polymer with only one water molecule in the metal coordination sphere; adapted from [38].

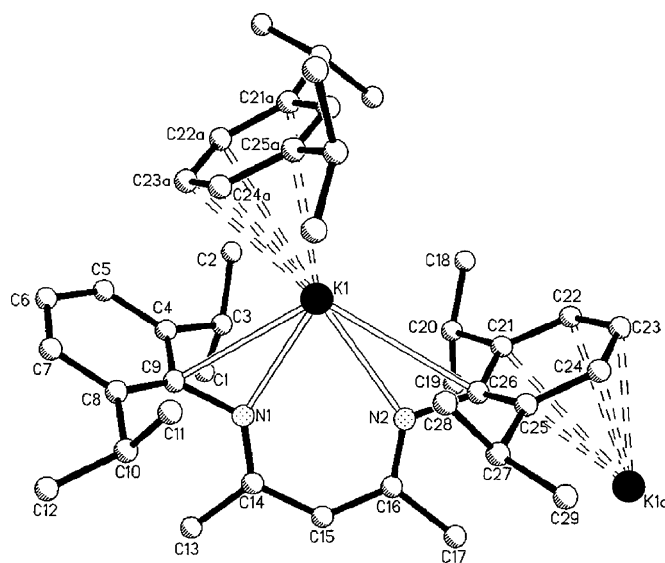


Fig. 18. 1D structure of $\text{K}[(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{NC}(\text{Me})\text{C}(\text{H})\text{C}(\text{Me})\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)]$; adapted from [39].

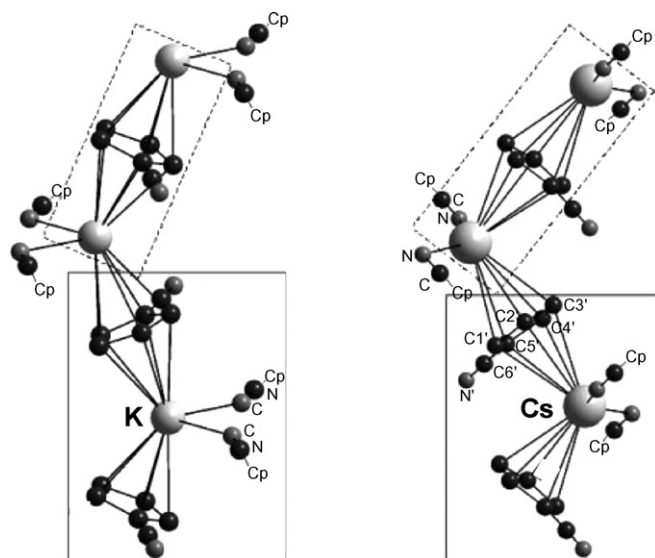


Fig. 19. Zig-zag chains of cyanocyclopentadienyl alkali salts (K left, Cs right); adapted from [40].

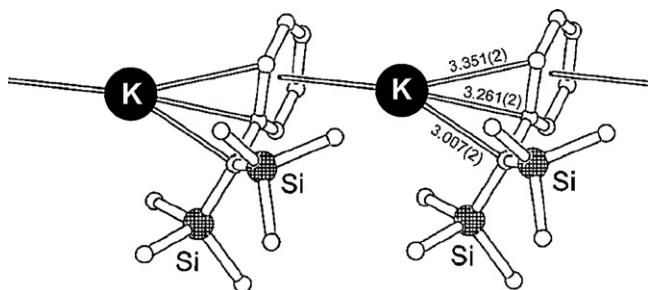


Fig. 20. Typical solid-state structure of aryl-potassium interactions; adapted from [43].

phosphine and borane rests [46]. The related potassium compound yields then a complicated sheet structure in which additional K–H bonds seem to stabilize the structure (Fig. 22).

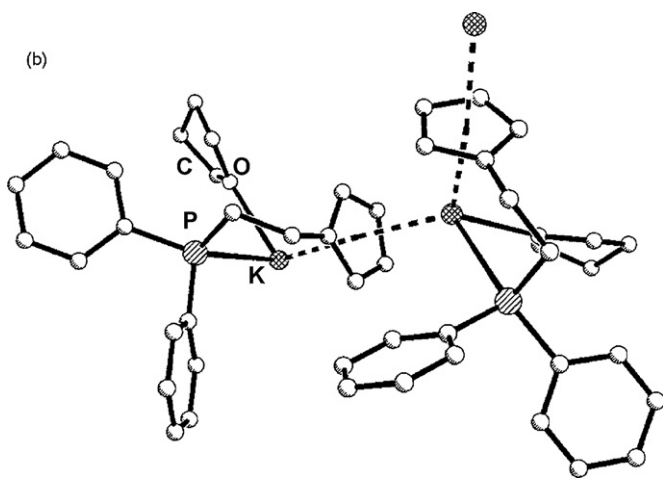
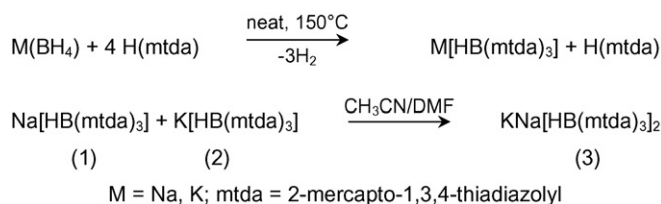


Fig. 21. 1D structure of [(THF)K(C₅H₄CH₂CH₂PPh₂)]; by permission of the Royal Society of Chemistry from [44].



Scheme 5. Different coordination polymers obtained with Na and K; by permission of the Royal Society of Chemistry from [47].

2.5. Sulfur donor ligands

Alkali metal coordination polymers with solely sulfur atoms as donors, have not been reported in the literature so far. However, as shown in some of the previous examples, the combination of different metal donor types allows the selective coordination of different metal ions to different donor sites, as anticipated from Pearson's hard-soft acid–base theory. Thus, the Janus scorpiate ligand [HB(mtda)₃[−]] (mtda = mercaptothiadiazolyl) contains both sulfur and nitrogen atoms. This feature can be exploited for the controlled construction of homo- and hetero-metallic (hard-soft) alkali metal coordination polymers (Scheme 5) [47]. Remarkably, in the case of sodium, coordination polymers with both acentric (with NaS₃N₃H kernels) and centric (with alternating NaN₆ and NaS₆H₂ kernels) chains are found in the same crystal (where the centricity is defined by the relative orientations of the BH-bonds of the ligands along the lattice) (Fig. 23). For the homometallic potassium congener, the larger cation size, compared to sodium, induced significant distortions and favored a polar arrangement of ligands in the resulting coordination polymer chain. An examination of the solid-state structure of the mixed alkali metal salt system revealed that synergistic binding of smaller sodium cations to the nitrogen portion and of the larger potassium cations to the sulfur portion of the ligand minimizes the ligand distortions relative to the homometallic coordination polymer counterparts, a design feature of the ligand that likely assists in thermodynamically driving the self-assembly of the heterometallic chains. The similarity of the solution analytical data regardless of the cation indicates that the salts are likely dissociated in solution rather than maintaining their solid-state polymeric structures.

Thiophosphonates combine the coordination of sulfur atoms with the one of oxygen donors, within the same ligand. Thus, the ligand [ArP(O*t*Bu)S₂][−] (Ar = 4-anisyl) may coordinate with both donor atoms to alkali metal ions in ethereal solvents to yield mostly one-dimensional coordination polymer compounds (Scheme 6 and Fig. 24) [48].

In terms of networks and nodes, moving from groups 1 to 2 metals halves the number of nodes and so decreases connectivity for the same ligand types.

3. Group 2 metal compounds

Passing from groups 1 to 2 metal ions, the charge density of the cations increases. Also, many alkaline earth metal compounds are hygroscopic. For these reasons, many of the species

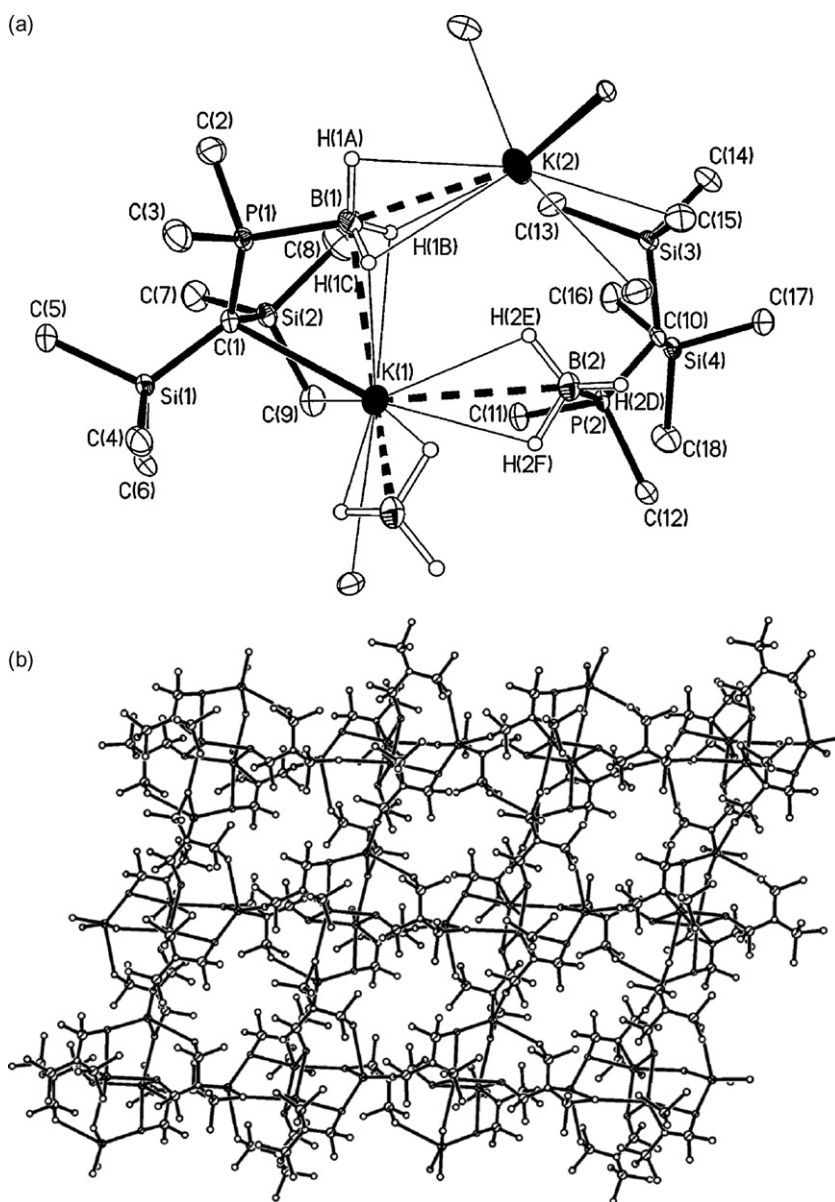
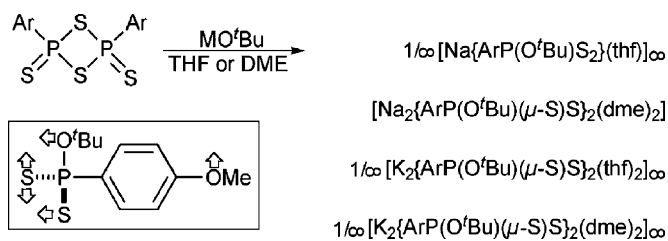


Fig. 22. 2D structure of $[(\text{Me}_3\text{Si})_2\{\text{Me}_2\text{P}(\text{BH}_3)\}\text{C}]\text{K}$; adapted from [46].

do contain water molecules, either directly linked to the metal ions, or H-bonded to the formed structure in some way.

Until recently, the chemistry of alkaline earth metals has been a largely underdeveloped area of coordination chemistry. There have been a few studies on the coordination behavior of these metals in both aqueous and non-aqueous media. The alkaline

earth metals play an important role in the biochemistry of virtually all living organisms. They are distributed in most cells and tissues, often in considerable concentrations, and a constant supply is indispensable for unrestricted performance of biological functions. Magnesium and calcium are the most prominent alkaline earth metals in biological systems. Magnesium is present solely as the solvated or complexed dication Mg^{2+} , basically as a part of the osmotic equilibria in and outside of the cells and in all tissues. Magnesium cations induce or stabilize tertiary structures or enhance certain enzyme functionalities. Calcium is the most prominent metal involved in structural biology. It is the main constituent of bones and teeth. These two metal ions play an essential role in the activation of enzymes, complexation with nucleic acids, nerve impulse transmission, muscle contraction, and carbohydrate metabolism. A range of model complexes containing these two metals have been prepared as probes to elucidate the mode of binding of these metals. The



Scheme 6. Reaction of thiophosphonates with alkali metal ions; adapted from [48].

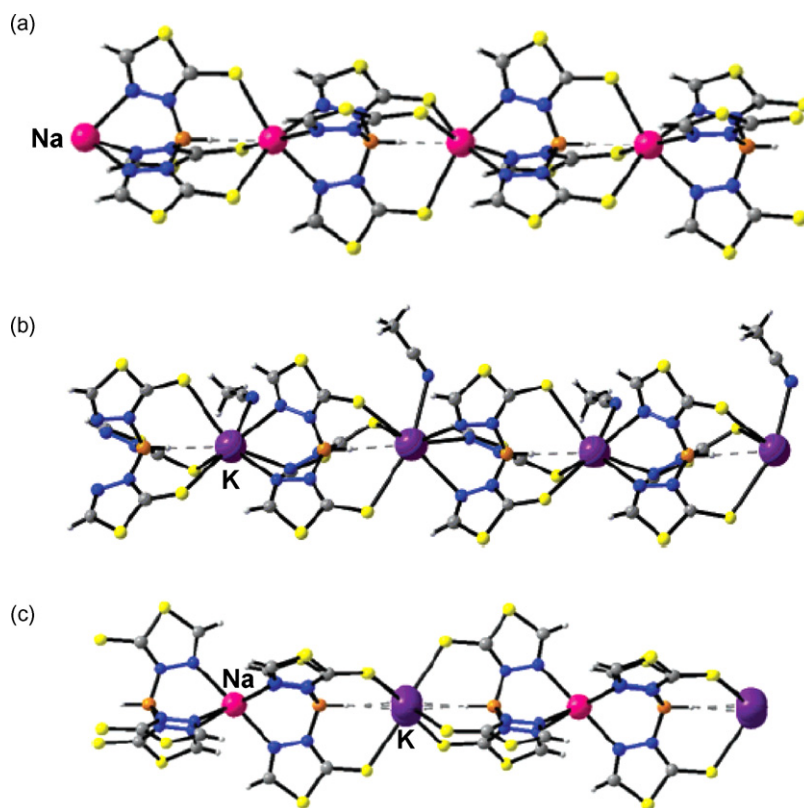


Fig. 23. Polymeric 1D structures of $M[\text{HB}(\text{mtda})_3]^-$, (a) $M = \text{Na}$; (b) $M = \text{K}$; (c) $M = \text{Na/K}$; adapted from [47].

studies have focused on the use of aspartate, glutamate, orotate, or pyroglutamate ligands as careful investigation of the calcium or magnesium binding sites on proteins has shown that the acidic groups of L-aspartic acid and L-glutamic acid are the key anchoring positions for these ions. On the other hand, barium and strontium are considered as *trace elements* in the body. Strontium is rated nontoxic, and traces of it appear to be essential, though the reason for this is not yet known. Barium causes typical heavy metal poisoning even at low concentrations if soluble compounds are applied. Barium and strontium metals have been known as antagonists for potassium and calcium, respectively. In the process of binding to various sites, the ions compete with other common metal ions, some of which are antagonists through a different specificity. This specificity is predominantly governed by the charge and size of the cation, as well as by

the resulting effective coordination number and geometry. An improved understanding of the function of biological cations is thus to be expected from a detailed study of the coordinating properties of the metals competing with various ligating groups.

3.1. Neutral oxygen donor ligands

Similar to alkali metal ions, group 2 metal compounds can be treated with for instance neutral oxygen donor ligands to “cut out” fragments from the three-dimensional salt structure. This has been exemplified in the studies on alkaline earth metal iodides, which are still quite soluble in organic solvents which may act also as coordinating ligands. In these cases, it is important to control the quantity of water present, as water is a solvent

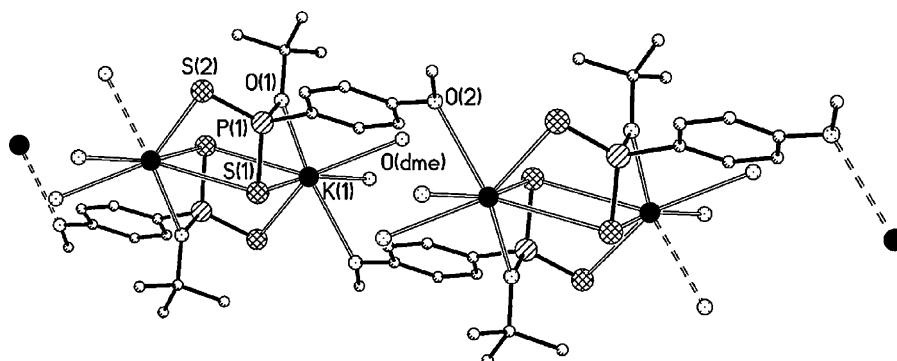


Fig. 24. Section of the 1D structure of $[\text{K}_2\{\text{ArP}(\text{OrBu})(\mu\text{-S})_2(\text{dme})_2\}]$; by permission of the Royal Society of Chemistry from [48].

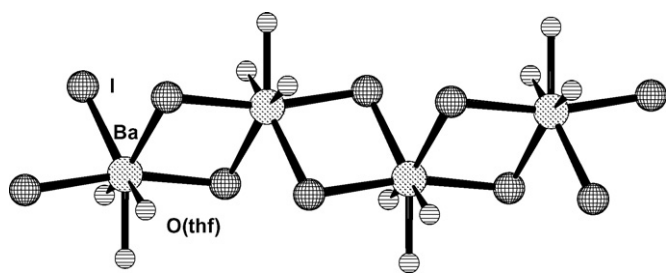


Fig. 25. 1D structure of $[\text{BaI}_2(\text{thf})_3]$ [55].

able to dissociate the mainly ionic bonds in alkaline earth metal salts [49–54].

Thus, it has been shown that one-dimensional coordination polymer compounds can be obtained with low concentrations of THF, used as chemical scissors to yield $[\text{BaI}_2(\text{thf})_3]$ (Fig. 25) [55].

Similarly, by controlling the ratio of O-donor solvents, a series of low-dimensional barium iodide solvates were isolated [56]. This strategy could be transferred to alkaline earth triflate $\text{Ba}(\text{OTf})_2$ [57]. In these salt derivatives, the metal ions are still directly coordinated by the anions and show excerpts from their initial solid-state structure. Other neutral solvents are however able to cleave the cation–anion contacts and to coordinate the cations completely, leaving the anions out of the first coordination sphere of the cation. Water is such a solvent, and thus, can replace one or both anions from the first coordination sphere of the cation. As cation-coordinated water is a hydrogen bond donor ligand, low-dimensional polymer structures can be designed as a function of the number of coordinating water molecules [58]. As an example, the H-bonded one-dimensional polymer $[\text{Ca}(\text{H}_2\text{O})_2(\text{diglyme})_2](\mu\text{-I})_2$ is cited [58–62].

Instead of using single metal ions as nodes to be connected into 1D, 2D or 3D-motifs, cluster units can be used as well. Thus, replacing terminal, monodentate O-donor cluster ligands such as THF by polydentate O-donors, such as DME (dimethoxy ethane), the latter may displace the terminal ligands and bridge two cluster units into 1D chains of mixed metal $[\text{SrLi}_6(\text{OPh})_8(\text{thf})_4]$ -clusters (Fig. 26) [63].

3.2. Anionic oxygen donor ligands

3.2.1. Beta-diketonates

Beta-diketonates of alkaline earth metal ions received prominent attention when High-Tc superconductors were discovered. One synthesis of such oxide materials is *via* metal organic chemical vapor deposition (MOCVD) or the sol–gel technique. For the

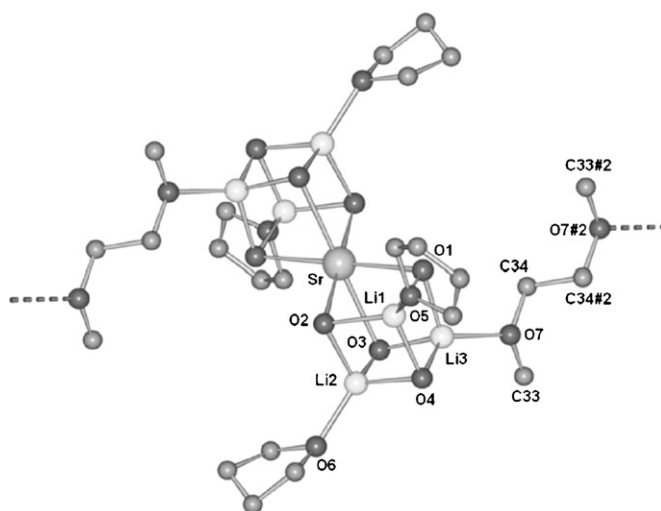
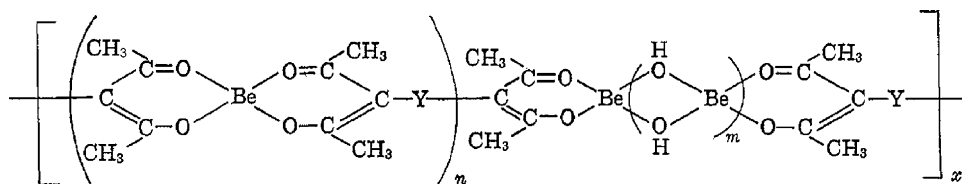


Fig. 26. 1D structure of $(\mu\text{-dme})[\text{SrLi}_6(\text{OPh})_8(\text{thf})_4]$ (green: Sr, red: O, yellow: Li and grey: C) [63].

first technique, volatile species are necessary. It turned out that beta-alkoxides are well suited, because they form cluster-like compounds in which the alkaline earth metal ions are surrounded by the organic ligands and turn out to be volatile at relatively low temperatures. From this property, the reader may deduce that these compounds do not form coordination polymer network. However, some cases are known, for which polymer structures are obtained. Thus, beryllium, the smallest of the alkaline earth metal ions, has a low coordination number of four, which in the case of bis-beta-diketones leads to a one-dimensional chain structure (Scheme 7) [64].

3.2.2. Alkoxides

Another group of alkaline earth metal compounds studied in the same context are the alkoxides. Unless multifunctional alcohols' and sterically crowded alkyl or aryl groups are employed these compounds are generally polymeric insoluble solids, which are poorly characterised from a structural point of view. The reactions of these compounds with small molecules such as CO_2 and SO_2 have been relatively neglected although organo-magnesium compounds are known to react with SO_2 to give sulfinic acids after hydrolysis, while calcium oxide is used to scrub flue gases and for the desulfurisation of iron ores. In contrast, the corresponding reactions of the class 'b' or soft metal alkoxides of palladium, platinum and rhodium with SO_2 have been investigated in more detail. Structural studies of these complexes reveal, as expected, S-coordinated SO_2 moieties. In a communication by Arunasalam et al., the reactions



Scheme 7. 1D-coordination network of beryllium bis-beta-diketonates; adapted from [64].

of $[\text{Mg}(\text{OMe})_2]$, and $[\text{Ca}(\text{OMe})_2]_n$ with SO_2 are described, which lead to one-dimensional polymers, with good solubility in organic solvents and which have interesting structural features in the solid state [65]. Thus, the reaction of $\text{SO}_2(\text{g})$ with a suspension of $[\text{M}(\text{OMe})_2]$, ($\text{M} = \text{Mg}$ and Ca) in methanol yields the crystalline compounds, $[\text{M}(\text{O}_2\text{SOMe})_2(\text{MeOH})_2]$, ($\text{M} = \text{Mg}$, Ca). The insertion reaction is of high yield and the X-ray crystal structure of the second complex reveals that it is a chain polymer with eight-coordinated Ca -ions and the methylsulfito anions acting as both chelating and bridging ligands.

3.2.3. Carboxylates

Carboxylates were also among the species investigated as precursors for oxide materials, using sol-gel techniques. However, many of these precursors may lead to the formation of mixed alkaline earth metal carboxylates and oxides. This is why this research was not further pursued. However, dicarboxylates have found a large field of application in the construction of coordination polymer arrays, especially the more rigid ligands, as they are useful building blocks for porous networks with metal ions throughout the periodic system [66].

A semi-rigid ligand, benzene-1,4-dioxyacetate, L , leads to the three-dimensional coordination polymer networks $[\text{M}(\text{L})\text{H}_2\text{O}]$, $\text{M} = \text{Ca}$, Sr , Ba [67]. Both $\text{Ca}(\text{L})\text{H}_2\text{O}$ and $\text{Sr}(\text{L})\text{H}_2\text{O}$ crystallize in the monoclinic space group $P2_1/c$ while $\text{Ba}(\text{L})\text{H}_2\text{O}$ in the monoclinic space group $P2_1$. As determined by X-ray single-crystal analysis, in these compounds each metal ion is coordinated by eight O atoms: four from different carboxylate groups, two from one carboxylate group, one from the ether oxygen and one from one water molecule (Fig. 27). Each ligand coordinates to five alkaline earth metal ions through one of its ether oxygen atoms and two carboxylate groups adopting novel bridging coordination modes to give rise to a 3D network. The luminescence analysis shows that the Ca - and Sr -compounds exhibit fluorescence in the solid state at room temperature.

A claim for rational design based on metal ion coordination and H-bonding for the construction of polymer structures with alkaline earth metal ions is the use of bicyclic bis-lactam-

dicarboxylate ions as bricks for two-dimensional compounds [68]. The products are obtained by transmetallation of the alkali salts by alkaline earth halides to yield different compounds depending on the H-bonding capacity and the metal ion size (Fig. 28).

The slightly more rigid zwitterionic 1,3-bis(carboxymethyl)-imidazolium forms with SrCO_3 in water a two-dimensional structure between the layers of which are found sheets of water molecules intercalated (Fig. 29) [69].

The very rigid 2,6-naphthalenedicarboxylate (ndc) reacts in a solvothermal process with magnesium nitrate in either water or DMF [70]. Whereas in the presence of water molecules preferred coordination of H_2O and dmf in $[\text{Mg}(\text{dmf})_2(\text{H}_2\text{O})_4]\text{ndc}$ hinders the formation of extended three-dimensional networks, a porous network structure is obtained in the absence of water to yield the three-dimensional metal-organic framework of $[\text{Mg}_3(\text{ndc})_3(\text{dmf})_4]$ (Fig. 30). The latter is microporous with pores accessible to H_2 , O_2 , N_2 and CH_4 , and with a Langmuir surface area of $520 \text{ m}^2 \text{ g}^{-1}$ and a hydrogen adsorption capacity of 0.78 wt.% at 77 K and 760 Torr. The metal-organic framework crystallizes in the space group $C2/c$ [$a = 13.451(3)$, $b = 18.043(4)$, $c = 20.937(5)$ Å, $\beta = 99.79(3)^\circ$] with trinuclear magnesium clusters connected to six dicarboxylate ligands that link the clusters into a three-dimensional network. In contrast to $[\text{Mg}_3(\text{ndc})_3(\text{def})_4]$ ($\text{def} = N,N$ -diethylformamide), the dmf molecules coordinated to magnesium in $[\text{Mg}_3(\text{ndc})_3(\text{dmf})_4]$ not only cause a distortion of the network but induce accessibility for the adsorption of nitrogen. So, only small structural changes induced by coordinating dmf molecules play a key role in adjusting the pore size of the network and are responsible for the size exclusion of nitrogen. Due to the low weight of magnesium, the design of Mg -MOFs with higher specific surface areas is, in principle, feasible, although identification of suitable structural building units allowing for a high porosity remains a challenge, for which the use of large rigid dicarboxylates and larger Mg -clusters might be a solution.

A systematic study of larger flat aromatic ligands with two carboxylic groups and beryllium and magnesium ions lead to a

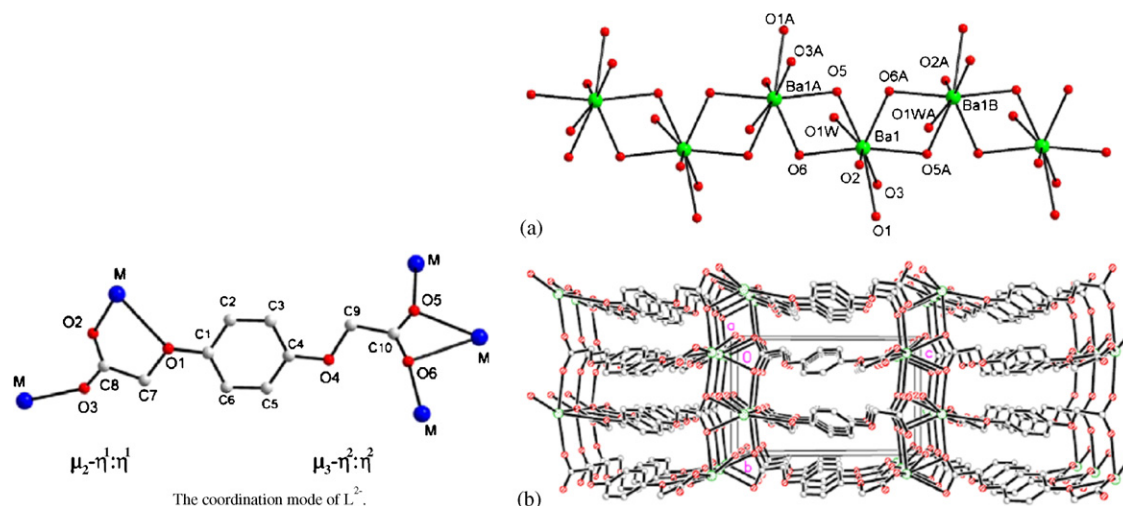


Fig. 27. Coordination mode of the dicarboxylate ligand (left) and Ba-coordination polymer (right) of $\text{Ba}(\text{L})\text{H}_2\text{O}$, L = benzene-1,4-dioxyacetate [67].

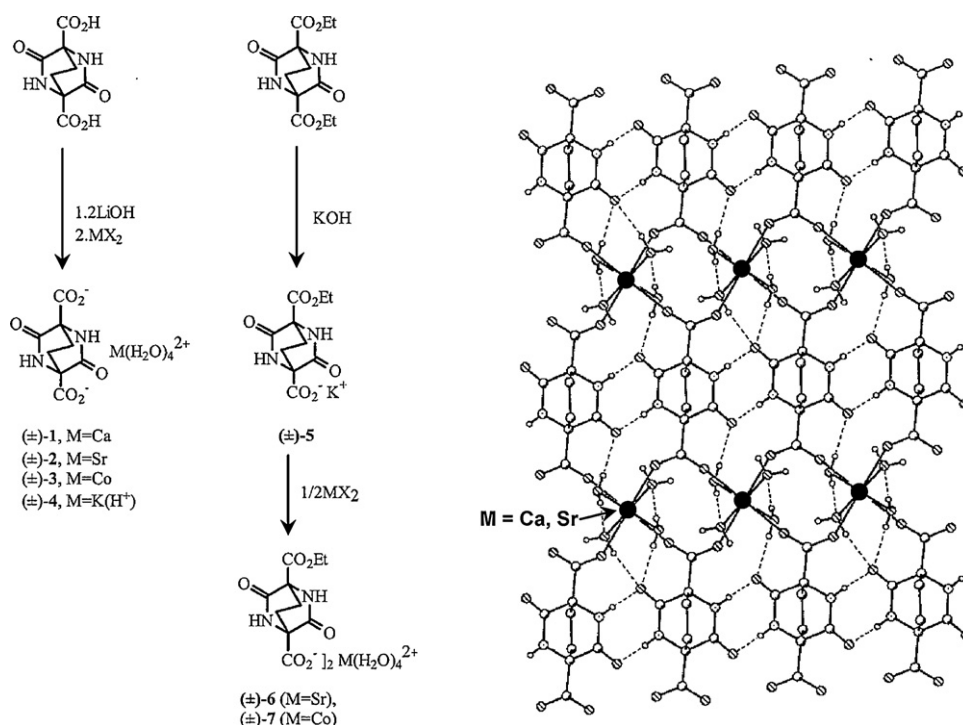


Fig. 28. 2D structure of $[M(C_8H_8O_6N_2)_2(H_2O)_4]$, $M = Ca, Sr$; adapted from [68].

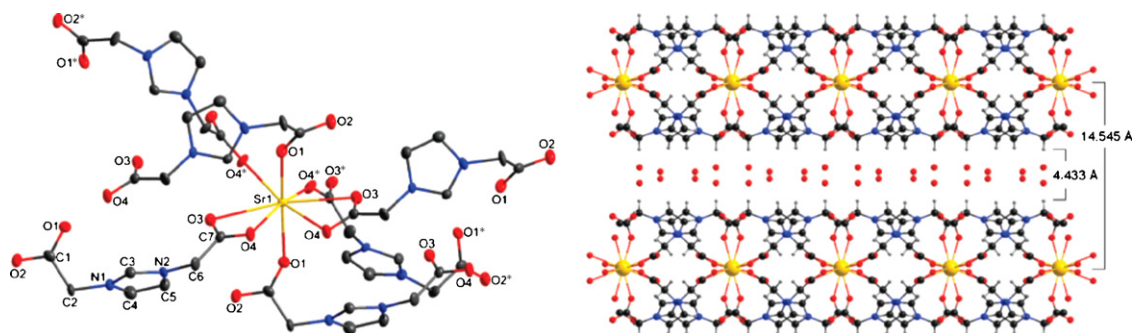


Fig. 29. 1,3-Bis(carboxymethyl)-imidazolium as O-donor ligand to Sr-ions in a layered structure [69].

large number of different metal organic frameworks with good hydrogen absorption properties [71].

Increasing the number of carboxylate functions to three in the flexible 1,3,5-triacetic acid (bta), layered structures of $[Ca_3(bta)_2(H_2O)_8] \cdot 3H_2O$ and $[Ba_3(bta)_2(H_2O)_8]$ are obtained

(Fig. 31) .[72] Each bta^{3-} ligand coordinates to Ca^{2+} or Ba^{2+} ions using two of three carboxylate groups adopting different coordination modes. The noncoordinated carboxylic group forms hydrogen bonds with an adjacent network to generate a three-dimensional structure. The complexes showed photo-

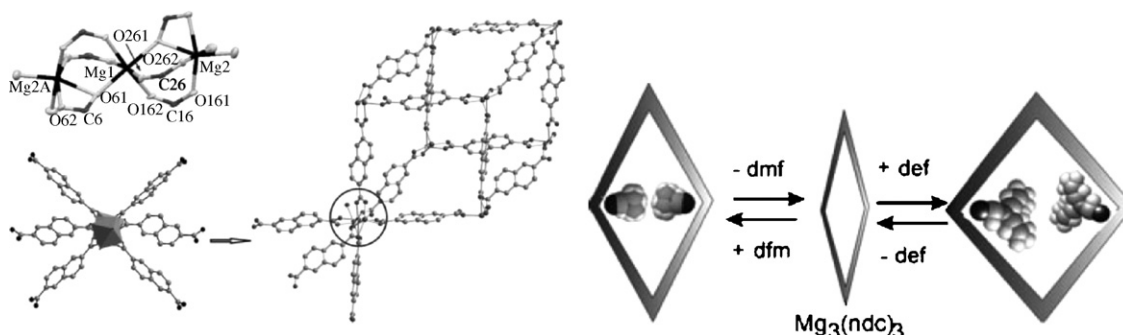


Fig. 30. 2,6-Naphthalenedicarboxylate as rigid ligand in the construction of porous and yet flexible metal-organic frameworks [70].

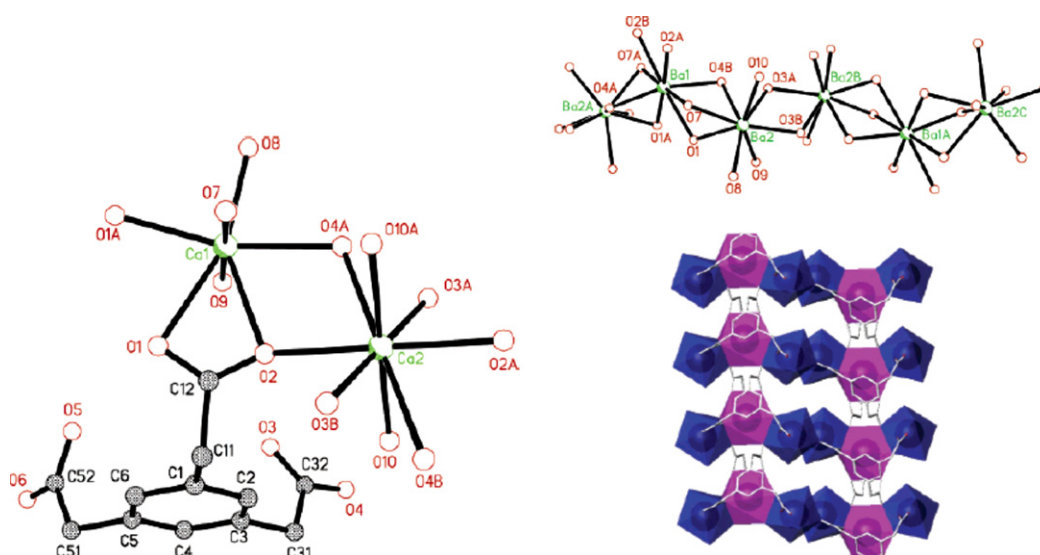


Fig. 31. 2D structures obtained with 1,3,5-triacetic acid (bta); left: coordination to the calcium ions in $[\text{Ca}_3(\text{bta})_2(\text{H}_2\text{O})_8]\cdot 3\text{H}_2\text{O}$; right: details and schematic representation of $[\text{Ba}_3(\text{bta})_2(\text{H}_2\text{O})_8]$; adapted from [72].

luminescence in the solid state at room temperature. Probably, water-free compounds with this ligand type would lead to higher dimensional structures.

Finally, ligands with four carboxylic functions, such as naphthalene-1,4,5,8-tetracarboxylate-hydrates (NTC), react with alkaline earth metal chlorides to yield $[\text{Ca}(\text{NTC})(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}$, $[\text{Sr}(\text{NTC})(\text{H}_2\text{O})_2]\cdot 2\text{H}_2\text{O}$, $[\text{Sr}_2(\text{NTC})_2(\text{H}_2\text{O})_8]\cdot \text{H}_2\text{O}$, and $[\text{Ba}(\text{NTC})(\text{H}_2\text{O})_2]$ (Fig. 32) [73]. The NTC in the first two compounds is tridentate, leading to two-dimensional layers, and in the fourth pentadentate leading to a three-dimensional network, forming bonds to the cations using the oxygen atoms of the carboxylate and one oxygen atom of anhydride groups. In the third compound the cations are associated only *via* the oxygen atoms of carboxylate groups to form a chain structure.

Among the alkoxides, the carbonate anion can also be included. As many gastropods and bivalves use calcium carbonate to build their shells, and/or to form nacre, this mineral has been under investigation for the better understanding of how these animals can construct very robust structures [74]. A guanidinium-templated new carbonate-based network with sodalite topology could thus be realized with magnesium and calcium ions [75]. Among alkaline earth metal carbonates, $[\text{Mg}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4]\cdot x\text{H}_2\text{O}$ and

$[\text{Ca}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{K}_3[\text{N}(\text{CH}_3)_4]\cdot 3\text{H}_2\text{O}$ were isolated. In these structures, pairs of guanidinium cations are associated with the hexagonal windows of the sodalite cages, and alkali metal cations are associated with their square windows. While the Mg-compound is derived from a face-centered structure, the calcium compound has a body-centered basis. The calcium ions have four close carbonate oxygen donors and four other more distant ones, while magnesium has an octahedral environment consisting of two bidentate chelating carbonate ligands and two *cis* monodentate carbonate ligands (Fig. 33) [75].

3.2.4. Phosphonates

A very early example of polymeric phosphonates with alkaline earth metal ions was actually reported in 1962. Thus, the smallest alkaline earth metal ion, beryllium, is used for the generation of one-dimensional coordination polymer based on diphenylphosphonate, $[\text{Be}(\text{OPPh}_2)_2]$ (Scheme 8) [76].

Since then, the investigation of phosphonates has more focused on the more closely to nature related phosphonates. Also, polyphosphonic acids have attracted significant attention in recent years due to their utility in supramolecular chemistry and crystal engineering [77]. Polyphosphonates are

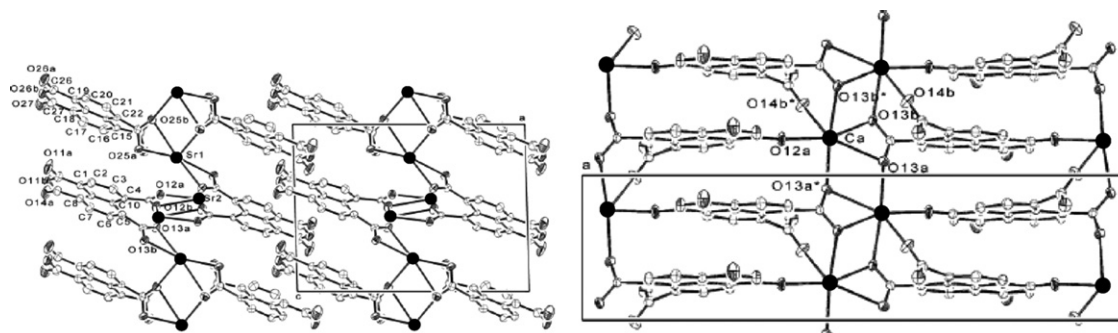


Fig. 32. 1D (left) and layered structure (right) of $[\text{Sr}_2(\text{NTC})_2(\text{H}_2\text{O})_8]\cdot \text{H}_2\text{O}$ and $[\text{Ca}(\text{NTC})(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}$, respectively; adapted from [73].

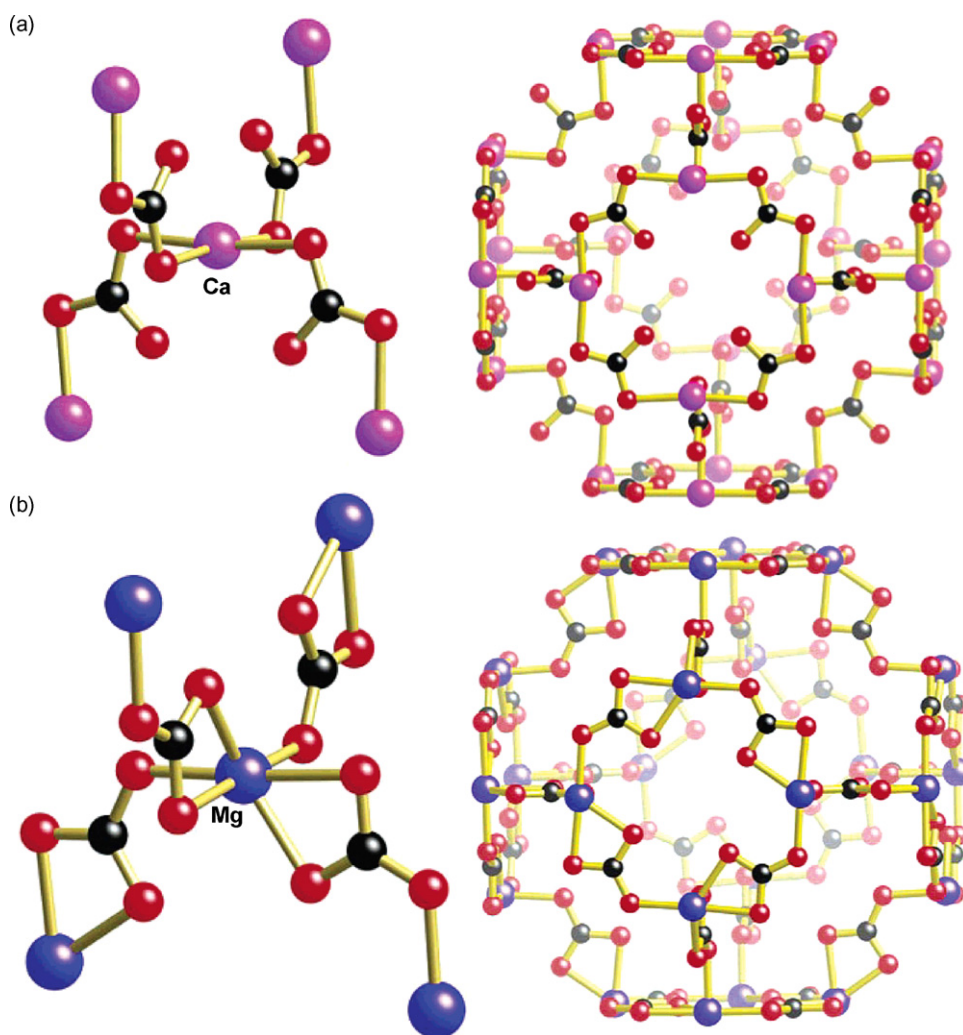
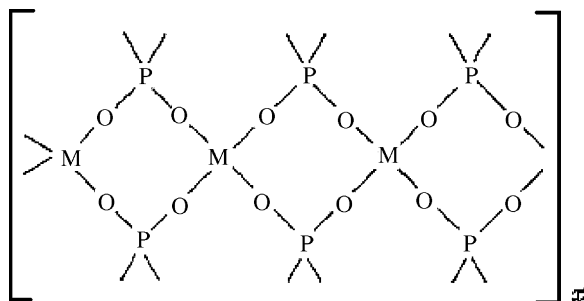


Fig. 33. Environments of alkaline earth metal ions and carbonate ligands in (a) $[\text{Ca}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{K}_3[\text{N}(\text{CH}_3)_4] \cdot 3\text{H}_2\text{O}$, which is representative of the BC structural class, and (b) $[\text{Mg}_6(\text{CO}_3)_{12}(\text{CH}_6\text{N}_3)_8]\text{Na}_3[\text{N}(\text{CH}_3)_4] \cdot 2\text{H}_2\text{O}$, which is representative of the FC structural class; adapted from [75].

also used extensively in an array of industrial applications such as chemical water treatment, oilfield drilling, minerals processing, corrosion control, and metal complexation and sequestration. Metal phosphonates commonly form pillared-layered inorganic–organic hybrid materials and microporous solids. Their properties can be useful for intercalation, catalysis, sorption, and ion exchange. One example is the amino-tris(methylenephosphonic) acid (H_6AMP). At low pH, this

ligand loses two protons, with all phosphonate groups being deprotonated while the amino function carries a proton. This ligand can react easily with the alkaline earth metal cations Mg, Ca, Sr, and Ba. $\text{Mg}[\text{HN}(\text{CH}_2\text{PO}_3\text{H})_3(\text{H}_2\text{O})_3]$ forms zig-zag chains in which the Mg-ions are bridged by two of the three phosphonate groups. The third phosphonate group is non-coordinated and involved in hydrogen bonding. A three-dimensional (3D) polymer is obtained with strontium, having the composition $[\text{Sr}(\text{H}_4\text{AMP})]$. The Sr-atoms are seven-coordinate, with five monohapto and one chelating AMP ligands. In the 3D barium polymer, $[\text{Ba}(\text{H}_4\text{AMP})(\text{H}_2\text{O})]$, the two crystallographically independent Ba-ions are 9- and 10-coordinated by phosphonate and H_2O oxygen atoms (Fig. 34). All bridging oxygen atoms belong to phosphonate moieties that act as chelates for one Ba^{2+} and form 4-membered rings. The crystal structure of the barium compound is characterized by the complete absence of hydrogen bonds.

With the more rigid phosphates containing strategically placed bulky *ortho*-amide groups (Scheme 9), one-dimensional chain structures can be obtained just as well as zero-dimensional cyclic complexes. This has been shown by



Scheme 8. 1D-phosphonate network of beryllium [76].

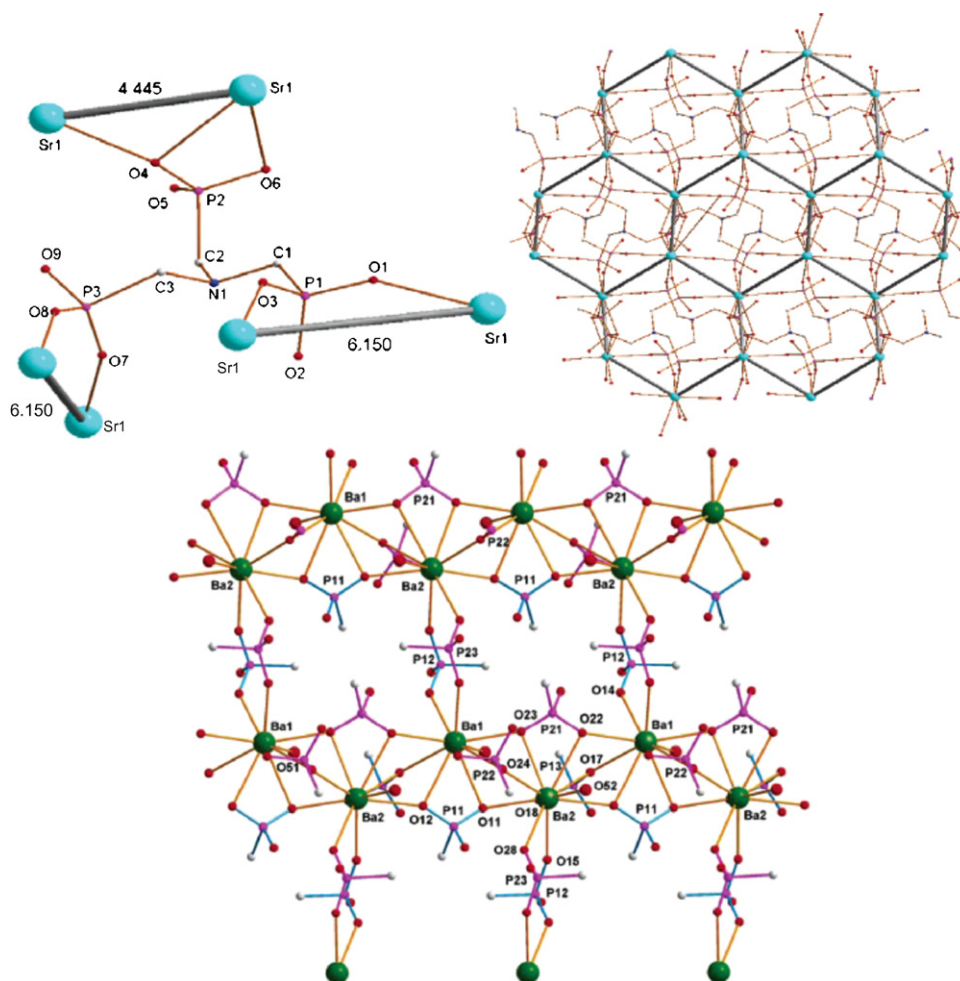
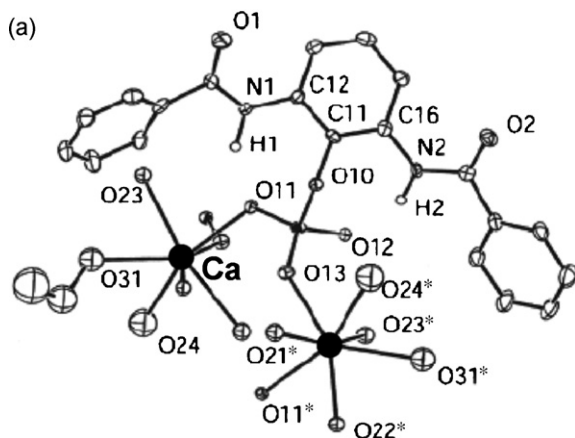


Fig. 34. Coordination of Sr-ions and network of $[\text{Sr}(\text{H}_4\text{AMP})]$ (top); 3D structure of $[\text{Ba}(\text{H}_4\text{AMP})(\text{H}_2\text{O})]$ (amino-tris(methylenephosphonic) acid = H_6AMP); adapted from [77].

Onoda et al in the synthesis of the polymer $[\text{Ca}\{\text{O}_3\text{POC}_6\text{H}_3-2,6-(\text{NHCOPh})_2\}(\text{H}_2\text{O})_4(\text{EtOH})]$, which extends into a one-dimensional zig-zag chain, and of a cyclic octameric structure of $[\text{Ca}_8\{\text{O}_3\text{POC}_6\text{H}_3-2,6-(\text{NHCOPh})_2\}_8(\text{dmf})_8(\text{H}_2\text{O})_{12}]$ (Fig. 35) [78]. The zig-zag structure transformed into a cyclic octanu-

clear structure due to the change of coordination of DMF and the intermolecular hydrogen-bond network. The ligand design with amide groups is an intriguing approach for the regulation of intramolecular and intermolecular hydrogen bonds. The synthesis of Ca^{2+} complexes using strategically designed bulky amide ligands will become very important for understanding biomineral Ca^{2+} structures found in biological systems and also for expanding new Ca^{2+} cluster chemistry.



Scheme 9. Coordination of the phosphonate to the metal ions Ca^{2+} ; by permission of the Royal Society of Chemistry from [78].

3.2.5. Sulfonates

In terms of anionic oxygen donor ligands to alkaline earth metal ions in polymeric scaffolds, the sulfonates have been quite well studied. Thus, a family of organosulfonates has been reported by Côté et al. [79]. They have developed new solids, which, in contrast to more typical crystal engineering approaches, are sustained by the assembly of building blocks that are coordinatively adaptable rather than rigid in their bonding preferences. The ligand, 4,5-dihydroxybenzene-1,3-disulfonate, L, progressively evolves from a 0D, 1D, 2D, to a 3D microporous network with the Group 2 cations Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} (Fig. 36). This trend in dimensionality can be explained by considering factors such as hard-soft acid/base principles and cation

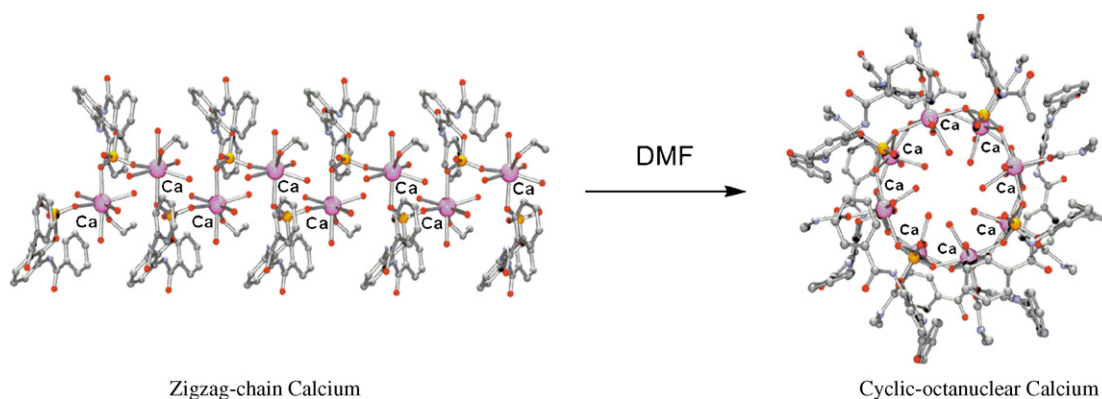


Fig. 35. Transformation of a 1D structure into a ring-type structure upon addition of DMF as ligand [78].

radii, a rationalization, which follows salient crystal engineering principles.

With H_2S at 50°C , a mass increase of 7.5% was observed for the barium compound, corresponding to the uptake of 0.93 equivalents of H_2S with respect to the equivalent of expelled water. Additional evidence for the sorption of H_2S was obtained using a gravimetric analysis. A sample of $[\text{Ba}(\text{L})(\text{H}_2\text{O})](\text{H}_2\text{S})_x$ was prepared by mono-dehydrating the initial barium compound in a N_2 purged flask, followed by H_2S purging. After removing excess H_2S , the sample was dissolved in 1 M $\text{Pb}(\text{NO}_3)_2$. A highly insoluble black PbS precipitate formed instantaneously, indicating H_2S in the sample. Quantification of the precipitate

showed 0.62 equivalent of H_2S was included by $[\text{Ba}(\text{L})(\text{H}_2\text{O})]$. A lower measured capacity by this method than by the thermobalance is to be expected due to loss of H_2S during sample handling. Significantly, no other guests showed any uptake, implying selectivity for H_2S .

Incomplete deprotonation of tris-sulfonates leads to robust cationic frameworks with channels between pillaring ligands in which reside the chloride anions of $[\text{Ba}_2(\text{L})(\text{H}_2\text{O})\text{Cl}]$ (Fig. 37). This barium compound contracts slightly upon dehydration but retains its overall structural motif to 420°C . Significantly, the chloride ions of the structure can be exchanged in 80% yield for fluoride ions in a facile manner. This exchange is quantified by

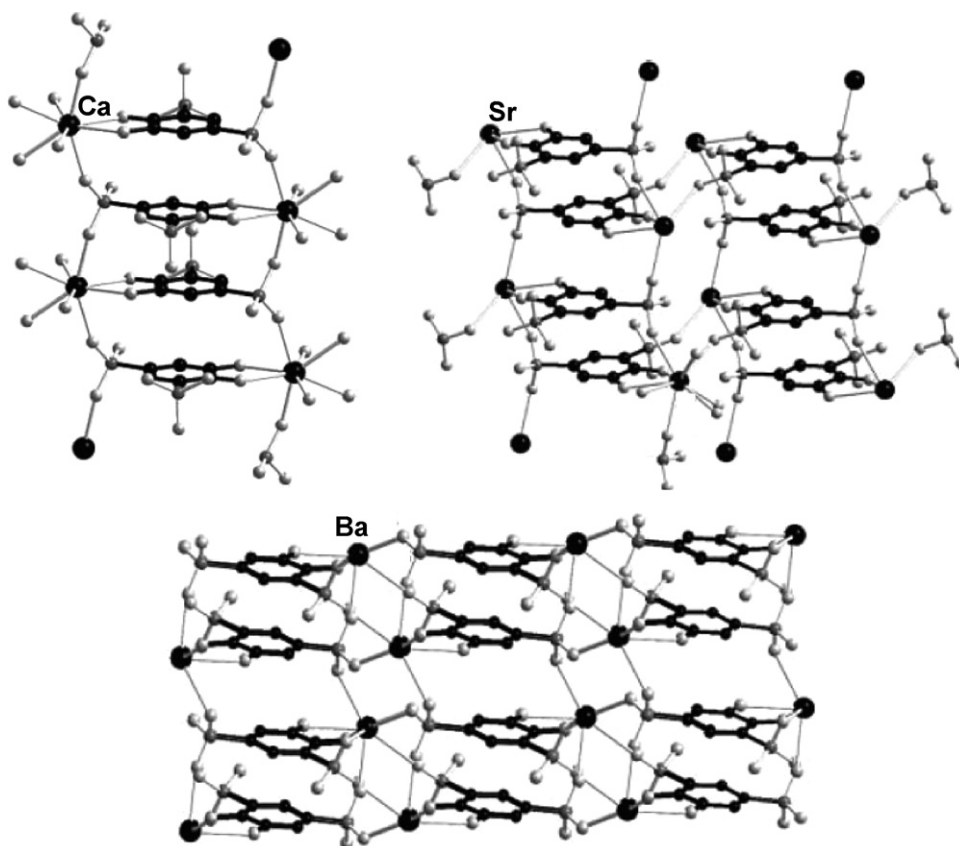


Fig. 36. One-, two- and three-dimensional structures of the calcium, strontium and barium sulfonates, respectively; adapted from [79].

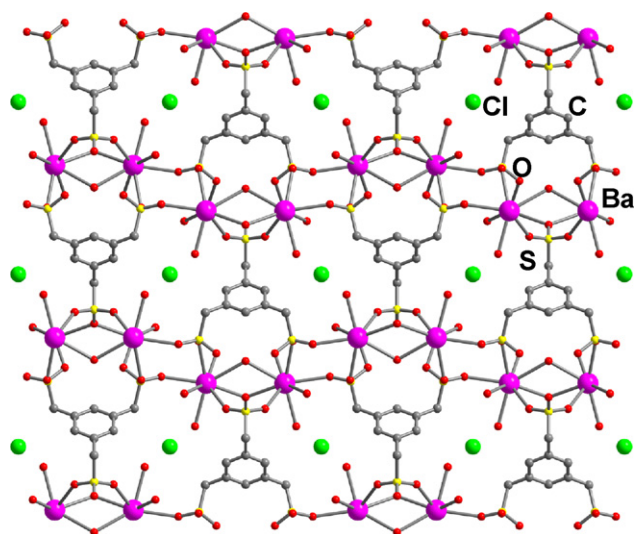


Fig. 37. Structure of $[\text{Ba}_2(\text{L})(\text{H}_2\text{O})\text{Cl}]$ down the a -axis with Cl^- in the channels [80].

elemental analyses, gravimetric determination, and ^{19}F NMR spectroscopy. Confirmation of retention of structure is provided by standardized powder X-ray diffraction experiments. This last point is notable as the F-analogue of the structure is not attainable by a direct synthesis. These results illustrate one of the hallmark features of supramolecular chemistry that a robust and functional framework can result through cooperative interactions between more weakly interacting units [80].

3.3. Mixed N- and O-donors

Self-assembly is an increasingly viable method for the quick and efficient construction of large molecular architectures. Porphyrins are particularly suitable building blocks for non-covalent synthesis due to their attractive photophysical, spectroscopic, geometrical, catalytic, and synthetic properties [81]. Furthermore, the magnesium complex of porphyrin is responsible for photosynthesis. Thus, a mixture of 1:1 magnesium dicatechol porphyrin MgL and pyridine-3-boronic acid self-assembles into a one-dimensional coordination polymer (Scheme 10). The boronic acid acts as N- and O-donor in a bridging function towards two magnesium cations.

Another group of simultaneous N- and O-donating ligands of biological importance are the amino acids. A series of calcium α -aminocarboxylates was prepared by

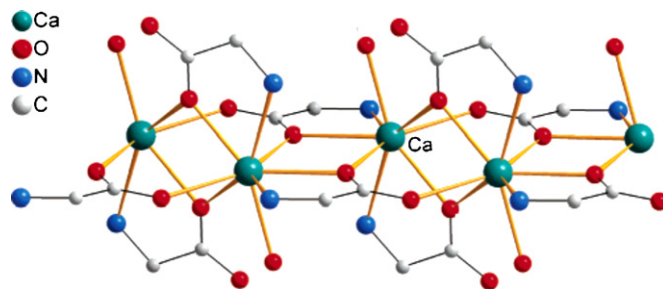
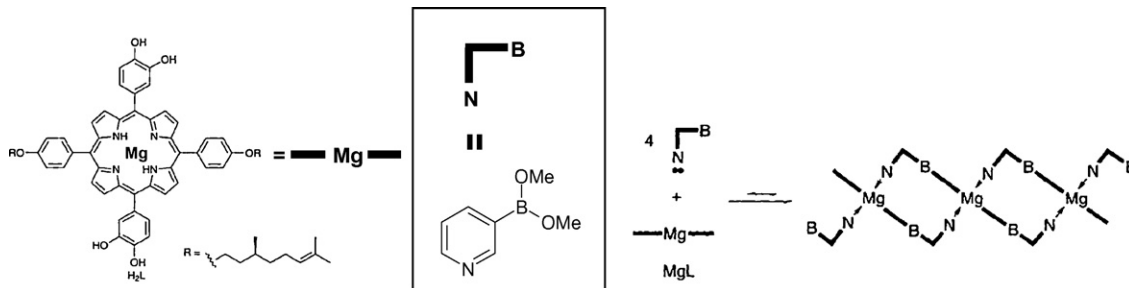


Fig. 38. 1D chain structure of $[\text{Ca}(\text{gly})_2]\text{H}_2\text{O}$; adapted from [82].

refluxing aqueous solutions/suspensions of calcium hydroxide and the respective α -amino acid [82]. The colorless, crystalline hydrates $\text{Ca}(\text{gly})_2 \cdot \text{H}_2\text{O}$ (Fig. 38), $\text{Ca}(\text{ala})_2 \cdot 3\text{H}_2\text{O}$, $\text{Ca}(\text{val})_2 \cdot \text{H}_2\text{O}$, $\text{Ca}(\text{leu})_2 \cdot 3\text{H}_2\text{O}$, $\text{Ca}(\text{met})_2 \cdot n\text{H}_2\text{O}$ ($n=2$), and $\text{Ca}(\text{pro})_2 \cdot \text{H}_2\text{O}$ have been isolated in yields between 29 and 67% (gly = glycinate, ala = rac-alaninate, val = rac-valinate, leu = rac-leucinate, met = rac-methioninate, pro = rac-prolinate). The compounds are readily soluble in water. The 0.10 M solutions have a pH of ca. 11, which is consistent with a noticeable degree of dissociation. The ^{13}C NMR spectra point to carboxylate coordination in solution, but no indication of nitrogen coordination was found. The complete single-crystal X-ray structure analyses of the first four derivatives reveal that all aminocarboxylate ligands are N,O-chelating. Crystals of the alanine derivative consist of mononuclear complexes, while the other five compounds form three different types of one-dimensional coordination polymers. Structural diversity is also observed with the binding modes of the aminocarboxylate ligands and the calcium environment. Besides terminal aminocarboxylate coordination, there are three different types of aminocarboxylate bridges. The calcium ions are seven- or eight-coordinate in N_2O_5 and N_2O_6 coordination environments, respectively; one or three water molecules are part of the first ligand sphere of each metal ion. The crystal structures support conjectures about the existence of the yet undetected solution species $[\text{Ca}_x(\text{aa})_{2x}(\text{H}_2\text{O})_n]$ ($\text{aa} = \alpha$ -aminocarboxylate). For example, $x=1$ is realized in crystalline $[\text{Ca}(\text{ala})_2 \cdot (\text{H}_2\text{O})_3]$, and in $[\text{Ca}_2(\text{leu})_4(\text{H}_2\text{O})_4]$ complexes ($x=2$) are linked to infinite chains by bridging aqua ligands.

Sulfonylamines represent yet another type of ligand with combined O- and N-donor ligands. As for alkali metal ions, their alkaline earth metal derivatives have been studied and possess one-dimensional polymeric structures in the case of the com-



Scheme 10. Porphyrin (left), boronic acid (middle) and one-dimensional Mg-polymer (right), adapted from [81].

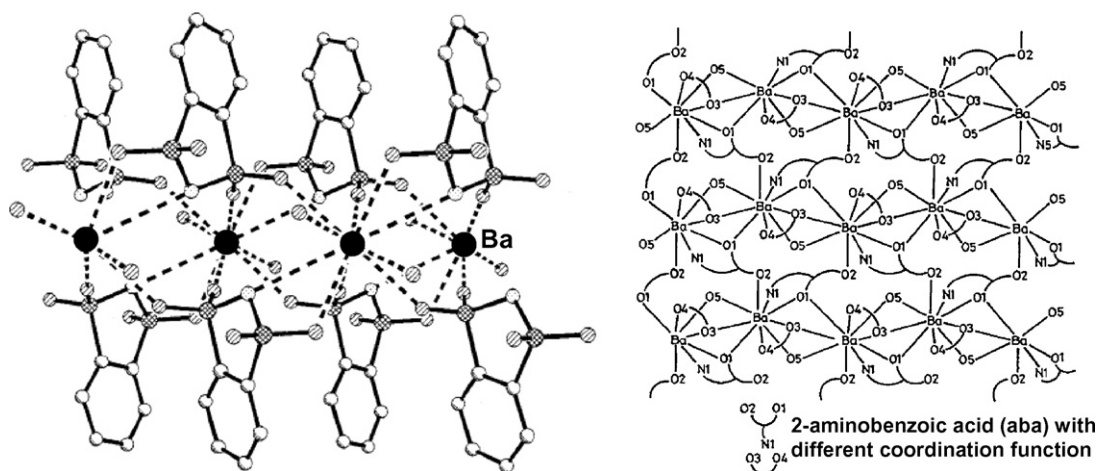
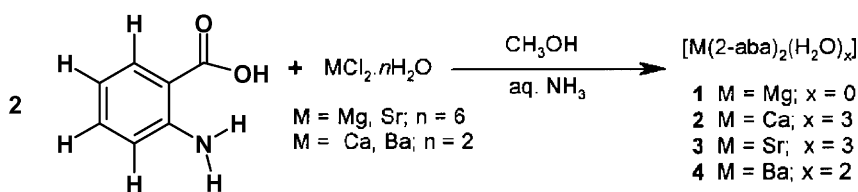


Fig. 39. 1D structure of $[\text{Ba}(\text{BSA})_2(\text{H}_2\text{O})_2]$ (left) and 2D network of $[\text{Ba}(2\text{-aba})_2(\text{OH}_2)]$ (right); adapted from [83].



Scheme 11. 2-Aminobenzoic acid with the amino function in the meta position for perfect chelate formation with Mg, Ca, Sr and Ba; adapted from [84].

combination of barium cations with benzene-1,2-di(sulfonyl)amine (BSA) (Fig. 39) [83].

Combining one carboxylic group with an amino function within a ligand may lead to additional coordination of the latter to the metal ions, depending on the size of the cations and the reaction conditions. Thus, 2-aminobenzoic acid has the amino function placed in the meta position, allowing for a perfect chelate formation when possible (Scheme 10) [84]. Reactions of alkaline earth metal chlorides with 2-aminobenzoic acid (2-abaH) in a 1:2 ratio in a MeOH/H₂O/NH₃ mixture leads to the formation of anthranilate complexes $[\text{Mg}(2\text{-aba})_2]$, $[\text{Ca}(2\text{-aba})_2(\text{OH}_2)_3]$, $[\{\text{Sr}(2\text{-aba})_2(\text{OH}_2)_2\}\text{H}_2\text{O}]$, and $[\text{Ba}(2\text{-aba})_2(\text{OH}_2)]$ (Scheme 11). Alternatively, these products can also be obtained starting from the corresponding metal acetates. The solid-state structures of calcium, strontium and barium metal anthranilates have been established by single-crystal X-ray diffraction studies (Fig. 40). While the calcium ions are hepta-coordinated, the strontium and barium ions reveal a coordination number of 9 apart from an additional weak metal–metal interaction along the polymeric chains. The carboxylate groups show different chelating and bridging modes of coordination behavior in the three complexes. Interestingly, apart from the carboxylate functionality, the amino group also binds to the metal centers in the case of strontium and barium complexes. However, the coordination sphere of calcium in its compound contains only O donors. All three compounds form polymeric networks in the solid state with the aid of different coordinating capabilities of the carboxylate anions and O–H and N–H hydrogen bonding interactions.

As mentioned earlier, the calcium coordination polymer with 2-aminobenzoic acid features only oxygen donation towards the cation [84]. The barium derivative $[\text{Ba}(2\text{-aba})_2(\text{OH}_2)]$ however, has the ligands in two different coordination modes, one of which is based on solely O-donation, while the second ligand molecule also involved the N-atom in metal ion coordination.

Investigation of the effect of pH in carboxylic acid systems is of particular importance because it helps us to understand the correlation between the reaction acidity and the structure dimensionality. Combining two carboxylic groups with N-donors, as in 3,5-pyrazoledicarboxylic acid (H₃pdc), should lead to diverging coordination of the ligand and thus to polymeric structures as a function of the pH, because carboxylic groups can be deprotonated, N-atoms additionally protonated. The acidity levels of the reactions can be adjusted not only by adding basic solvents but also by introducing basic precursors, such as $\text{Ca}(\text{OH})_2$,

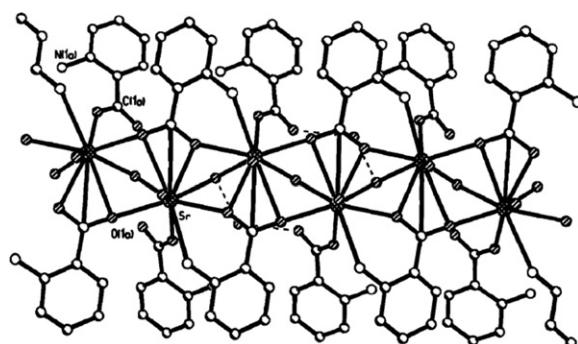


Fig. 40. The Sr-compound $[\{\text{Sr}(2\text{-aba})_2(\text{OH}_2)_2\}\text{H}_2\text{O}]$; adapted from [84].

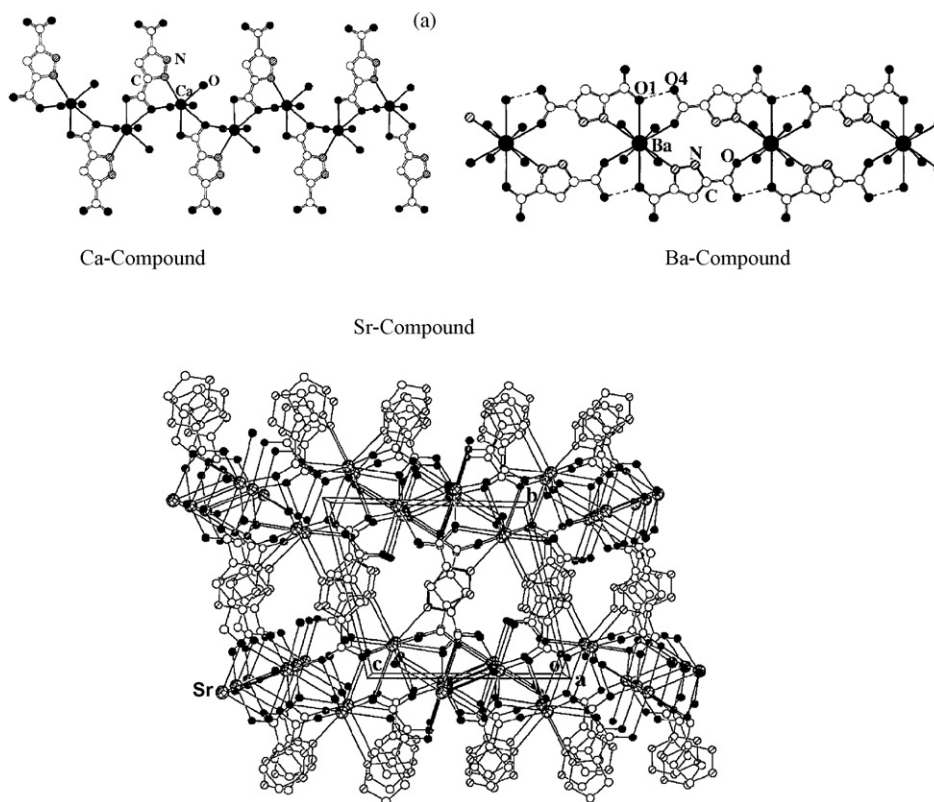


Fig. 41. Crystal structures of the Ca-, Ba- and Sr-structures obtained with 3,5-pyrazoledicarboxylic acid as coordinating bridging ligand; adapted from [85].

$\text{Sr}(\text{OH})_2$, and $\text{Ba}(\text{OH})_2$. Indeed, several alkaline earth metal coordination polymers were obtained as a function of pH and thus deprotonation grade of the ligand [85]. At a lower pH level three one-dimensional structures $[\text{Ca}(\text{Hpdc})(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$, $[\text{Ca}(\text{Hpdc})(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$, which are pseudo-polymorphs (or solvates), and $[\text{Ba}(\text{H}_2\text{pdc})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ were obtained by evaporation of the solutions resulting from hydro(solvo)thermal reactions of MCl_2 ($\text{M} = \text{Ca}, \text{Ba}$) with H_3pdc in water or in water/ Et_3N at 150°C for 3 days. The first two compounds are based on zig-zag chains of metal ions bridged by a single Hpdc^{2-} ligand, whereas the barium structure consists of linear chains of metal centers bridged by two H_2pdc^- ligands. At higher pH levels (pH 4–6), the three-dimensional polymers $[\text{M}(\text{Hpdc})(\text{H}_2\text{O})]$ ($\text{Ca}, \text{Sr}, \text{Ba}$) were isolated by reactions of MCl_2 ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) with H_3pdc in water/ Et_3N or in $\text{M}(\text{OH})_2$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) with H_3pdc in water under hydro(solvo)thermal conditions (150°C , 3 days). Calcium and strontium are seven- and nine-coordinated in their respective compounds, while barium is nine- and ten-coordinated (Fig. 41). It was observed that the increase in pH resulted in a higher connectivity level of ligands, which in turn leads to a higher dimensionality of the crystal structures.

At lower pH levels, alkaline earth metal elements show a high tendency to coordinate with water molecules, resulting in a high water-to-metal ratio, thus limiting their ability to form structures of higher dimensionality as rare-earth metals and cadmium. The comparisons among different metal–pdc species also show that the hydrogen atom attached to the pyrazole ring of the dicarboxylate cannot be deprotonated in either rare-earth or alkaline-earth metal compounds.

3.4. N-donor ligands

Neutral N-donor ligands are, just as neutral O-donors, able to stabilize low-dimensional coordination polymers of alkaline earth metal salts. The polymer structures are generated in most cases by bridging halides, while the N-donor molecules step in as terminal ligands to reduce dimensionality of the initial polymer structure [86].

Even though that 4,4'-bipyridine is a widely used ligand in transition metal ion coordination, examples with alkali and alkaline earth metal ions are rather scarce due to the general preference of block s elements towards oxygen. Complete elimination of oxygen donors leads however to alkaline earth metal compounds, in which the metal ions are entirely coordinated by N-atoms. This is especially true for the larger metal ions, as they have a lower charge density and are softer than their smaller homologues. However, steric bulk of the ligand needs to be sufficient to stabilize the coordination.

Monoanionic heteroallylic ligand systems $[\text{R}-\text{N}-\text{E}-\text{N}-\text{R}]^-$ ($\text{E} = \text{Si}(\text{R}_2), \text{S}(\text{R}_2)$ or $\text{S}(\text{R}), \text{C}(\text{R}),$ and $\text{P}(\text{R}_2)$) are versatile chelating substituents both in main group and transition metal chemistry as they provide sufficient steric demand and solubility to the products [87]. Their application is only limited by the rigid bite of the ligands as the N–N distance cannot be tuned to the various radii of different metals. The $\text{NP}(\text{R}_2)\text{N}^-$ chelate in classical aminoiminophosphoranates is extended by additional coordination sites in the organic substituents (e.g., 2-pyridyl (Py) instead of phenyl (Ph)). $\text{Py}_2\text{P}\{\text{N}(\text{H})\text{SiMe}_3\}(\text{NSiMe}_3)$ is the starting material for a new class of complexes as the

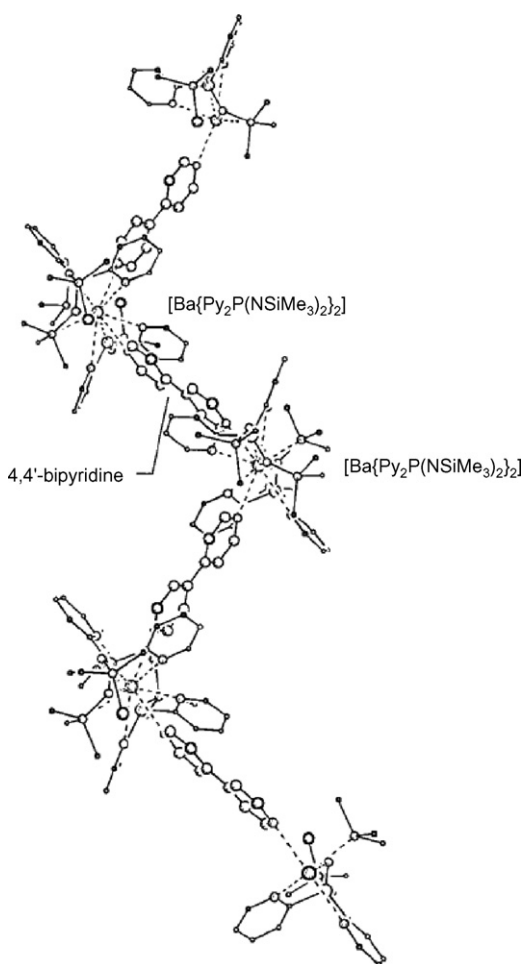


Fig. 42. 4,4'-Bipyridine as bridging ligand for the formation of a 1D-polymer of $[(4,4'\text{-bipy})\text{Ba}\{\text{Py}_2\text{P}(\text{NSiMe}_3)_2\}_2]$; adapted from [87].

deprotonated ligand contains along with the NPN-chelate the pyridyl ring nitrogen atoms to generate a side selective Janus face ligand. In $[(\text{THF})\text{Sr}\{\text{Py}_2\text{P}(\text{NSiMe}_3)_2\}_2]$ and $[(4,4'\text{-bipy})\text{Ba}\{\text{Py}_2\text{P}(\text{NSiMe}_3)_2\}_2]$ both pyridyl rings are involved in metal coordination but only one imido nitrogen atom. Hence, the classical $\text{NP}(\text{Ph}_2)\text{N}^-$ chelating ligand is converted into a $\text{NP}(\text{Py}_2)\text{N}^-$ tripodal ligand. Whereas the strontium compound is a zero-dimensional compound due to its smaller radius and terminal THF-coordination, the bridging bipyridine ligand in the barium compound allows the formation of a one-dimensional coordination polymer (Fig. 42).

While the 4,4'-bipyridine is a linear directing ligand, tetrakis(imidazolyl)borate points into the four corners of a tetrahedron [88]. With magnesium, calcium and strontium, the compounds of general composition $\text{M}[\text{B}(\text{Im})_4]_2(\text{H}_2\text{O})_2$ ($\text{M}=\text{Mg}, \text{Ca}, \text{Sr}$) are obtained with the same coordination environment about the metal ions. However, the three compounds have different network structures with different degrees of hydrogen bonding; the Mg material forms a two-dimensional network and the Ca and Sr compounds form one-dimensional chains (Fig. 43).

The formation of interlaced squares in $\text{Mg}[\text{B}(\text{Im})_4]_2(\text{H}_2\text{O})_2$ versus one-dimensional chains in the $\text{Ca}[\text{B}(\text{Im})_4]_2(\text{H}_2\text{O})_2$ and $\text{Sr}[\text{B}(\text{Im})_4]_2(\text{H}_2\text{O})_2$ structures results from how the borates can link together metals in either a one- or two-dimensional network. As can be seen in the three metal-organic networks presented in this report, the nature of the metal ion can be used to tune the structure of the solid. In the cases presented here, a combination of the radius of the metal and its electronic character affect the topology of the resultant solid. Several parameters change as one goes down the group, including the closed/open conformation of the borate, the geometry of the imidazoles about the metal center, and the lengths of the metal-ligand bonds. These variations in geometries and hydrogen bonding result in differences between the magnesium structure, which adopts a brick wall layered pattern, and the calcium and strontium structures, which form one-dimensional square chains.

3.5. Carbon donor ligands

As discussed for the alkali metal ions, the larger alkaline earth metal ions also have an increased tendency to interact with aromatic π -systems when available. A general reaction pathway to such metal-organic compounds is the use of the alkali-organic compound and its reaction with alkaline earth metal halides under elimination of alkali halide in an organic solvent. Thus, indenyl (Ind) and its derivative, bisisopropyl-indenyl (Ind2i) react as potassium salts with alkaline earth metal iodides to yield $[(\text{Ind})_2\text{M}(\text{thf})_n]$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}$; $n=1$ for Sr and Ba; $n=2$ for Ca) and $[(\text{Ind2i})_2\text{M}(\text{thf})_n]$ ($n=1$ for Ca; $n=2$ for Sr and Ba) under KI elimination [89]. All complexes are air-sensitive solids, and while the calcium and barium compounds are monomeric, the strontium complex is an infinite coordination polymer, $[(\text{Ind})_2\text{Sr}(\text{thf})]$, with both terminal (Sr-C) 2.94 Å (av) and bridging (Sr-C) 3.07 Å (av) indenyl ligands (Fig. 44).

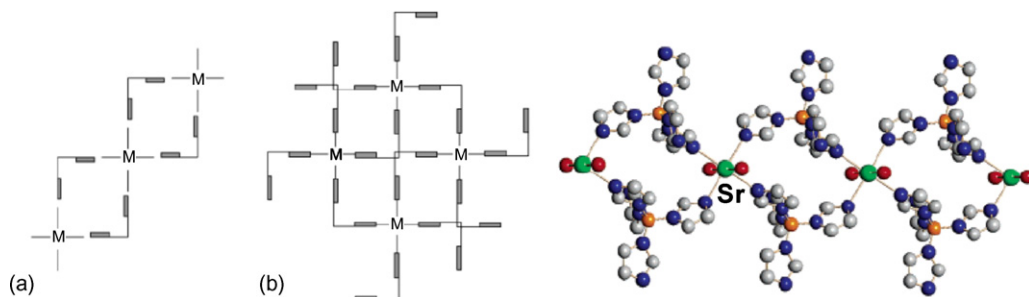


Fig. 43. Different networks obtained with Ca and Sr (left, a, and right), and Mg (b) and tetrakis(imidazolyl)borate; adapted from [88].

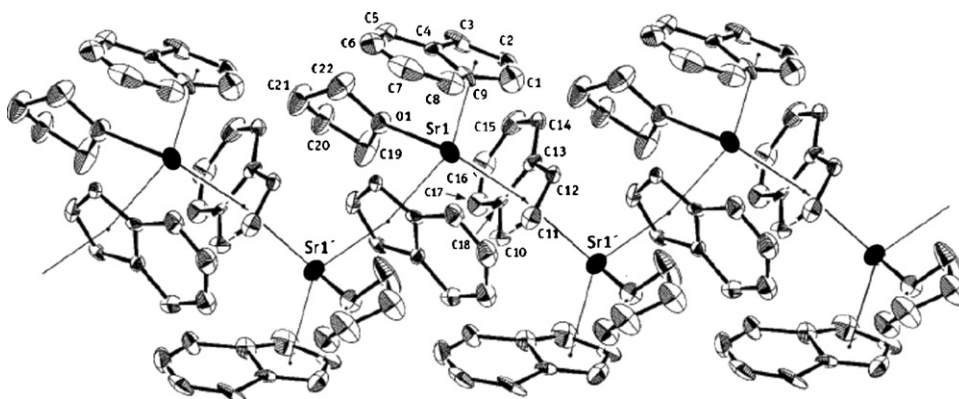


Fig. 44. 1D structure of $[(\text{Ind})_2\text{Sr}(\text{thf})]$; adapted from [89].

Such a *trans*-metallation, using alkali reagents and alkaline earth metal halides in order to eliminate alkali iodide seems however not always successful [90]. Thus, the generation of $[1,2,4\text{-tris}(\text{trimethylsilyl})\text{-cyclopentadienyl}]$ metal iodides $(\text{Cp}_3\text{Si})\text{MI}(\text{thf})_n$ ($\text{M} = \text{Ca}$, $n = 1$; $\text{M} = \text{Sr}$, Ba , $n = 2$) are isolated from the 1:1 reaction of $\text{K}[\text{Cp}_3\text{Si}]$ and MI_2 in THF, but the yields range from very good (79%) when $\text{M} = \text{Ca}$ to poor (26%) when $\text{M} = \text{Ba}$. In the case of $\text{M} = \text{Sr}$, Ba , substantial amounts of $\text{K}[\text{Cp}_3\text{Si}]$ are recoverable at the end of the reaction. No redistribution of $(\text{Cp}_3\text{Si})\text{MI}(\text{thf})_n$ into $(\text{Cp}_3\text{Si})_2\text{M}$ and $\text{MI}_2(\text{thf})_n$ is observed in either THF or aromatic solvents at room temperature. Both $(\text{Cp}_3\text{Si})\text{CaI}(\text{thf})$ and $(\text{Cp}_3\text{Si})\text{SrI}(\text{thf})_2$ crystallize from THF/toluene as iodide-bridged dimers, while the organobarium complex $(\text{Cp}_3\text{Si})\text{BaI}(\text{thf})_2$ crystallizes from THF/toluene as a coordination polymer containing both linear and near-linear (177.8°) Ba-I-Ba links in a zig-zag motif; this is an unprecedented arrangement for bridging iodide ligands (Fig. 45).

3.6. Sulfur donor ligands

Combination of carboxylate groups with sulfur donor groups such as thiols, additional coordination of sulfur to the

cations may be observed in the case of the correct design of the ligand. Treating alkaline earth metal chlorides with the ligand 2-mercaptobenzoic acid (Scheme 12), extended polymer structures $[\text{Ca}(\text{DTBB})(\text{H}_2\text{O})_2 \cdot 0.5(\text{C}_2\text{H}_5\text{OH})]$, $[\text{Sr}(\text{DTBB})(\text{H}_2\text{O})_2 \cdot 0.5(\text{C}_2\text{H}_5\text{OH})]$, and $[\text{Ba}_2(\text{DTBB})_2(\text{H}_2\text{O})_2 \cdot 0.5\text{H}_2\text{O}]$ are obtained, in which the ligand underwent thiol oxidation to form 2,2'-dithiobis(benzoic acid) (H_2DTBB) as a bridging ligand [91]. The calcium and strontium coordination polymers are isomorphous with the DTBB ligands acting as hexadentate ligands. Both compounds have a channel structure in which solvent ethanol molecules are included. In the barium compound, a complex three-dimensional coordination polymer where both the carboxylate and the sulfur groups of the DTBB ligands (which are hepta- and octadentate) coordinate to the metal, is observed (Fig. 46).

While the coordination is exclusively through the carboxylate groups of the DTBB ligands in the case of hard metal ions such as calcium and strontium, the disulfide linkage also participates in the metal binding in the case of the softer barium ion. The binding of disulfide linkage to barium ion may have some role to play in heavy metal poisoning by barium in physiological systems. This observation probably needs to be further investigated in future studies.

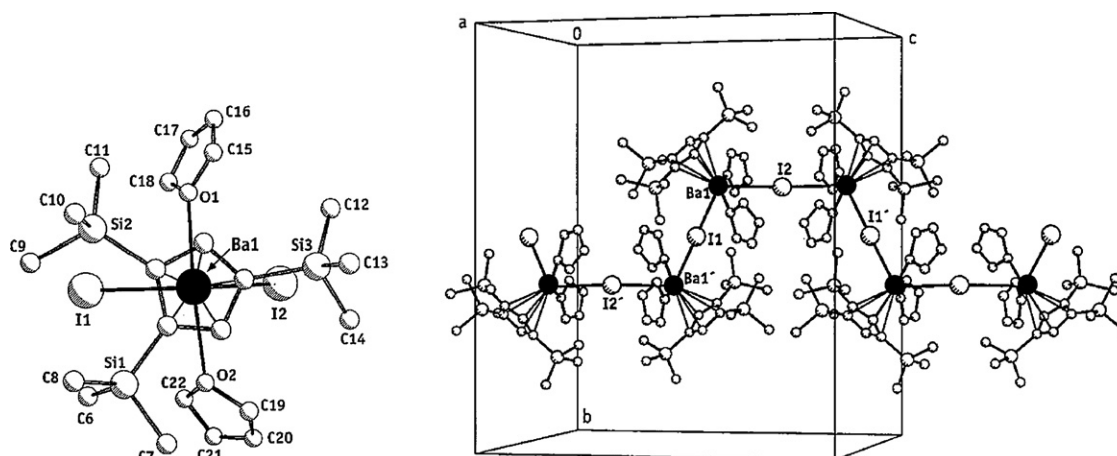
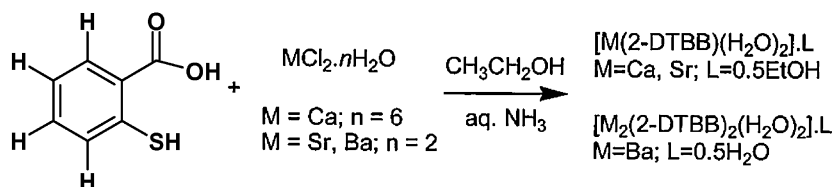


Fig. 45. 1D-coordination polymer of $(\text{Cp}_3\text{Si})\text{BaI}(\text{thf})_2$ (Asymmetric unit left, polymer arrangement right); adapted from [90].



Scheme 12. Reaction of 2-mercaptobenzoic acid with alkaline earth metal chlorides; adapted from [91].

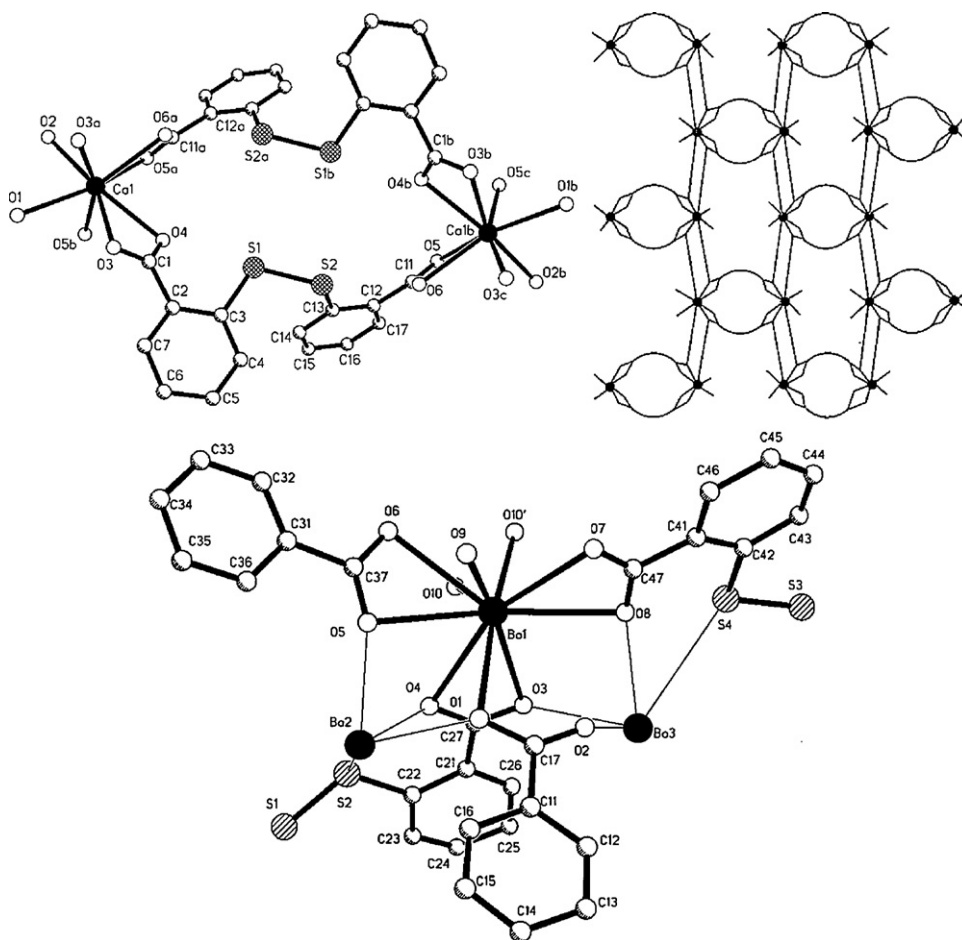


Fig. 46. 2-Mercaptobenzoic acid as O-donor ligand to Ca (top) and as O- and S-donor to Ba; adapted from [91].

4. Conclusions

4.1. Alkali metal coordination polymer networks

The construction of different dimensional coordination polymer networks based on alkali or alkaline earth metal ions is mainly based on anionic oxygen donor ligands. Even though a number of results have been found in the literature, most results seem to be based on serendipitous discoveries rather than systematic constructions.

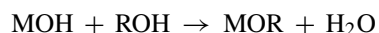
The synthesis of alkali metal coordination polymers can be achieved using a salt and forming low-dimensional structures with neutral donor ligands, the latter acting as chemical scissors on the initial material. With anionic ligands, several synthetic methods to access polymeric structures with alkali metals are possible. Examples for the formation of alkoxides are sum-

marised here, but which are also transferable to other ligand systems:

Reactions of metals and alcohols	$\text{M} + \text{ROH} \rightarrow \text{MOR} + (1/2)\text{H}_2$
Reactions of metals hydrides with alcohols	$\text{MH} + \text{ROH} \rightarrow \text{MOR} + \text{H}_2$
Metal-carbon bond cleavage reactions	$n\text{BuLi} + \text{ROH} \rightarrow \text{LiOR} + n\text{BuH}$
Reactions of metal dialkyl amides with alcohols	$\text{M}\{\text{N}(\text{SiMe}_3)_2\} + \text{ROH} \rightarrow \text{MOR} + \text{HN}(\text{SiMe}_3)_2$

The interest in these reactions clearly relies on the fact that the secondary product is volatile, allowing easy purification of the product.

Reactions of metal hydroxide with alcohols :



The water formed during this reaction has to be eliminated by azeotropic distillation, for instance with NaOH dissolved in a mixture ethanol/benzene under reflux. The more acidic phenols allow formation of most group 1 phenoxides more readily by simple heating of the hydroxide in dried ethanol, followed by recrystallization.

For the smaller and thus harder alkali cations, lithium and sodium, the cations are coordinated by the donor atoms of the ligand, and the dimensionality of the resulting solid-state structure can be governed by the capacity of the ligand to bridge between the metal ions, i.e. its steric demand as well as its number and position of donor sites.

Potassium aryloxides KOR, as well as the heavier analogues rubidium and cesium, often possess polymeric structures due to the large ionic radius and the low charge of the cation, giving them a relatively soft character. In general, such adducts with less sterically demanding ligands present solvated polymeric structures, while by increasing the steric bulk, unsolvated polymers may be observed. Usually, the large cations are then also π -bonded to the aryl rings of the neighboring ligand to fill their unsaturated coordination sites.

Summarising the situation for alkali metal ions containing coordination polymer structures, even though a large number of materials are used as their group 1 metal salts, the structures of the latter are often not investigated in detail, ignoring the cations as simple “spectator” ions. However, this is an issue worth investigating in order to better understand the properties of these solid-state compounds. Few of the examples mentioned above have been investigated in this respect, and first recent results show that a certain design in the construction of alkali metal coordination polymer structures can be achieved by a) using (rigid) bridging ligands with two or more coordination sites, and/or b) template molecules to generate voids in the solid-state structures, and/or c) the use of alkali metal aggregates as nodes of a low-dimensional network to yield porous materials with large cavities.

4.2. Alkaline earth metal coordination polymer networks

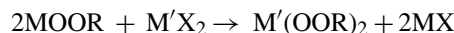
The alkaline earth metal ions have received more attention, probably due to the research on group 2 metal containing precursors for oxide as well as biomimetic materials. In terms of networks and nodes, moving from group 1 to 2 metals halves the number of nodes and so decreases connectivity for the same ligand types.

Again by serendipity, many polymeric species have been discovered, but also more systematic studies have been made including a series of group 2 cations and comparing the structures obtained. There is however no clear trend in the evolution of structural features with respect to the metal ion size. One expects that the larger the cation, the higher its coordination number and thus the structure will display a higher dimension. However, some of the above examples show isostructural compounds for calcium, strontium and barium despite the softer character of barium compared to calcium. Some trends are still applicable, as for the alkali metal ions. Thus, the larger the cation, the lower its charge density, and the higher its tendency to com-

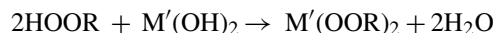
plete its coordination sphere by π -interactions with aromatic ligands.

With neutral O- and N-donor ligands, several low-dimensional networks were isolated and characterized, using the ligands as chemical scissors. The generation of anionic ligands can be summarised in the following methods, exemplified by carboxylates:

- Reaction of alkali carboxylate with group 2 halide:



- Reaction of carboxylic acid with group 2 hydroxide:



The latter reaction can be fine-tuned as a function of the pH, as the systematically described studies showed. This is especially interesting in the case of ligands with more than one functional group to be deprotonated. Then, the bridging functionality of the ligands can be switched on or off as a function of the pH, and thus the dimensionality of a coordination polymer network can be tuned.

Highlights in the generation of coordination polymer networks in terms of functionality are the rigid dicarboxylate derivatives with Mg_3 -units as nodes that show a porosity and thus host-guest behaviour in the solid state, the use of amino acids and their derivatives as ligands on group 2 ions for a better understanding of biological systems, and the alkoxides which are able to react with CO_2 and SO_2 to yield new products.

For both, alkali and alkaline earth metal MOFs, the presence of water molecules in the coordination sphere of the metal ions strongly influences the final structures. Water molecules are highly attracted to s-block ions, and are small enough to coordinate easily to any of the metal ions. This is due to the fact that groups 1 and 2 metal ions usually are able to rapidly exchange their neutral ligands in solution, and that, if water is present, the latter may then often bind to the metal ions in a stronger fashion than another neutral ligand.

All in all, the formation of metal–organic frameworks (MOFs) with alkali and alkaline earth metal ions has not been exhaustively investigated. Whereas mostly solution synthesis or autoclave techniques for groups 1 and 2 coordination polymers are employed, microwave and solid-state synthesis are still scarce for these kinds of networks. Additionally, applications in many, very different fields are possible, and therefore such investigations should be continued.

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