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An unusual linker and an unexpected node: $CaCl_2$ dumbbells linked by proline to square lattice networks[†]

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Four new structures from $CaCl_2$ and proline are reported, all with an unusual Cl-Ca-Cl moiety. Depending on stoichiometry and the chirality of the amino acid, this metal dihalide fragment represents the core of a mononuclear Ca complex or may be linked by the carboxylate to extended structures. A cisoid coordination of the halide atoms at the calcium cation is encountered in a chain polymer. In the 2D structures, $CaCl_2$ dumbbells act as nodes and are crosslinked by either enantiomerically pure or racemic proline to square lattice nets. Extensive database searches and topology tests prove that this structure type is rare for MCl_2 dumbbells in general and unprecedented for Ca compounds.

1 Introduction

Ligands with carboxylate groups are commonly used in coordination chemistry as they can be reliably coordinated to oxophilic cations and show a plethora of coordination modes. Cations without predominant d-orbital ligand-field influence may show coordination ranging from single terminal η^1-coordination to simultaneously bridging and chelating μ_2-η^2:η^1 or μ_3-η^1:η^2:η^1 modes (Fig. 1). While the usage of polycarboxylato ligands leads to a variety of coordination polymers, monocarboxylate ligands repeatedly form coordination compounds with a small number of unique motifs. Among these the paddlewheel and the 'basic zinc acetate' as an octahedral node are the most noted and can function as structural building units[1]. Crosslinking to extended network structures is achieved via additional coordination sites.

Aminoacids may be used as anionic ligands offering the carboxylate as well as the amino group as binding sites. An alternative use in their zwitterionic form may show the same coordination behaviour as other carboxylates but directly allows for secondary interactions by providing a hydrogen-bond donor group. An overview about the coordination diversity of even the simplest amino acid glycine has been given by Fleck[2]. In a recent communication, Zaworotko and coworkers[3] reported coordination polymers of zwitterionic amino acids and Li salts; the amino acids in this study also comprise proline. When the carboxylato moiety of amino acids is combined with salts of the oxophilic Ca(II) cation, a variety of new products are conceivable. An overview about calcium-carboxylate interactions and their characteristic geometries has been published by Einspahr and Bugg[4]. In view of the biocompatibility of the calcium dication, its coordination polymers with O donor ligands have not only found attention with respect to crystal engineering[5] but also with medical applications in mind[6].

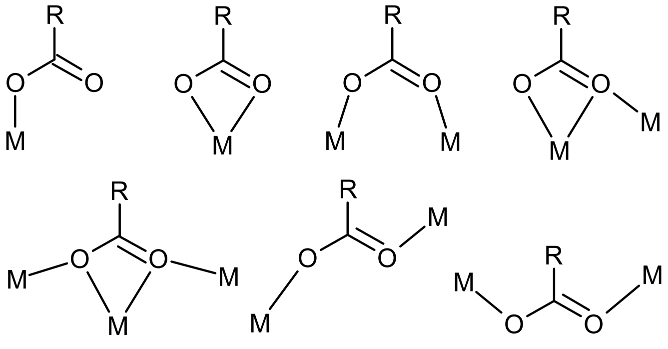

Fig. 1 Coordination modes of carboxylato ligands often observed for cations without predominant d-orbital ligand-field influence[1].

Only a few structures containing amino acids and Ca cations have been reported, mostly derivatives of the simplest and achiral amino acid glycine. Among these, the majority includes glycine in zwitterionic form with simple anions such as chloride[7–9], bromide[10], iodide[11,12] or nitrate[13]. Two Ca-glycinates as well as a valinate and a leucinate obtained at higher pH-values show the chelating behaviour of deprotonated amino acids towards calcium cations[14]. Further struc-

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[†] Electronic Supplementary Information (ESI) available: Crystallographic information files, checkCIF report, further illustrations (displacement ellipsoid plots, simplified network structures), further information on the modification of GTECS3D and CSD-searches, refcode lists. See DOI: 10.1039/b000000x/

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tures were reported for valine[15] and aspartic acid[16].

From this small pool of structural data general trends may be deduced: a) the calcium cation is oxophilic as shown by a small number of Ca-non-O-contacts in the coordination sphere b) amino acids may simultaneously be engaged as chelating and bridging groups c) aqua ligands are very popular in Ca coordination.

We present the structures of four new compounds synthesised from $CaCl_2$ and either racemic or enantiopure proline. Depending on stoichiometry, different products are obtained. In contrast to the trends mentioned above, all four structures include rather unusual Cl-Ca-Cl moieties. Furthermore two of the presented compounds exhibit an unexpected two-dimensional network structure. Focussing particularly on these structural motifs, a profound database search has been performed, *i.e.* a large subset of the Cambridge Structural Database has been investigated. In this context, our geometrical analyses do not only recur to established tools such as the coordination number but also address dimensionality and topology. The constantly increasing number of extended structures represents a major challenge for comparison and classification of connectivity-related, yet chemically and crystallographically different species; we meet this challenge by the "network approach"[17,18]. For this purpose, we use customized algorithms which allow for automatic simplifications followed by a graph theoretical approach.

2 Experimental

2.1 Syntheses

All four products were obtained from aqueous solutions. ***1a*** was synthesised by dissolving 0.4 mmol $CaCl_2 \cdot x\,H_2O$ (44 mg) and 0.4 mmol DL-proline (46 mg, 1:1 molar ratio) in 0.25 mL H_2O. Single crystals formed after one week of storage at ambient temperature and reduced pressure in a desiccator. Crystals of the other products were obtained under the same conditions but with different stoichiometries. ***1b*** formed from a reaction with 2 equivalents DL-proline per $CaCl_2$. ***2a*** was also obtained from a 1:2 stoichiometry but with enantiopure L-proline and ***2b*** with a 1:1 $CaCl_2 \cdot x\,H_2O$ to L-proline ratio (see Fig. 2). All compounds except ***1a*** can alternatively be synthesised in quantitative yield by grinding the reactants in the stoichiometry of the target products with a drop of water.

2.2 Crystallographic Characterisation

Suitable single crystals were mounted on glass fibers. Intensity data were collected at 100 K in ω-scan mode on a Bruker D8 goniometer with a Bruker SMART APEX CCD detector using Mo-Kα-radiation ($\lambda = 0.71073$ Å) from an Incoatec microsource with multi-layer optics. Temperature control was achieved by using an Oxford Cryostream 700. Data were processed with SAINT+[19] and corrected for absorption by multiscan methods with SADABS[20]. The structures were solved by direct methods (using SHELXS-97[21]) and refined on F^2 with SHELXL-97/13[21]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms connected to carbon were placed in idealised positions and included as riding.

The hydrogen atoms of the protonated amino group were located in difference Fourier maps and restrained to similar N—H distances with $U_{iso}(\mathrm{H}) = 1.2\,U_{eq}(\mathrm{N})$ in all structures. Hydrogen atoms connected to oxygen in ***1b*** and ***2b*** were restrained to similar O—H distances with $U_{iso}(\mathrm{H}) = 1.2\,U_{eq}(\mathrm{O})$.

2a showed two maxima for C4 in a difference Fourier map. Split positions were assigned and their occupancy refined whilst their sum was constrained to unity.

Phase purity of the products could be confirmed by powder X-ray diffraction (see Fig. 3). Measurements were done at the Institute of Inorganic Chemistry, RWTH Aachen University, using a Stoe imageplate detector IP-PSD. Flat samples were measured in transmission using Cu-Kα_1-radiation at ambient temperature.

2.3 Database Analysis

Database searches were performed using the Cambridge Crystallographic Database (CSD version 5.34, including updates until Feb 2013). All searches were restricted to error-free structures without disorder for which 3D-coordinates were available. Structures determined from powder diffraction were excluded. Information about entries with calcium and chloride in general where obtained from a search for structures containing at least one Ca—Cl-distance below 3 Å (155 results) followed by manual screening. The evaluation of the calcium coordination geometry was based on structures containing Ca atoms in general (1306 entries). The built-in connectivity function of the Conquest program[22] was used to evaluate the number of connected atoms. We are aware of the fact that a small fraction of structures might have been wrongly categorized, either because of an erroneous connectivity assignment or simply in borderline cases of bonding slightly longer than common thresholds.

For the topology investigations, two subsets of the Cambridge Crystallographic Database were created for further investigation by using the following criteria:

A: The central atom was chosen as "any metal" with exactly 6-fold coordination. Four of the coordinated atoms were set to be N, O, S, P, Se or C. The other two coordinating groups were set to be either two halides, cyanates, thiocyanates or isothiocyanates. This search yielded 9628 entries.

B: The central atom was again "any metal" coordinated by four carboxylate groups: Carbon atom with exactly 3 con-

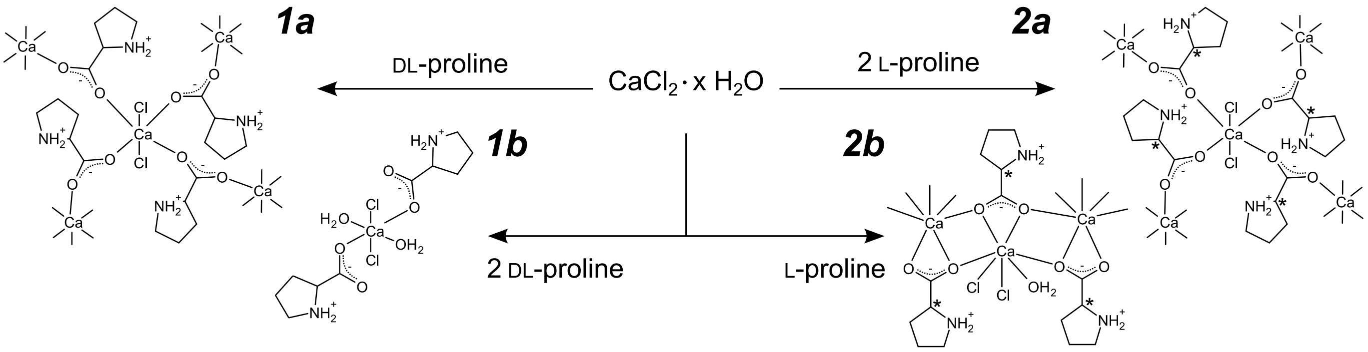

Fig. 2 Schematic representation and naming convetion for reactions and crystal structures determined in the context of this work.

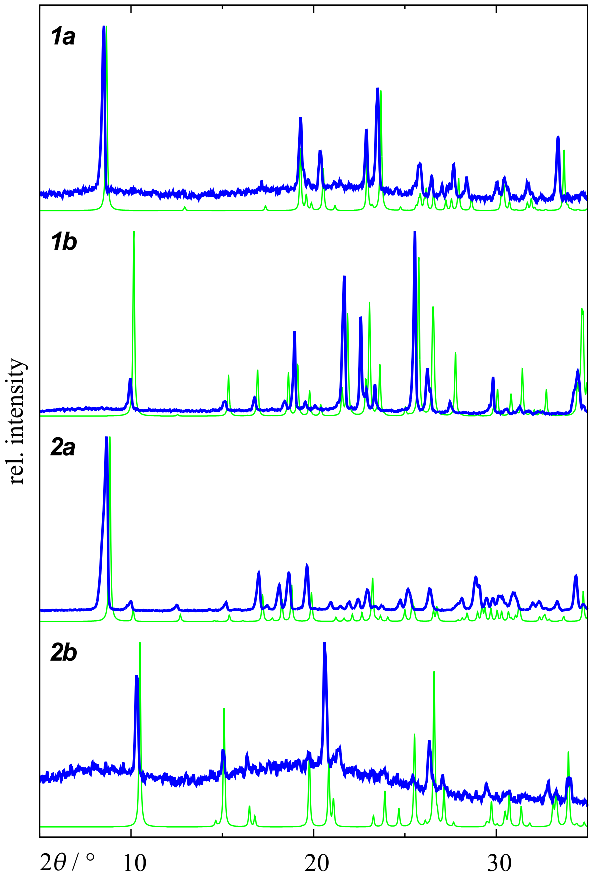

Fig. 3 Experimental (blue) and simulated (green) X-ray powder diffractograms of all structures.

nected atoms – two oxygen atoms connected by any bond and an additional single bonded carbon or hydrogen atom. At least one of the carboxylate groups may be bridging to another metal center. A total of 4934 entries was found.

The structures were sorted with respect to the dimensionality of connected moieties with the help of a scripted customized version of the topology program GTECS3D[23] which allowed batch processing. For each structure an adjacency matrix was calculated based on the standard bonding radii used in the CSD (see corresponding sources[24–26]); from these data the dimensionality of this structure was directly accessible. Deviations from results of other software that allows for determination of the dimensionality (*e.g.* TOPOS[27] or PLATON[28]) may be explained by slightly different tabulated radii. In a first step, nodes with less than two bonds, i.e. terminal or isolated atoms, were eliminated. Secondly, nodes with exactly 2 neighbours were reduced to edges connecting these two adjacent nodes. This procedure was repeated twice in order to comply with slightly more complex structural motifs such as bipyridine ligands. Our process corresponds to the process of automated simplification of the adjacency matrix available in the very popular TOPOS[27] program. Finally, extended point and vertex symbols compliant to Blatov *et al.*[29] were derived. We note that the simplification of certain motifs following a standard algorithm does not necessarily result in the most intuitive network, in particular when nodes of higher connectivity accumulate. An entirely manual evaluation of many thousand extended structures would, however, require a prohibitive amount of time and most likely suffer from human errors and inconsistencies. Only results valid within these limitations will be discussed. Refcodes of the results as well as a short evaluation and comparison to the results of a recent TOPOS-based study on 2D networks[30] are provided as supporting information, a full list is available on request. GTECS3D is available for download from www.gtecs.rwth-aachen.de and the customised version on request.

3 Discussion

3.1 Structural Description

Four different phase pure solids could be obtained by combining $CaCl_2$ and proline under varying conditions. Reactions

Table 1 Crystal data and refinement results of all Products. The datacollection of ***1b*** is of lesser quality due to the intergrown nature of the crystalline solid.

	1a	***1b***	***2a***	***2b***
Empirical formula	$C_{10}H_{18}CaCl_2N_2O_4$	$C_{10}H_{22}CaCl_2N_2O_6$	$C_{10}H_{18}CaCl_2N_2O_4$	$C_5H_{11}CaCl_2NO_3$
Formula weight (g/mol)	341.24	377.28	341.24	244.13
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Crystal description	colourless plate	colourless block	colourless needle	colourless plate
Crystal size (mm)	0.31 x 0.27 x 0.05	0.20 x 0.16 x 0.06	0.20 x 0.09 x 0.04	0.23 x 0.21 x 0.08
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	10.6806(15)	5.8720(19)	7.6518(12)	6.9732(6)
b (Å	9.1982(13)	17.422(6)	9.7084(15)	11.7268(11)
c (Å)	7.5204(11)	7.957(3)	19.982(3)	12.1168(11)
β (°)	107.139(2)	104.233(5)	90	90
V ($Å^3$)	706.01(17)	789.0(4)	1484.4(4)	990.83(15)
Z	2	2	4	4
μ (mm^{-1})	0.833	0.763	0.793	1.141
Total/unique reflectoins	9265/1713	8140/1418	17580/2979	14215/2605
Variables refined	94 (1 restraints)	109 (2 restraints)	194 (6 restraints)	121 (2 restraints)
R_{int}	0.0484	0.0655	0.0749	0.0407
wR_2 (all/obs)	0.0711/0.0686	0.1633/0.1596	0.0783/0.0747	0.0557/0.0542
R_1 (all/obs)	0.0320/0.0283	0.0690/0.0613	0.0434/0.0358	0.0238/0.0227
Goof	1.027	1.090	1.040	1.044
Diff. peak/hole (e $Å^{-3}$)	0.370/-0.246	1.199/-0.386	0.266/-0.225	0.444/-0.229
Flack parameter	-	-	0.03(5)	0.02(3)
CCDC#	971721	971722	971723	971724

with racemic proline yield compounds ***1a*** and ***1b***. Structures ***2a*** and ***2b*** form from enantiopure proline and build necessarily chiral solids. Crystallographic parameters of all structures are listed in Table 1.

From both racemic proline and L-proline, the closely related coordination networks ***1a*** and ***2a*** are obtained. The racemic network ***1a*** crystallises in the monoclinic spacegroup $P2_1/c$ with an asymmetric unit consisting of CaCl(DL-proline) with Ca on Wyckoff position 2*a*. The unit cell of the chiral analogue ***2a*** is about twice the size and orthorhombic with space group $P2_12_12_1$ resulting in an asymmetric unit of $CaCl_2$(L-proline)$_2$. In both structures, the distorted octahedral coordination sphere of the Ca metal is occupied by four equatorial carboxylate-O atoms and two axial chloride ligands (Fig. 4). Ca—O distances range from 2.260(2) to 2.343(2) Å in ***2a*** whereas in ***1a*** only a small difference between the two independant Ca—O distances is found, reflecting a slightly more regular octahedral geometry. All values are in line with the distances reported by Einspahr and Bugg[4]. The only symmetry-independent Ca—Cl distance in ***1a*** is about the same length as the shorter one in ***2a*** (see Table 2). Whereas the Cl-Ca-Cl dumbbell arrangement in ***1a*** must be linear for reasons of symmetry, a significant distortion is found in its enantiopure analogue ($160.23(3)°$).

Two lower dimensional hydrates were found by altering the reaction stoichiometry. ***1b*** was obtained from DL-proline and crystallises in a monoclinic lattice with space group $P2_1/n$. The asymmetric unit consists of one proline, one water and one chloride ligand coordinated to a calcium atom on Wyckoff position 2*a*. Therefore, a very similar coordination sphere to the aforementioned structures is found; two carboxylate coordination sites are replaced by the aqua ligands forming a centrosymmetric elongated octahedron.

Table 2 Selected bond lengths in Å of ***1a***, ***1b***, ***2a*** and ***2b***.

1a		***1b***	
Ca(1)···O(2)^{i}	2.3079(11)	Ca(1)···O(3)	2.342(3)
Ca(1)···O(1)	2.3329(11)	Ca(1)···O(1)	2.357(3)
Ca(1)···Cl(1)	2.7375(5)	Ca(1)···Cl(1)	2.7333(13)
2a		***2b***	
Ca(1)···O(3)	2.260(2)	Ca(1)···O(3)	2.3090(14)
Ca(1)···O(4)^{ii}	2.273(2)	Ca(1)···O(2)^{iv}	2.3777(12)
Ca(1)···O(2)^{iii}	2.298(2)	Ca(1)···O(2)	2.4176(12)
Ca(1)···O(1)	2.343(2)	Ca(1)···O(1)^{v}	2.4989(12)
		Ca(1)···O(1)	2.6700(12)
Ca(1)···Cl(1)	2.7380(10)	Ca(1)···Cl(1)	2.6982(6)
Ca(1)···Cl(2)	2.7522(10)	Ca(1)···Cl(2)	2.7425(6)

Symmetry codes: *i* x,-y+1/2,z-1/2; *ii* x+1/2,-y+5/2,-z;
iii x-1/2,-y+3/2,-z; *iv* x+1/2,-y+3/2,-z+1; *v* x-1/2,-y+3/2,-z+1

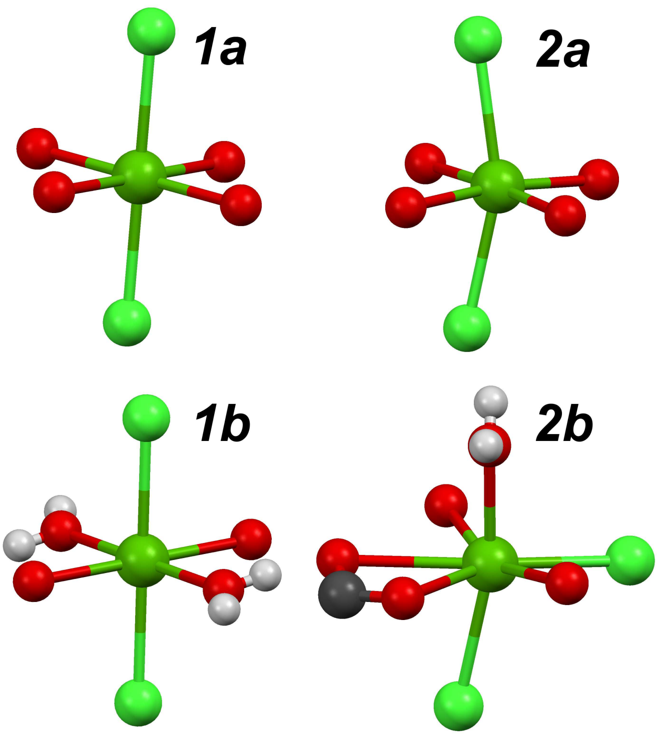

Fig. 4 Coordination environment of the central Ca cation in all four products.

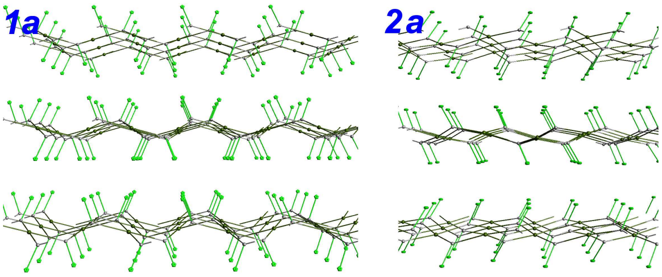

Fig. 5 Simplified side view of the network layers in ***1a*** and ***2a***. Proline rings have been simplified to light green pentagons. All terminal atoms or groups were omitted for clarity.

2b stands out because of its higher coordination number and exceptional Ca:proline ratio (1:1). Asymmetric units of $CaCl_2(H_2O)_2$(L-proline) form the orthorhombic structure ($P2_12_12_1$). A μ_3-η^1:η^2:η^1-carboxylate and two symmetry equivalents in total contribute to 4 coordination sites at the central calcium cation; together with two chlorides and one water ligand, an overall sevenfold coordination is achieved. The polyhedron can be described as a pentagonal bipyramid with the water and one chloride in axial positions. Thus the chlorido ligands occupy *cis* coordination sites in contrast to the other three structures where the *trans* isomers have been found. The Ca—Cl bond in the pentagonal plane is only 2.6982(5) Å and therefore the shortest among the four reported structures.

With respect to the dimensionality of these coordination compounds, ***1b*** is a molecular structure highly resembling that of a previously reported manganese analogue[31], although the packing and weak interactions between the molecules differ. ***2b*** on the other hand forms a one-dimensional coordination polymer extending along the shortest unit cell axis (a = 6.9732(6) Å). Its connectivity with regard to the μ_3-η^1:η^2:η^1-carboxylate bridging and the resulting chain resembles a structure reported for a calcium chloride glycine complex[9] that exhibits a unit cell axis of comparable length along the expansion direction of the polymer (6.8980(14) Å).

For both anhydrous structures (***1a*** and ***2a***) the equatorial carboxylates O,O'-μ_2-η^1:η^1 bridge into four directions and yield two topologically equivalent network structures. When each proline linker is reduced to a 2-connecting edge, the underlying net of **sql** topology (also known as {4,4} network) is perceived. While the layers extend parallel to the shortest two unit cell axes in both structures, the stacking direction is manifested in the longest cell axes. The homochiral compound ***2a*** may be described by alternating network layers (ABAB) whereas ***1a*** is built by only one centrosymmetric and necessarily heterochiral layer (see Figure 5). Although their unit cells are metrically similar, only a topological and no group-subgroup relationship exists. An evaluation of the uniqueness of these network motifs will be presented in section 3.2.

Hydrogen bonds can be found in all structures; a synopsis is provided in Table 3. In the enantiopure network ***2a*** a bifurcated hydrogen bond is formed by N(2)—H(2B), overall resulting in an higher number of stabilising interactions than in the racemic network.

Notably, in ***1a*** and ***2a*** these hydrogen bonds are confined to the layers defined by coordinative bonds; no short interlayer contacts occur. In contrast, the one-dimensional coordination polymer ***2b*** is crosslinked to a three-dimensional hydrogen-bonded framework and the racemic mononuclear coordination compound ***1b*** is engaged in a two-dimensional network of hydrogen bonds.

The hydrogen-bond deficient structure ***1a*** packs more efficiently than its chiral analogue ***2a*** (73.8% vs. 69.9% space filling). Superior space filling in heterochiral crystals has been initially postulated by Wallach and Liebisch[32] and explained by Brock *et al.*[33]; we have confirmed this relationship for homo- and heterochiral molecular crystals[34], salts[35] and coordination polymers[36].

3.2 Database Search

A database search underlines the uncommon features of our structures with respect to Ca coordination by chloride and, in

Table 3 Hydrogen bonds of ***1a***, ***1b***, ***2a*** and ***2b***.

D—H···A	D—H [Å]	H···A [Å]	D···A [Å]	D—H···A [°]
1a				
N(1)—H(1B)···Cl(1)^{i}	0.895(15)	2.318(15)	3.1198(15)	149.2(16)
1b				
N(1)—H(1A)···O(2)^{ii}	0.89(5)	1.97(5)	2.810(5)	158(5)
N(1)—H(1B)···Cl(1)^{iii}	0.89(4)	2.51(4)	3.208(4)	136(4)
O(3)—H(3A)···Cl(1)^{iii}	0.83(5)	2.31(5)	3.128(4)	168(5)
O(3)—H(3B)···O(2)^{iv}	0.82(4)	1.94(4)	2.745(4)	168(5)
2a				
N(1)—H(1A)···Cl(2)^{v}	0.91(2)	2.18(2)	3.083(3)	171(3)
N(1)—H(1B)···Cl(1)	0.90(2)	2.35(2)	3.187(3)	155(3)
N(2)—H(2A)···O(1)^{vi}	0.92(3)	2.37(3)	3.232(3)	156(2)
N(2)—H(2B)···O(2)^{vii}	0.91(3)	2.24(3)	2.948(3)	134(3)
N(2)—H(2B)···Cl(1)^{viii}	0.91(3)	2.77(2)	3.353(2)	124(2)
2b				
N(1)—H(1A)···Cl(1)^{ix}	0.87(2)	2.28(2)	3.0360(15)	146.0(18)
N(1)—H(1B)···Cl(2)^{x}	0.879(17)	2.290(17)	3.1557(15)	168.3(18)
O(3)—H(3C)···Cl(1)^{xi}	0.78(2)	2.33(2)	3.0771(14)	161(2)
O(3)—H(3D)···Cl(2)^{xii}	0.79(2)	2.37(2)	3.1570(15)	176.0(17)

Symmetry codes: ^{i} x,y,1+z ; ^{ii} 1+x,y,z ; ^{iii} 1-x,-y,-z ; ^{iv} x,y,-1+z ; ^{v} -1/2+x,3/2-y,-z ; ^{vi} -1/2+x,5/2-y,-z ; ^{vii} x,-1+y,z ; ^{viii} 1/2+x,5/2-y,-z ; ^{ix} 1/2+x,3/2-y,1-z ; ^{x} 1-x,-1/2+y,3/2-z ; ^{xi} 1-x,-1/2+y,1/2-z ; ^{xii} -1/2+x,3/2-y,1-z ;

particular, the formation of the carboxylato-based **sql** nets.

Overall, the carboxylate coordination in all structures is unexceptional; the three different coordination modes and all Ca—O—C—O geometries are well known motifs. However, among the 54 structures discussed by Einspahr and Bugg[4], only 5 include chloride and none of them a chloride-calcium contact. Expanding this aspect, the database documents 143 structures with calcium and chloride of which only 31 include Ca-Cl-bonding. Among these, 18 have at least two Ca—Cl bonds, and in only 7 cases *trans* configured $CaCl_2$ dumbbells are encountered.

Among the most frequent coordination numbers, 6 and 8 are slightly favoured (see Fig. 6). Based on the 356 entries with 6 coordinated calcium, an investigation of the coordinated atom types underlines the strong preference for Ca-O contacts. In 58 % of the structures, the coordination sphere of the Ca atom is exclusively occupied by oxygen. Only 15 % are coordinated by four oxygen atoms as in the structures ***1a***, ***1b*** and ***2a*** discussed here. While the mononuclear composition as found in ***1b*** and the one dimensional polymer from ***2b*** are common motifs for carboxylates, the two dimensional networks stand out and represent a rare architecture not only for calcium compounds.

A majority of 82.4 % among the many structures with 6-coordinated metal (9628 structures defined as set A, cf. Experimental) correspond to discrete molecular ("zero-

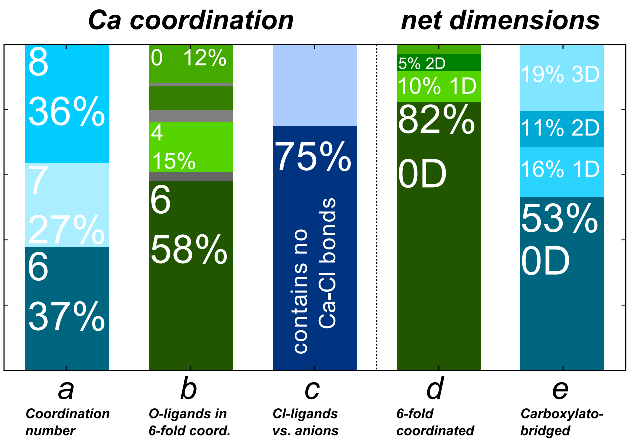

Fig. 6 Histograms describing calcium coordination (left). ***a:*** Coordination number (CN) based on 923 entries containing Ca atoms with CN 6 to 8. ***b:*** Number of Ca—O bonds in 6-coordinated Ca complexes based on 356 entries. ***c:*** Percentage of structures without direct Ca—Cl bonds based on 155 entries which include both Ca and Cl atoms. Histograms describing network dimensionality. ***d:*** Dimensionality of coordination compounds with sixfold-coordination based on 9628 entries (subset A). ***e:*** Dimensionality of coordination compounds with carboxylate bridging based on 4934 entries (subset B).

dimensional") structures. Most of the higher dimensional structures extend in only one dimension (9.5 %). Only 5.4 % of the investigated structures form coordination networks in two and 2.6 % in three dimensions. The majority (53 %) of the two dimensional networks corresponds to an automatically deducible **sql**-topology, similar to the structures ***1a*** and ***2a*** presented here. The high abundance of **sql** networks in general is well documented and discussed by Mitina and Blatov[30]. Very recently, these authors have investigated a large subset of the CSD with alternative algorithms and derived similar relative occurrences.

When only those complexes are considered which feature carboxylato ligands (4934 structures defined as set B, cf. Experimental), two dimensional structures are slightly more abundant (11 %); this may be due to the large number of structures based on polycarboxylates, ligands which easily lead to crosslinking. However, only 1 % among the almost five thousand structures correspond to simple **sql**-topology. A manual investigation of this subset reveals that only 16 structures are exclusively based on bridging by carboxylates as found in ***1a*** and ***2a***. Their majority are derivatives of formic acid, and only one structure for an amino acid[37] has been reported. None of the carboxylato-bridged **sql** nets involves metal coordination by halides.

4 Conclusion

Our diffraction results and a connectivity search in the Cambridge Structural Database confirmed that the direct coordination of two chlorido ligands to a Ca cation in all four new structures is unexpected. Extensive searches based on a dedicated topology program were required to evaluate the second uncommon feature in two of our solids, namely the formation of **sql** nets exclusively subtended by monocarboxylato ligands. In addition to the versatile coordinative bonds of the carboxylate and the hydrogen donor functionality of the ammonium group, chirality makes a welcome extra in amino acid chemistry. In the case of our **sql** nets, enantiomerically pure and racemic proline result in structures not related by a simple group-subgroup concept: rather, they provide crystallographically different versions of the same topology. In future work, we will extend the chemical and graph theoretical toolbox in order to make such topological comparisons more general, more reliable and user-intuitive and even faster.

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Extensive database searches using the network approach underline that sql-topology is unusual for carboxylato bridged networks.