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An unusual linker and an unexpected node: CaCl₂ dumbbells linked by proline to form square lattice networks†

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Four new structures based on CaCl₂ and proline are reported, all with an unusual Cl-Ca-Cl moiety. Depending on the 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 form extended structures. A cisoid coordination of the halide atoms at the calcium cation is encountered in a chain polymer. In the 2D structures, CaCl₂ dumbbells act as nodes and are crosslinked by either enantiomerically pure or racemic proline to form square lattice nets. Extensive database searches and topology tests prove that this structure type is rare for MCl₂ dumbbells in general and unprecedented for Ca compounds.

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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 or μ_3 - η^1 : η^2 : η^1 modes (Fig. 1). While the usage of polycarboxylato ligands leads to a variety of coordination compounds with a small number of unique motifs. Among these the paddlewheel and the 'basic zinc acetate' as octahedral nodes are the most noted and can function as structural building units.¹ Crosslinking to form extended network structures is achieved *via* additional coordination sites.

Amino acids may be used as anionic ligands offering the carboxylate as well as the amino group as binding sites. As an alternative, their zwitterionic form can be used, which may

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show the same coordination behaviour as other carboxylates; however a zwitterion directly allows for secondary interactions by providing a hydrogen-bond donor group. An overview of the coordination diversity of even the simplest amino acid glycine has been given by Fleck.² In a recent communication, Zaworotko and coworkers³ reported coordination polymers of zwitterionic amino acids and Li salts; the amino acids in this study also include proline. When the carboxylato moiety of amino acids is combined with salts of the oxophilic $Ca(\pi)$ cation, a variety of new products are conceivable. An overview of 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 attracted attention not only with respect to crystal engineering⁵ 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

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[†] Electronic supplementary information (ESI) available: Crystallographic information files, checkCIF reports, further illustrations (displacement ellipsoid plots and simplified network structures), further information on the modification of GTECS3D, and CSD searches and refcode lists. CCDC 971721– 971724. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce42357c

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 include glycine in zwitterionic form with simple anions such as chloride,^{7–9} bromide,¹⁰ iodide^{11,12} or nitrate¹³ anions. 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 structures have been reported for valine¹⁵ 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 and c) aqua ligands are very popular in Ca coordination.

We present the structures of four new compounds synthesised from CaCl₂ and either racemic or enantiopure proline. Depending on the 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 make use of 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 using 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 $CaCl_2 \cdot xH_2O$ (44 mg) and 0.4 mmol _{DL}-proline (46 mg, 1:1 molar ratio) in 0.25 mL of H₂O. 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 of DL-proline per CaCl₂. **2a** was also obtained from a 1:2 stoichiometry but with enantiopure L-proline and **2b** with a 1:1 CaCl₂·*x*H₂O 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 using a Bruker D8 goniometer with a Bruker SMART APEX CCD detector using Mo-K α radiation ($\lambda = 0.71073$ Å) from an Incoatec microsource with multi-layer optics. Temperature control was achieved using an Oxford Cryostream 700. Data were processed using SAINT+¹⁹ and corrected for absorption by multi-scan methods using SADABS.²⁰ The structures were solved by direct methods (using SHELXS-97²¹) and refined on F^2 using 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 $U_{iso}(H) = 1.2U_{eq}(N)$ in all structures. Hydrogen atoms connected to oxygen in **1b** and **2b** were restrained to similar O-H distances with $U_{iso}(H) = 1.2U_{eq}(O)$. **2a** showed two maxima for C4 in the difference Fourier map. Split positions were assigned and their occupancy refined whilst their sum was constrained to unity.

Phase purity of the products was confirmed by powder X-ray diffraction (see Fig. 3). Measurements were done at the Institute of Inorganic Chemistry, RWTH Aachen University, using a Stoe imaging plate detector IP-PSD. Flat samples were measured in transmission using Cu-K α_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 errorfree structures without disorder for which 3D-coordinates were



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



diffractograms of all structures.

available. Structures determined from powder diffraction were excluded. Information about entries with calcium and chloride in general was 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 program²² 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 because in borderline cases, the bonds are slightly longer than common threshold values.

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 two other 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, the carbon atom of which has exactly 3 connected 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 the connected moieties with the help of a scripted customized version of the topology program GTECS3D²³ which allowed batch processing. For each structure an adjacency matrix was calculated based on the standard bonding radii used in the CSD (see corresponding sources²⁴⁻²⁶); from these data the dimensionality of each structure was directly accessible. Deviations from results of other programs that allow for determination of the dimensionality (e.g. $TOPOS^{27}$ or PLATON²⁸) may be explained by slightly different tabulated radii. In the 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 cover 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 TOPOS²⁷ program. Finally, extended point and vertex symbols according to the definitions by 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, particularly when nodes of higher connectivity accumulate. An entirely manual evaluation of many thousands of 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 networks³⁰ are provided as supporting information and 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 CaCl₂ and proline under varying conditions. Reactions 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 space group $P2_1/c$ with an asymmetric unit consisting of CaCl(DL-proline) with Ca on the Wyckoff position 2a. The unit cell of the chiral analogue 2a is about twice the size of 1a and is orthorhombic with space group $P2_12_12_1$ resulting in an asymmetric unit of CaCl₂(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

	1a	1b	2a	2b
Empirical formula	C10H18CaCl2N2O4	C ₁₀ H ₂₂ CaCl ₂ N ₂ O ₆	$C_{10}H_{18}CaCl_2N_2O_4$	C ₅ H ₁₁ CaCl ₂ NO ₃
Formula weight (g mol ⁻¹)	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)	$0.31 \times 0.27 \times 0.05$	$0.20 \times 0.16 \times 0.06$	$0.20 \times 0.09 \times 0.04$	0.23 imes 0.21 imes 0.08
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$
a (Å)	10.6806(15)	5.8720(19)	7.6518(12)	6.9732(6)
<i>b</i> (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)
$\beta(\circ)$	107.139(2)	104.233(5)	90	90
$V(\mathbf{A})^3$	706.01(17)	789.0(4)	1484.4(4)	990.83(15)
Z	2	2	4	4
$\mu (\mathrm{mm}^{-1})$	0.833	0.763	0.793	1.141
Total/unique reflections	9265/1713	8140/1418	17 580/2979	14 215/2605
Variables refined	94 (1 restraint)	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

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

2.260(2) to 2.343(2) Å in 2a, whereas in 1a only a small difference between the two independent 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



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

in 1a must be linear for reasons of symmetry, a significant distortion is found in its enantiopure analogue $(160.23(3)^{\circ})$.

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

2b stands out because of its higher coordination number and exceptional Ca : proline ratio (1 : 1). The asymmetric units of CaCl₂(H₂O)₂(μ -proline) form the orthorhombic structure (*P*2₁2₁2₁). A μ_3 - η^1 : η^2 : η^1 -carboxylate and two symmetry

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

	1b	
2.3079(11)	Ca(1)…O(3)	2.342(3)
2.3329(11)	$Ca(1)\cdots O(1)$	2.357(3)
2.7375(5)	$Ca(1)\cdots Cl(1)$	2.7333(13)
	2b	
2.260(2)	Ca(1)…O(3)	2.3090(14)
2.273(2)	$Ca(1)\cdots O(2)^d$	2.3777(12)
2.298(2)	$Ca(1)\cdots O(2)$	2.4176(12)
2.343(2)	$Ca(1)\cdots O(1)^e$	2.4989(12)
	$Ca(1)\cdots O(1)$	2.6700(12)
2.7380(10)	$Ca(1)\cdots Cl(1)$	2.6982(6)
2.7522(10)	$Ca(1)\cdots Cl(2)$	2.7425(6)
	2.3079(11) 2.3329(11) 2.7375(5) 2.260(2) 2.273(2) 2.298(2) 2.343(2) 2.7380(10) 2.7522(10)	$\begin{array}{c c} 1b \\ \hline 2.3079(11) & Ca(1)\cdots O(3) \\ 2.3329(11) & Ca(1)\cdots O(1) \\ 2.7375(5) & Ca(1)\cdots Cl(1) \\ \hline \\ \hline \\ \hline \\ 2b \\ \hline \\ 2.260(2) & Ca(1)\cdots O(3) \\ 2.273(2) & Ca(1)\cdots O(2)^d \\ 2.298(2) & Ca(1)\cdots O(2) \\ 2.343(2) & Ca(1)\cdots O(1)^e \\ & Ca(1)\cdots O(1) \\ 2.7380(10) & Ca(1)\cdots Cl(1) \\ 2.7522(10) & Ca(1)\cdots Cl(2) \\ \hline \end{array}$

Symmetry codes:^{*a*} x, -y + 1/2, z - 1/2. ^{*b*} x + 1/2, -y + 5/2, -z. ^{*c*} x - 1/2, -y + 3/2, -z. ^{*d*} x + 1/2, -y + 3/2, -z + 1. ^{*e*} x - 1/2, -y + 3/2, -z + 1.

equivalents in total contribute to 4 coordination sites at the central calcium cation, and 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 atom 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 has 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 μ_3 - η^1 : η^2 : η^1 -carboxylate bridging and the resulting chain resemble a structure reported for a calcium chloride glycine complex⁹ 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 $O,O'-\mu_2-\eta^1:\eta^1$ 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 a {4,4} network) is observed. While the layers extend parallel to the two shortest unit cell axes in both structures, the stacking direction is manifested in the longest cell axes. The homochiral compound 2a may be described as alternating network layers (ABAB) whereas 1a is built of only one centrosymmetric and necessarily heterochiral layer (see Fig. 5). Although their unit cells are metrically similar, only a topological and no groupsubgroup 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 summary is provided in Table 3. In the enantiopure network 2a a bifurcated hydrogen bond is formed by N(2)-H(2B), overall resulting in a 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



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

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

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D-H···A	D-H [Å]	H…A [Å]	D…A [Å]	D−H…A [°]
1a				
$N(1)-H(1B)\cdots Cl(1)^{a}$	0.895(15)	2.318(15)	3.1198(15)	149.2(16)
1b				
$N(1)-H(1A)\cdots O(2)^{b}$	0.89(5)	1.97(5)	2.810(5)	158(5)
$N(1)-H(1B)\cdots Cl(1)^{c}$	0.89(4)	2.51(4)	3.208(4)	136(4)
$O(3)-H(3A)\cdots Cl(1)^{c}$	0.83(5)	2.31(5)	3.128(4)	168(5)
$O(3)-H(3B)\cdots O(2)^d$	0.82(4)	1.94(4)	2.745(4)	168(5)
2a				
$N(1)-H(1A)\cdots Cl(2)^{e}$	0.91(2)	2.18(2)	3.083(3)	171(3)
$N(1)-H(1B)\cdots Cl(1)$	0.90(2)	2.35(2)	3.187(3)	155(3)
$N(2)-H(2A)\cdots O(1)^{f}$	0.92(3)	2.37(3)	3.232(3)	156(2)
$N(2)-H(2B)\cdots O(2)^{g}$	0.91(3)	2.24(3)	2.948(3)	134(3)
$N(2)-H(2B)\cdots Cl(1)^{h}$	0.91(3)	2.77(2)	3.353(2)	124(2)
2b				
$N(1)-H(1A)\cdots Cl(1)^{i}$	0.87(2)	2.28(2)	3.0360(15)	146.0(18)
$N(1)-H(1B)\cdots Cl(2)^{j}$	0.879(17)	2.290(17)	3.1557(15)	168.3(18)
$O(3)-H(3C)\cdots Cl(1)^k$	0.78(2)	2.33(2)	3.0771(14)	161(2)
$O(3)-H(3D)\cdots Cl(2)^{l}$	0.79(2)	2.37(2)	3.1570(15)	176.0(17)
	. h.			1

Symmetry codes:^{*a*} x, y, 1 + z. ^{*b*} 1 + x, y, z. ^{*c*} 1 - x, -y, -z. ^{*d*} x, y, -1 + z. ^{*e*} -1/2 + x, 3/2 - y, -z. ^{*f*} -1/2 + x, 5/2 - y, -z. ^{*g*} x, -1 + y, z. ^{*h*} 1/2 + x, 5/2 - y, -z. ^{*i*} 1/2 + x, 3/2 - y, 1 - z. ^{*j*} 1 - x, -1/2 + y, 3/2 - z. ^{*k*} 1 - x, -1/2 + y, 1/2 - z. l - 1/2 + x, 3/2 - y, 1 - z.

polymer 2b is crosslinked to a three-dimensional hydrogenbonded 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 Liebisch³² and explained by Brock et al.;³³ we have confirmed this relationship for homo- and heterochiral molecular crystals,³⁴ salts³⁵ 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 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 has a chloridecalcium 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 CaCl₂ 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

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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).

and 2a. While the mononuclear composition 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 ("zerodimensional") 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 dimensions and 2.6% in three dimensions. The majority (53%) of the two dimensional networks correspond 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 polycarboxylate ligands which easily leads to crosslinking. However, only 1% of 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**. The majority are derivatives of formic acid, and only one structure of an amino acid³⁷ 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 coordination bonds of the carboxylate and the hydrogen donor functionality of the ammonium group, chirality is a welcome extra in amino acid chemistry. In the case of our sql nets, enantiomerically pure and racemic proline results 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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