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Natural and synthetic metal oxalates – a topology approach

Coordination polymers based on $M^{n+}$ ions with three oxalates have the perfect geometry for forming the most symmetric of the 3-connected, 3D-nets, namely the chiral srs or (10,3-a) net. Intriguingly, in some cases less optimal nets are found. We describe the new noa-net above, and touch upon the crystal engineering questions of “why?” and “how to control?” these structures and network topologies. The tris-oxalates may also form the 2D hcb-net occasionally found in nature, and we similarly explore the topologies of these mineral oxalates, among these the new 3D hum-net above.
Natural and synthetic metal oxalates – a topology approach†

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Oxalates are found in minerals and in biology, are made in the laboratory, and are used on an industrial scale. They form coordination polymers and hydrogen bonded networks that often can be analysed using network topology. In this survey of known naturally occurring oxalates we note that, [Ca(C$_2$O$_4$)$_2$]·xH$_2$O, that seems to be the first known naturally occurring metal-organic framework, forming the four-connected crb-net (zeolite CRB). The natural oxalates are typically 3D, 2D or 1D coordination polymers, with extensive hydrogen bonding in the latter cases. For example, humboldtine and lindbergite form the new 3- and 8-connected net hum by combining the 1D structure with strong hydrogen bonds. Tris-oxalates rarely occur in nature but stepanovite, [MgH$_2$O]$_6$[Na(Fe(ox)$_3$)$_3$]·3H$_2$O, is an exception and forms hcb-nets (honeycomb 2D layers) with the hexaqua ions sealing any potential voids. Synthetic tris-oxalates on the other hand are well explored and normally form 2D hcb-nets or 3D chiral three-connected srs-nets. Theoretically a few other topologies should also be possible, and it was found that [Mn(R)-salmen(CH$_3$OH)CH$_3$CN][MnCr(ox)$_3$]·0.5CH$_3$OH·1.25CH$_3$CN forms the achiral three-connected lig-net, [Fe(2,6-bis(pyrazol-3-yl)pyridine)$_3$]MnCr(ox)$_3$]·2,6-bis(pyrazol-3-yl)pyridine·CH$_3$OH forms the likewise achiral nod-net and [Cu(trans[14]dien)]IKr(ox)$_3$]·3H$_2$O the rhs-net. A new binodal 3-connected net noa [with the derived 3c-, 4c- new net mys] was found in [Fe(tren(imid)$_3$)$_3$]$_2$[Mn$_{12.5}$(CH$_3$OH)$_3$Cr$_3$(ox)$_3$]·(CH$_3$OH)$_4$·0.75(H$_2$O)$_4$. The more complex [Fe(tren(imid)$_3$)$_3$]$_2$[Mn$_{2.5}$(CH$_3$OH)$_2$Cr$_3$(ox)$_3$]$_2$ forms a new three-nodal 3-connected daz-net.

Due to the possibility of the oxalate ion forming bridging chelates in two or more directions, and its many hydrogen bond accepting sites, oxalate compounds often form networks. The topological analysis of such networks has its origins in the work of Alexander Wells starting in the 1950s, gaining popularity by the analysis of coordination polymers and metal–organic frameworks (MOFs) in the 1990s and onwards.

Here, we report how well metal compounds with small oxalate ions (ox) lend themselves to such topological analysis. We will show the importance of network topologies in both the synthesis of new oxalate compounds and in the communication and understanding of known oxalates, both natural and synthetic.

We have investigated two cases, first the tris-oxalates, [M’M(ox)$_3$]$_2$, forming three-connected networks. These are known to produce 2D hcb-nets (honeycomb nets, Fig. 1 left) or the 3D chiral srs-nets (or (10,3)-a, Fig. 1 right), but geometrical considerations suggest that also a number of other 3-connected topologies should be conceivable, even though the srs-net appears to be the perfect fit for enantiomerically pure tris-oxalates.

We do not consider the four-connecting tetrakis-oxalates here if they are not naturally occurring, as these have been discussed elsewhere.

1. Introduction

Oxalic acid and oxalates date far back in human history, both found as a tasty part of numerous plants, and in painful and dangerous kidney and bladder stones. In industry, they are used in the separation of various metals, and other practical examples employing the ubiquitous C$_2$O$_4^{2-}$ unit are in artistic chemical photography processes and the anticancer drug oxaliplatin (trade name Eloxatin). But oxalates are also very much present in today’s cutting edge science.

Tri-potassium trioxalato-rhodium monohydrate was the focus of the first diffraction study of oxalates in 1927 (ZZZVZK) followed by beryllium oxalate trihydrate in 1928 (ZZZZQZK), and today the Cambridge Crystallographic Data Centre has collected over 6000 oxalate entries into the CSD.

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Secondly, we consider the natural oxalates, recently reviewed by Piro and Baran.17 Through the 2D tris-oxalate hcb-nets there is some overlap with the first group,18 and the rare Siberian mineral stepanovite had its 15 minutes of fame a few years ago19,20 when the structures were, unexpectedly, found to resemble "well-established magnetic and proton-conducting metal oxalate MOFs".21

2. Experimental

2.1 Materials and methods

2.1.1 Searching the Cambridge Structural Database (CSD). The CSD 5.40 (September 2019) was used. In all runs the Conquest software (version 2.0.2 or 2.0.3) was used. To compute bridging tris-oxalates, an [M$_3$O$_6$]$_2^-$ entity was used as a query, and to exclude the tetraakis-oxalates and only include extended networks, the central M was restricted to a maximum of 7 bonding atoms and at least one M–O bond was specified as polymeric.

2.1.2 Computational details. The network topologies discussed in this article were obtained using the freeware programs ToposPro22 and Systre23 operating on the original crystallographic information files for the compounds in question, or on files derived from these. Throughout we discuss the topologies using three-letter symbols in the web-based free Reticular Chemistry Structural Resource database, RCSR,24 as encouraged by IUPAC.25

3. Results and discussion

3.1 Tris-oxalates, [M′M(ox)$_3$]$_n$^

The Cambridge Structural Database in total contains 682 entries with a minimum of three bridging oxalates (15 added to the latest 5.40 tri-annual update, and at least 301 of these are tris-oxalate networks either with M = M’ or with different M and M’. A recent survey of srs-nets (Fig. 1) lists 91 tris-oxalates having the srs-network topology,26 and as not all of the remaining ones form the 2D hcb-net (Fig. 1), we wondered about these network topologies. Is there one particular topology that is the second “choice” or are there many possibilities? And are they all chiral as the srs-net?

In Table 1, we have collected the tris-oxalates from the CSD that form neither the srs nor hcb-net.

3.1.1 The lig-net. The lig-net (from LiGe, a Zintl phase with a three-connected Ge network) was identified by Blatov et al. in the coordination polymer [CdCl(tphp)(PPh$_3$Bz)], YINPEQ, where it is doubly interpenetrated.13 It was also briefly discussed as a rod-packing by Rosi et al.27 We found it in the metal-oxalate network in BEWVEG, [Mn(S)-salmen][(CH$_3$OH)$_2$][MnCr(ox)$_3$](CH$_3$Cl)$_3$0.350.35(1H$_2$O)]0.125,28 see Fig. 2.

Compared to the nets discussed by Öhrström & Larsson that were all formed from 10-gons as the shortest rings between nodes, the lig-net also forms 8-rings (point symbol 8·10 and vertex symbol 8·8·10, (ref.15)). This and other three-connected nets are discussed in detail in ref. 13.

3.1.2 The nod-net. The nod-net also forms 8-rings, but is a binodal net with the point symbol 8·8·10·10 and the vertex symbol 8·8·10·8·10·8·10. The metal-oxalate network in GURPTI, [Fe(sal$_2$-trien)][MnCr(ox)$_3$]CH$_3$OH,30 forms the nod-net, see Fig. 3.

3.1.3 The ths-net. The ths-net (from ThSi$_3$, also known as the 10,3-b net) is similar to the srs-net as it is also a 10,3-net, meaning that all the shortest rings are 10-gons. Its point symbol is 103 just as the srs, but the vertex symbols differ; 10$_5$·10$_2$·10$_2$ for srs versus 10$_2$·10$_2$·10$_4$ for ths (meaning that the number of different 10-gons forming the shortest circuits differ). A further difference is that ths is achiral and does not have the characteristic four-fold helices of srs, lig, nod, and some other 3-connected nets.

We found this net in for example [Cu(trans[14]dien)]KCr(ox)$_3$],31 where trans14-dien is 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene. In Fig. 4, it is shown (right) together with the ideal version of the ths-net (left).

3.1.4 The noa-net. While the preceding nets have all been described and found in various compounds (occurrence can be checked with ToposPro) we were surprised to find a new two-nodal three-connected net noa in RUGKIP (o-FAni)$_3$[DCH[18]crown-6](CH$_3$OH) Cr(oxalate)$_3$[MnCr(oxalate)$_3$]CH$_3$OH].32 This new net has point symbols 4·8·10 and 8·10$^2$ and again we see the characteristic four-fold helices in a racemic set-up, but this time connected by four rings. This enforces 90° angles in the network, and this is achieved by one of the Mn ions having one mono-coordinated oxalate ion and a methanol molecule completing the octahedron. The ideal net and the network in RUGKIP are presented in Fig. 5.

It has not escaped us that the noa-net is an augmented form of a three- and four-connected net with the four connected nodes in the centre of the squares. Somewhat surprisingly this is not the known jph-net16 but yet another new topology, mrs, with point symbols 6·8·4 and 6·8·$^{2}$·10. They differ again, just as lig and nod, in the arrangement of the four-fold helices of opposite chirality, see ESIFig. S1.

3.1.5 The daz-net. To finish off this section we want to comment on a more complicated structure, [Fe$^6$(tren-
the achiral daz net resembles the srs net, only with a zigzag motif added between helices along the z-axis. It is also related to the likewise chiral binodal noj net that essentially is an srs net with the zigzag motif inserted between all helices.

It is currently not known if there are similar versions of the achiral lig and noj nets.

We note, however, that the analysis of the structure using the daz net greatly simplifies the task and renders a very irregular 3D oxalate network into a reasonably understandable geometrical object.

3.1.6 Geometrical requirements of the nets. Topology is invariant to bending, squeezing and twisting as long as no bonds are broken. Many nets can be adjusted so that the dihedral angles between nodes more or less match what is needed between two tris-oxalate complexes. A detailed analysis of some of these geometries is found in ref. 15. Here, in Table 2, we note the ideal densities (as the number of vertices per unit volume) of these nets.

From this point of view it can be noted that the srs net has a very good fit to the oxalate networks, (see ref. 13 and 15 for details) and counter ions like {M[1,10-bipyridine]}

3.1.7 Rationale for topology choice of the system. In the studies surveyed, there has been no single reason pointed out responsible for which network topology any system will adopt. Unfortunately, we cannot point out a single factor either. The following discussion is a summary and a few comments on the rationales given in each individual paper.
For clarity, Lewis structures and space filling models of the individual cations are presented in Fig. S2.†

BEWVEG and BEWVOQ are typical examples. The authors demonstrated that using the same cation, [Mn(R)-salmen]⁺ or [Mn(S)-salmen]⁻, the 3D oxalate network depends on the choice of solvent.28 When crystallized in acetonitrile, a 2D hcb-net resulted (BEWVIK and BEWUW) instead of the 3D lig-net obtained from dichloromethane. Pertinent differences between the two structures are the configuration of the two phenoxy arms and the presence of different solvent molecules coordinated to MnII in the two apical positions of the structure, [Mn(R/S)-salmen(CH₂OH)₂]⁺ for lig, whereas the hcb ones contain [Mn(R/S)-salmen(CH₂CN)₂]⁺ together with [Mn(R/S)-salmen(CH₃OH)₂]⁻.

VINHOR and VINHIL33 on the other hand, both lig-nets, get their network from the heptacoordinated MnII ions in each structure. The difference between these structures is that in VINHOR all the Mn atoms are heptacoordinated, and in VINHIL the second crystallographically independent Mn atom is hexacoordinated with a strong trigonal distortion of its octahedral coordination, which give rise to the presence of O–Mn–O angles of 154.6° instead of 180° expected for an octahedral coordination. The methanol in these two complexes is attached to the trioxalate network. Another remark on these two compounds is that the smaller number of cations necessary (+2 vs. +1 in i.e. BEWVEG) to compensate the negative charge of the oxalate network produces a more irregular network with heptacoordinated MnII ions coordinated to solvent molecules, and a more open structure with pores filled with disordered solvent molecules.

The nod-net in EDATOT34 may be related to a solvent effect. There is a presence of many interstitial solvent molecules since only one Fe complex is present per Mn/Cr pair, and results in no extra anions needed to stabilize the complex. The lower occupancy of cations and anions inside the anionic network could be the main cause for losing the enantiopure character of these systems.

Combining [FeIII(5-Xsal₂-trien)]⁺ (X = NO₂ or CH₃O) with the MnIII CrIII oxalates resulted in two different networks.35 The cation [FeIII(5-NO₂sal₂-trien)] gave a 2D hcb-net (PUWZIZ) since the electron withdrawing group favors π⋯π stacking interactions between phenyl rings of neighboring cationic complexes. In contrast, in PUWZOX the phenyls are not face to face. This is explained by the presence of the methoxy

| Net  | Alt. name | Point symbol | Density a  |
|------|-----------|--------------|-----------|
| srs  | 10,3-a    | 10³         | 0.3536    |
| lig  | 6°10-a    | 6°-10; 6°-10 | 0.3536    |
| nod  | 6°10-b    | 6°-10; 6°-10 | 0.3535    |
| bto  | 10,3-c    | 10³         | 0.5132    |
| ths  | 10,3-d    | 10³         | 0.4218    |
| utp  | 10,3-d    | 10³         | 0.4218    |
| noj  | 8,3-d     | 8°³-8°³     | 0.3241    |

Table 2 Densities, as the number of vertices per unit volume, of some selected, ideal, nets. Data from the RCSR

a Number of vertices per unit volume.
groups that hinders the face to face orientation of the neighboring rings. The dihedral angles, $\alpha$, between the least-squares planes of the two phenoxy rings of the hcb-net are $\alpha = 89.002^\circ$ ([Fe1] complex) and $\alpha = 94.248^\circ$ ([Fe2] complex) and the dihedral angles, $\alpha$, between the phenoxy rings in PUWZIZ forming the nod-net are for [Fe1A], [Fe1B] and [Fe2] 110.47, 100.41 and 105.55$^\circ$, respectively. The dihedral angles, $\alpha$, between the least-squares planes of the two phenoxy rings have very different values in the 2D or 3D structures. Thus, the two phenoxy rings in the 2D compound (PUWZIZ) are closer to 90$^\circ$, the ideal value for an octahedral complex.

### 3.1.8 The absence of interpenetration for these systems.

The intergrowth of two or more networks is a common feature for coordination polymers,12,13 and for the srs-net in particular many examples exist, see for instance ref. 41. However, in the tris-oxalate systems the srs-net is always negatively charged and two such nets interpenetrated in the same compound would require doubling the number of cations while at the same time leaving much less space for them. We believe that these two requirements are difficult to fulfil and therefore interpenetration is not observed in this class of compounds.

### 3.2 Naturally occurring metal oxalates

Metal oxalates from minerals come in a large variety, from the class of tris-oxalates we have seen in the preceding section, to more or less discrete molecular entities held together by hydrogen bonds. While the former are normally straight-forward to analyse, hydrogen bonded systems may be more ambiguous, and even simple metal oxalates may use multiple bonding sites on the oxalates, making some of these systems equally challenging.36

In Table 3, we have assembled naturally occurring oxalates according to Piro and Baran17 with the network analysis performed by our group. We have mainly concentrated on the 3D and 2D coordination polymers, but the very simple humboldtine and lindbergite, the Fe and Mn versions of two isostructural 1D [M(C2O4)(H2O)2] oxalates, have also been included. In this latter case, the coordination network is supplemented with strong hydrogen bonds between coordinated water and oxalate ions.

### 3.2.1 Stepanovite and zhemchuzhnikovite.

While stepanovite (OKUTUL03) [Mg(H2O)6][FeNa2(C2O4)3]·3H2O and zhemchuzhnikovite (OKUVAT02) [Mg(H2O)6][AlNa2(C2O4)3]·2H2O form the 2D hcb-net in very attractive structures, the hydrated metal ions ([Mg(H2O)6]2+) that completely fill the voids indicate that these are not real MOFs. The IUPAC definition states that a MOF should be ‘potentially porous’ and as the cations fill the perceived channels, it does not fit the bill. Nevertheless, forming a network of metal carboxylates does make them MOF-like in some aspects.

### 3.2.2 Weddellite.

Weddellite (also “weddelite”), on the other hand, has been reported to lose water without a change in morphology37 and is thus a potential candidate for a “natural” MOF. This compound, with a square antiprismic calcium ion coordinating three oxalate ions and two water molecules, has the approximate formula [Ca(ox)(H2O)3]·xH2O and the oxalates bridge the Ca$^{2+}$ ions as depicted in Fig. 7.

The crystal structure according to Tazzoli and Domenegetti38 (CSD code WHWLTB) is shown in Fig. 8 together with the crb-net formed.

### Table 3 Naturally occurring metal-oxalates according to Piro and Baran, and their networks

| Compound                  | Formula                  | Net  | Nodea |
|---------------------------|--------------------------|------|-------|
| 3D coordination networks  |                          |      |       |
| Weddellite                | [Ca(C2O4)(H2O)3]·xH2O   | crb  | Ca    |
| Natrosalate               | [Na2(C2O4)]             | fit  | Na, ox|
| Wheatleyite               | [Na2(Cu2C2O4)3(H2O)2]   | sdd  | Na    |
| Whewellite                | [Ca2(C2O4)2H2O]         | sqp  | Ca    |
| Novgorodavaite            | [Ca2Cl2(C2O4)2(H2O)2]   | sqp  | Ca    |
| 2D coordination networks  |                          |      |       |
| Zhemchuzhnikovite         | [Mg(H2O)6][AlNa2(C2O4)3]·2H2O | hcb  | Mg, Al|
| Stepanovite               | [Mg(H2O)6][FeNa2(C2O4)3]·3H2O | hcb  | Mg, Fe|
| Deveroite                 | [Ce2(C2O4)3(H2O)4]      | hcl  | Ce    |
| Coskrenite                | [Ce2(C2O4)(SO4)3(H2O)6] | hxl  | Ce    |
| 1D coordination networks  |                          |      |       |
| Humboldtine               | [Fe(C2O4)(H2O)3]        | humb | Fe, H2O|
| Lindbergite               | [Mn(C2O4)(H2O)3]        | humb | Mn, H2O|
| Levinsonite               | [Al(H2O)6][Y(C2O4)(SO4)3(H2O)3]·3H2O | —    | —     |
| Zugshunstite              | [Al(H2O)6][Ce(C2O4)(SO4)3(H2O)3]·3H2O | —    | —     |

a ox = oxalate centroid. b New topology.
The porosity of weddellite has not been rigorously proven. However, in a study using an environmental scanning electron microscope with a heating stage attached, no changes in the crystal morphology were observed as water was desorbed\(^{37}\) and recently detailed variable temperature single crystal and powder X-ray diffraction (XRD) has confirmed structural integrity up to 105–140 °C after which the structure collapses.\(^{39}\)

### 3.2.3 Natroxalate

In the crystal structure of natroxalate, [Na\(_2\)(C\(_2\)O\(_4\)\)] (CSD code NAOXAL – NAOXAL20), we no longer see distinct oxalate bridges, but rather a much more tightly packed system. In this compound every sodium ion binds to five oxalate ions, and every oxalate to ten sodium ions. The analysis is very straightforward, generating the 5 and 10 connected fit-net shown in Fig. 9.

![Fig. 9](image)

**Fig. 9** The 5 (Na\(^+\), pink) and 10 (oxalate centroids, green) connected fit-net in natroxalate, [Na\(_2\)(C\(_2\)O\(_4\)\)]. This is a tightly packed structure without voids.

### 3.2.4 Wheatleyite

Wheatleyite is a mixed-metal mineral with formula [Na\(_2\)Cu(C\(_2\)O\(_4\))\(_2\)]\(\cdot\)2H\(_2\)O (CSD code CUOXNAI) composed of layers of sodium ions doubly bridged by oxygens from either oxalate or water that are connected through the [Cu(C\(_2\)O\(_4\))]\(^{2−}\) bridge. This forms the six-connected sxd-net and the network in the wheatleyite structure is shown in Fig. 10 together with the most symmetric form of the net.

### 3.2.5 Deveroite

Deveroite, [Ce\(_2\)(C\(_2\)O\(_4\))\(_3\)]\(\cdot\)6H\(_2\)O (CSD code CEOXDH, also forms the 2D hcb-net despite Ce\(^{3+}\) being 9-coordinated. In contrast to stepanovite and zhemchuzhnikovite there are no counter ions that plug the empty space in the centre of the hexagons. However, the layers pack in an ABAB-fashion, with an offset, so that edges of layer A are in the middle of the hexagonal window of layer B, so no continuous open channels exist in this compound.

### 3.2.6 Whewellite

In whewellite, [Ca(C\(_2\)O\(_4\))\(_2\)\(\cdot\)H\(_2\)O]\(_2\)·xH\(_2\)O, water in pink. Top right: The crb-net formed. This is the only known naturally occurring metal–organic framework. Bottom: The ideal crb-net.

![Fig. 8](image)

**Fig. 8** Top left: Crystal structure of weddellite, [Ca(C\(_2\)O\(_4\))\(_2\)\(\cdot\)xH\(_2\)O, water in pink. Top right: The crb-net formed. This is the only known naturally occurring metal–organic framework. Bottom: The ideal crb-net.

**3.2.4 Wheatleyite.** Wheatleyite is a mixed-metal mineral with formula \([\text{Na}_2\text{Cu(C}_2\text{O}_4)_2]\cdot2\text{H}_2\text{O}\) (CSD code CUOXNAI) composed of layers of sodium ions doubly bridged by oxygens from either oxalate or water that are connected through the \([\text{Cu(C}_2\text{O}_4)]^{2−}\) bridge. This forms the six-connected sxd-net and the network in the wheatleyite structure is shown in Fig. 10 together with the most symmetric form of the net.

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**3.2.6 Whewellite.** In whewellite, \([\text{Ca(C}_2\text{O}_4)_2]\cdot\text{O}_2\) CSD code CALOXM, as in weddellite, we find a square antiprismatic calcium ion with two bis-chelating oxalate ions. One water and oxygen atoms from three other oxalate ions complete the coordination sphere, making every calcium ion a five-connected node in an sqp-net, see Fig. 11.
Inspecting this structure, one finds apparent voids, but they are all too small to be chemically significant.

3.2.7 Coskrenite. Coskrenite, $\text{[Ce}_2\text{(C}_2\text{O}_4\text{)}\text{(SO}_4\text{)}\text{H}_2\text{O)}_8\text{]}$, again forms a 2D network, a corrugated version of the six-connected $\text{hxl}$-net with lanthanoid ions (many possibilities exist) bridged by oxalates and sulfates. Structure data from entry 9004543 in the Crystallography Open Database.

3.2.8 Novgorodavaite. Novgorodavaite $\text{[Ca}_2\text{Cl}_2\text{(C}_2\text{O}_4\text{)}\text{H}_2\text{O)}_2\text{]}$ resembles whewellite in that it also forms a five-connected net with an $\text{sqp}$ topology, see Fig. 12. Structure data from entry 0012496 in the American Mineralogist Crystal Structure Database.

3.2.9 1D coordination polymers. The 1D coordination polymers are all straight chains with bis-chelating oxalates, M–oxalate–M. They all form hydrogen bonded networks, some more complex than others. Here, we consider only the isostructural humboldtite and lindbergite, the Fe and Mn versions of $\text{[M(C}_2\text{O}_4\text{)}\text{H}_2\text{O)}_2\text{]}$, respectively.

They have infinite bis-chelating –M–oxalate–M– chains with perpendicular coordinated water molecules, each hydrogen bonding to two oxalates. Taking the metal ions as one node and the water molecules as another, these structures form 3- and 8-connected nets. The water nodes are three-connected as they bind to the metal ion and then hydrogen bonds to two oxalates each. The metal ion node is eight connected as it binds to metal ions through coordination, two water molecules also via coordination, and then four waters via hydrogen bonds. This new topology $\text{hum}$ is shown in Fig. 13 (right) together with the structure of humboldtite.
4. Conclusions

Analysis of the CSD data indicates that synthetic 3D tris-oxalates occur in more than one network topology, even if the srs-net is by far the most common. The well-known nets nod, lig, and ths were found to occur, together with the new topologies noa and daz. It also suggests that, as different topologies have differently shaped and sized cavities, a rational approach to design compounds with other network topologies not encountered so far, should be possible.

Even so, the examples provided here give no clear guidance as how to perform such a rational design. Computational studies are in progress to address this question.

We also note that the issue may be more complex than a simple consideration of ideal geometries may suggest. Topologies stay the same even if bent, squeezed or otherwise distorted, as long as no bonds in the network are broken. Thus both the relative size and the shape of the empty space inside a particular network may be changed without changing the topology. Excellent examples are the “breathing” MOFs such as MIL-53. Indeed we suggest that it should be possible to calculate a figure of merit for each network topology on the relative energetic cost of different distortions to further enhance their utility as blueprints for the design of molecule based materials.

We also note that the synthetic tris-oxalates are often multi component systems where the network can interplay with one or more guests. Taking the network topology into consideration will be one important step in making the synthesis of such materials a more rational process.

The natural oxalates present a more complex picture, and in Fig. 14 we have tried to summarize and contrast them to the more symmetric synthetic analogues. The new net hum was described as a model for the bonding and structure in humboldtine and lindbergite.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 L. Öhrström and J. Covès, The Rubarb Connection and Other Revelations: The Everyday World of Metal Ions, Royal Society of Chemistry, London, 2018.
2 I. Huskić, N. Novendra, D.-W. Lim, F. Topić, H. M. Titi, I. V. Pekov, S. V. Krivovichev, A. Navrotsky, H. Kitagawa and T. Friščić, Chem. Sci., 2019, 10, 4923–4929.
3 F. Y. Yi, H. J. Yang, X. Zhao, P. Y. Feng and X. H. Bu, Angew. Chem., Int. Ed., 2019, 58, 2889–2892.
4 B. Zhang, P. J. Baker, Y. Zhang, D. Wang, Z. Wang, S. Su, D. Zhu and F. L. Pratt, J. Am. Chem. Soc., 2018, 140, 122–125.
5 M. Darawsheh, L. A. Barrios, O. Roubleau, S. J. Teat and G. Aromi, Angew. Chem., Int. Ed., 2018, 57, 13509–13513.
6 P. K. Tsobnang, E. Hastürk, D. Fröhlich, E. Wenger, P. Durand, J. L. Ngolui, C. Lecomte and C. Janiak, Cryst. Growth Des., 2019, 19, 2869–2880.
7 C. F. N. Gueñedzí, F. Capet, J. Ngouné, G. Bebga, M. Foulon and J. Nenwa, J. Coord. Chem., 2018, 71, 1483–1496.
8 G. W. Burgers and W. Bragg, Proc. R. Soc. London, Ser. A, 1927, 116, 553–586.
9 A. F. Wells, Three-dimensional nets and polyhedra, John Wiley & Sons, New York, 1977.
10 A. F. Wells, Acta Cryst., 1954, 7, 535–544.
11 O. M. Yaghi, M. O’Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, Nature, 2003, 423, 705–714.
12 V. A. Blatov, L. Carlucci, G. Giani and D. M. Proserpio, CrystEngComm, 2004, 6, 377–395.
13 L. Öhrström and K. Larsson, Molecule-Based Materials The Structural Network Approach, Elsevier, Amsterdam, 2005.
14 L. Öhrström, Chem. – Eur. J., 2016, 22, 13758–13763.
15 L. Öhrström and K. Larsson, Dalton Trans., 2004, 347–353.
16 L. Öhrström and K. Larsson, Molecule-Based Materials: The Structural Network Approach, Elsevier, Amsterdam, 2005, ch. 12.
17 O. E. Piro and E. J. Baran, Crystallogr. Rev., 2018, 24, 149–175.
18 I. Huskic and T. Friscic, Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater., 2018, 74, 539–559.
19 B. Smith, ‘Designer’ materials found deep in Siberian permafrost, Cosmos, 2016, 08 AUGUST.
20 E. Stoye, Naturally occurring MOFs found in coal mine minerals, Chemistry World, RSC, 2016, 19 AUGUST.
21 I. Huskic, I. V. Pekov, S. V. Krivovichev and T. Friscic, Sci. Adv., 2016, 2, 7.
22 V. A. Blatov, A. P. Shevchenko and D. M. Proserpio, Cryst. Growth Des., 2014, 14, 3576–3586.
23 O. Delgado-Friedichs and M. O’Keeffe, Acta Crystallogr., Sect. A: Found. Crystallogr., 2003, 59, 351–360.
24 M. O’Keeffe, M. A. Peskov, S. Ramsden and O. M. Yaghi, Acc. Chem. Res., 2008, 41, 1782–1789.
25 S. R. Batten, N. R. Champness, X. M. Chen, J. García-Martínez, S. Kitagawa, L. Öhrström, M. O’Keeffe, M. P. Suh and J. Reedijk, Pure Appl. Chem., 2013, 85, 1715–1724.
26 A. Mizuno, Y. Shuku and K. Awaga, Bull. Chem. Soc. Jpn., 2019, 92, 1068–1093.
27 N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O’Keeffe and O. M. Yaghi, J. Am. Chem. Soc., 2005, 127, 1504–1518.
28 M. Clemente-León, E. Coronado and M. López-Jordà, Dalton Trans., 2013, 42, 5100–5110.
29 V. A. Blatov, M. O’Keeffe and D. M. Proserpio, CrystEngComm, 2010, 12, 44–48.
30 M. Clemente-León, E. Coronado, M. López-Jordà, G. Mínguez Espallargas, A. Soriano-Portillo and J. C. Waerenborgh, Chem. – Eur. J., 2010, 16, 2207–2219.
31 H.-Y. Shen, W.-M. Bu, D.-Z. Liao, Z.-H. Jiang, S.-P. Yan and G.-L. Wang, Inorg. Chem., 2000, 39, 2239–2242.
32 T. Endo, K. Kubo, M. Yoshitake, S.-i. Noro, N. Hoshino, T. Akutagawa and T. Nakamura, *Cryst. Growth Des.*, 2015, 15, 1186–1193.
33 A. Ben Djamâa, M. Clemente-León, E. Coronado and M. López-Jordà, *Polyhedron*, 2013, 64, 142–150.
34 E. Coronado, J. R. Galán Mascarós, M. C. Giménez-López, M. Almeida and J. C. Waerenborgh, *Polyhedron*, 2007, 26, 1838–1844.
35 M. Clemente-León, E. Coronado and M. López-Jordà, *Dalton Trans.*, 2010, 39, 4903–4910.
36 C. Borel, M. Ghazzali, V. Langer and L. Öhrström, *Inorg. Chem. Commun.*, 2009, 12, 105–108.
37 J. T. Kloprogge, T. E. Bostrom and M. L. Weier, *Am. Mineral.*, 2004, 89, 245–248.
38 V. Tazzoli and C. Domeneghetti, *Am. Mineral.*, 1980, 65, 327–334.
39 A. R. Izatulina, V. V. Gurzhiy, M. G. Krzhizhanovskaya, M. A. Kuz'mina, M. Leoni and O. V. Frank-Kamenetskaya, *Cryst. Growth Des.*, 2018, 18, 5465–5478.
40 L. R. Parent, C. H. Pham, J. P. Patterson, M. S. Denny, S. M. Cohen, N. C. Gianneschi and F. Paesani, *J. Am. Chem. Soc.*, 2017, 139, 13973–13976.
41 M. Ghazzali, V. Langer, K. Larsson and L. Öhrström, *CrystEngComm*, 2011, 13, 5813–5817.