# Organically-templated metal sulfates, selenites and selenates

C. N. R. Rao,†* J. N. Behera and Meenakshi Dan

The literature on inorganic open-framework materials abounds in the synthesis and characterization of metal silicates, phosphates and carboxylates. Most of these materials have an organic amine as the template. In the last few years, it has been shown that anions such as sulfate, selenite and selenate can also be employed to obtain organically templated open-framework materials. This tutorial review provides an up-to-date survey of organically templated metal sulfates, selenites and selenates, prepared under hydrothermal conditions. The discussion includes one-, two-, and three-dimensional structures of these materials, many of which possess open architectures. The article should be useful to practitioners of inorganic and materials chemistry, besides students and teachers. The article serves to demonstrate how most oxy-anions can be used to build complex structures with metal–oxygen polyhedra.

## Introduction

Inorganic open-framework compounds constitute an important class of materials that has attracted much attention as evidenced by the vast number of research papers published in the last few years. Although work in this area started with aluminium silicates[1,2] because of their important uses in sorption and catalysis, much of the recent work pertains to the structure and characterization of open-framework metal phosphates and carboxylates. Both these families of open-framework materials have been reviewed recently.[3–7] Since open-framework silicates and phosphates can essentially be considered as resulting from different arrangements of the metal–oxygen polyhedra and the anion tetrahedra, it seemed rational to examine whether open-framework compounds similar to metal phosphates are readily formed by an oxy-anions such as the sulfate. The main difference between the last two anions and the silicate and phosphate ions relates to the formal oxidation states or the charge on the central atom. In the bonds formed with metals, sulfur would have a higher charge compared to Si–O–M or P–O–M bonds. The sulfate bonds are also least covalent. Sulfates should, however, form stable structures with relatively low valent metal ions. Sulfates rarely form rings unlike silicates and the latter polymerize readily. In spite of such factors, it was not obvious why the sulfate ion should not form open-framework structures with metal–oxygen polyhedra. Recent efforts in this direction have indeed been successful in isolating several organically templated open-framework metal sulfates. A few amine-templated metal selenites and selenates have also been reported recently.

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Many of these sulfates, selenites and selenates have open-framework structures.

The open-framework metal sulfates, selenites and selenates are synthesized under hydro/solvothermal conditions in the presence of organic amines. The organic amines play different roles, as true templates, as structure directors and as space fillers.[8,9] In some instances the parent amine is taken as part of the reaction mixture while in some others the amine is taken in the form of an amine sulfate which serves as the source of both the amine and the sulfate.[10] The use of amine sulfates as reaction precursors and their reactions with metal ions is in its infancy, unlike the use of amine phosphates in open-framework phosphate chemistry.[11,12] Organically templated metal sulfates, selenites and selenates possessing 1D inorganic chain structures, 2D layer structures, as well as 3D structures with channels have been synthesized and characterized. The inorganic frameworks are generally connected by hydrogen bonds to the protonated amine molecules and the extra framework water molecules when present. In this article, we briefly review the present status of the organically templated metal sulfates, selenites and selenates of different dimensionalities.

## One-dimensional metal sulfates

**Single-stranded chain.** This simple topology is found in $[Zn(SO_4)(H_2O)_2(C_{10}N_2H_8)]$, **I**, which consists of chains formed by $[ZnO_4N_2]$ octahedra and $[SO_4]$ tetrahedra joined by common vertices.[13] The octahedral coordination around the zinc center is provided by two μ-O groups from two adjacent sulfate ligands in the chain and two nitrogens from the chelating 2,2′-bipyridine ligand. Each sulfate ligand uses two oxygen atoms to link two $ZnO_4N_2$ octahedra each of which, in turn, shares vertices with two $SO_4$ groups. This generates the –Zn–O–S–O–Zn– wire-like chain shown in Fig. 1a. Two adjacent chains interact through hydrogen bonds formed by the aqua ligand and terminal S=O bonds. A similar single stranded structure has been found in a vanadium sulfates.[14,15] The $[M(TO_4)\phi_4]$ chain backbone is the simplest possible 1D structure and is the basic motif in the mineral chalcanthite.[16]

**Double-stranded chain.** This topology is found in $[H_2N(CH_2)_2NH_2][FeF_3SO_4]$, **II**, comprising strictly alternating

FeF$_3$O$_3$ octahedra and SO$_4$ tetrahedral units, to form a four-member ring ladder as shown in Fig. 1b.[17] The ladder runs along the *a*-axis with the FeF$_3$O$_3$ octahedra sharing vertices with triply-bridging SO$_4$ groups. The structure can be viewed as a $[M(TO_4)\phi_4]$ chalcanthite chain, polymerized by the corner-sharing of polyhedra from the adjacent chains to form the (O–T) ladder. The structure of the mineral banattite, $[Cu^{2+}(SO_4)(H_2O)_3]$, is based on a skewed arrangement of chalcanthite chains where it forms six membered rings as in **II**. The formation of octahedral–tetrahedral (O–T) ladder in the metal sulfate family is noteworthy as there is only one other report of an O–T ladder in the literature,[18] unlike the relative large number of T–T ladders.[19–22] It is possible that higher dimensional structures can be obtained from these ladder structures as in the case of the zinc phosphates.[23]

**Kröhnkite-type chain.** In $[HN(CH_2)_6NH][(VO)_2(OH)_2$-$(SO_4)_2].H_2O$, **III**, there are five-coordinated vanadium sites [V(1) and V(2)] with the square-pyramidal geometry with the
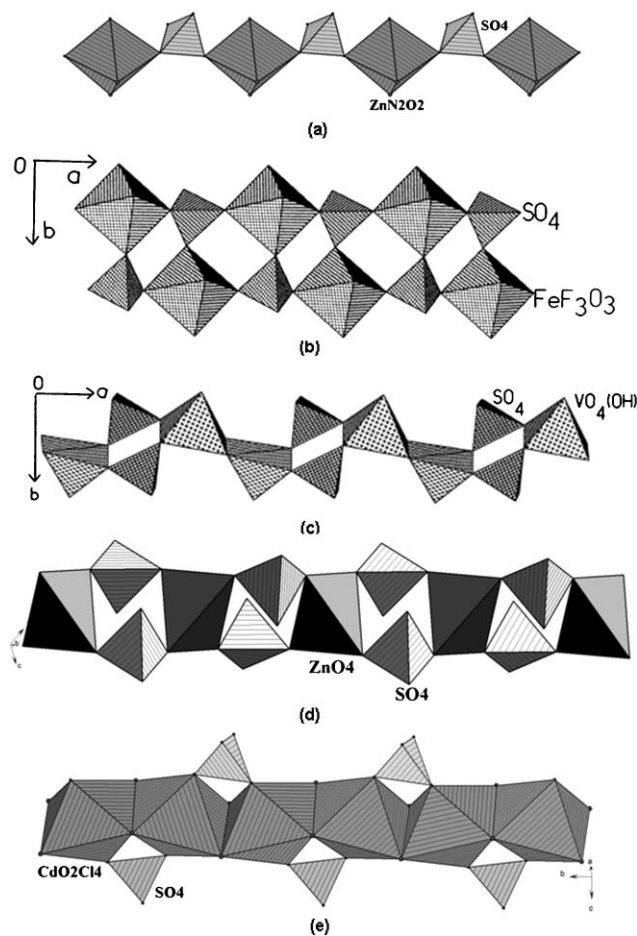


**Fig. 1** (a). Strands of ZnN$_2$O$_4$ octahedra and SO$_4$ tetrahedra forming wire like chains in $[Zn(SO_4)(H_2O)_2(2,2′-bpy)]$, **I**, from ref. 13. (b) Double stranded chains of $[FeF_3(SO_4)]_n^{2n-}$ in **II**, from ref. 17. (c) Kröhnkite-type chain motif of $[(VO)_2(OH)_2(SO_4)_2]_n^{2n-}$ in **III**, from ref. 15. (d) View of the $[Zn(SO_4)_2]_n^{2n-}$ units along the *b*-axis showing the chains of corner sharing '4-ring' built from ZnO$_4$ and SO$_4$ tetrahedra in **IV**, from ref.13. (e) Linerite- type chain of $[CdCl_2(SO_4)]_n^{2n-}$ in **V**, redrawn from ref. 10.

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basal plane defined by the oxygens of adjacent sulfate groups, two hydroxyl donors and a terminal oxide group.[15] Two square-pyramids, $V(1)O_3(OH)_2$ and $V(2)O_3(OH)_2$, share a common edge via two hydroxyl oxygens, with their apices on the opposite sides of the basal plane, to form $V_2O_8$ dimers. These dimers are capped by the sulfate tetrahedra by sharing the corners to form four-membered rings which propagate along the a-axis (Fig. 1c). This structure is related to that of the mineral kröhnkite $Na_2Cu^{II}(SO_4)_2 \cdot 2H_2O$.[16] Kröhnkite-type compounds contain infinite $[M(XO_4)_2(H_2O)_2]$ chains, where M is a divalent (Mn, Fe, Co, Ni, Cu, Zn or Cd) or a trivalent (Al, Fe or In) cation and X is pentavalent (P or As) or hexavalent (S, Se, Cr or Mo). In these chains, the $MO_6$ octahedra are corner-linked to bridging $XO_4$ tetrahedra to give the 1D-chains. The kröhnkite chain topology with tetrahedral atoms has been observed in open-framework metal phosphates[24–26] as well as in some metal sulfates and selenates.[27] The common occurrence of the kröhnkite-type chain is probably because the corner-link between the $MO_6$ and $SO_4$ groups is flexible, involving little steric constraint.

**Chain consisting of four-membered rings.** A typical case is that of $[Zn(SO_4)_2(H_2O)_2]^{2-}$, **IV**, consisting of infinite zinc sulfate chains containing four-membered rings obtained from strictly alternating $ZnO_4$ and $SO_4$ tetrahedral units, which are linked through their corners (Fig. 1d).[13] Two oxygen atoms of a $SO_4$ unit bridge adjacent $ZnO_4$ units while the other two form terminal S=O groups. Tetrahedra-based one-dimensional metal phosphates with a chain topology formed by $MO_4$ (M = Al, Ga and Zn) and $PO_4$ tetrahedra are known.[28–32] Such a corner-shared chain structure has been considered to be a precursor to 3D open-framework metal phosphates.[33,34]

**Linarite-type chain.** Four linear cadmium sulfates of linarite topology have been reported recently.[10,35] In the linarite chain, $[CdX_2SO_4]^{2-}$, **V**, $CdX_4O_2$ (X = Cl, Br) octahedra share edges in a trans-fashion with the sulfate tetrahedra grafted on to the chain as a symmetrical bridge. Two Cd–μ-X– Cd linkages between adjacent Cd atoms lead to infinite linear chains of trans edge-sharing $CdX_4O_2$ octahedra. Two of the sulfate oxygens bond to adjacent cadmium sites of the edge-shared $CdX_4O_2$ in the common symmetrical bridging mode, forming a synthetic analogue of the linarite chain[36] (Fig. 1e). In linarite, $Pb^{2+}[Cu^{2+}(OH)_2(SO_4)]$, octahedra share two trans edges to form a $[M\varphi_4]$ chain. This is decorated by flanking tetrahedra that adopt a staggered arrangement on either side of the chain. The structure of wherryite, $Pb_7^{2+}[Cu^{2+}(OH)(SO_4)(SiO_4)]_2(SO_4)$, is based on linarite chains that are decorated by $(SiO_4)$ tetrahedra. The $[M(TO_4)_2\varphi]$ chains extend along the c-axis and pack along the vertices of a primitive orthogonal plane lattice. The additional $SO_4$ groups that do not link to the $(Cu^{2+}\varphi_6)$ octahedra are linked by [7]- and [8]- coordinated $Pb^{2+}$ cations. Infinite chains of $M(TO_4)\Phi_2$ stoichiometry in the linarite group of minerals are rare and occur in layered metal phosphates[37–39] such as tsumcorite and bermanite.

**Butlerite-type chain.** Open-framework metal sulfates form the $[M(TO_4)\varphi_3]$ chain which is the basic motif of butlerite,[40] wherein tetrahedra alternate along the chain and link to the

trans vertices of the octahedra. The structure of $[H_2N(CH_2)_4NH_2][MF_3SO_4]$ (M = V, Fe), **VI**, consists of $MF_4O_2$ octahedra sharing vertexes with similar neighbors through the fluorine (Fig. 2a).[15] The sulfate tetrahedra are bridged onto the trans vertex of the metal octahedra along the chain. The trans orientation of the bridging F atom creates a zigzag {–F–M–F–M–} backbone to the linear chain of $MF_4O_2$ octahedra. In the sulfate tetrahedra, two oxygens bond to the adjacent M-sites of the vertex-shared $MF_4O_2$ octahedra in a symmetrical bridge, the remaining two forming terminal S=O bonds. The individual chains are held together by hydrogen bond interactions involving diprotonated amine molecules. A similar chain of cis corner-sharing octahedra occurs in fibroferrite, $[Fe^{3+}(OH)(H_2O)_2(SO_4)][H_2O]_3$, giving rise to a helical configuration. In butlerite $[Fe^{3+}(OH)(H_2O)_2(SO_4)]$, parabutlerite, $[Fe^{3+}(OH)(H_2O)(SO_4)]$, and fibroferite, the
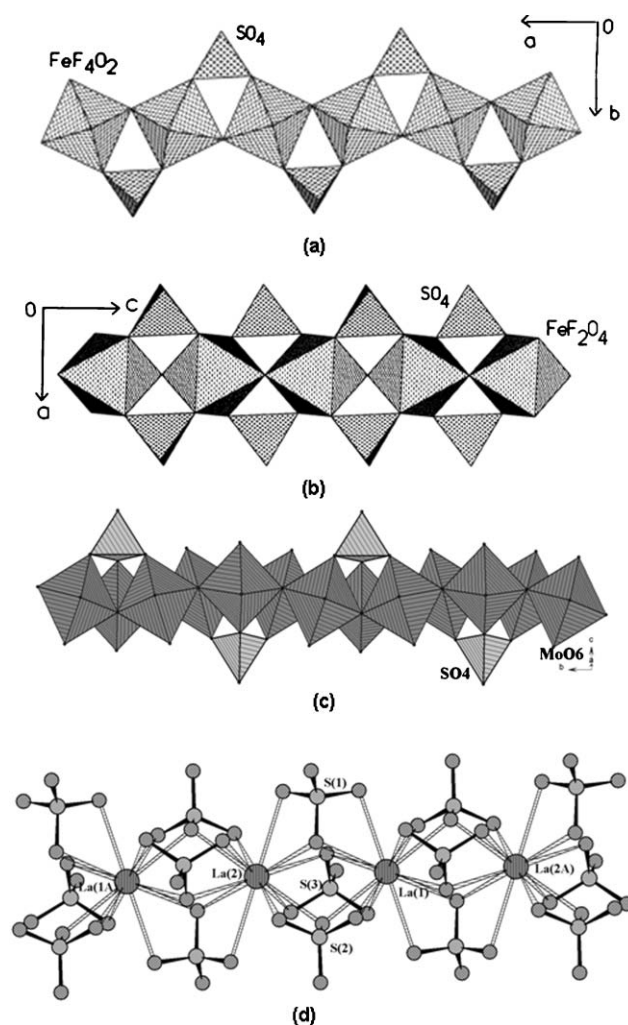


**Fig. 2** (a). Butlerite-type chains with alternating up-down bridging of sulfate tetrahedron in $[MF_3SO_4]^{2-}$, **VI**, from ref. 15. (b) Tancoite-type chains in metal sulfates in **VII**, from ref. 17. (c) α-Molybdena backbone in molybdenum sulfate, $[(MoO_3)_3(SO_4)]_n^{2n-}$, **VIII**, redrawn from ref. 46, copyright (2004) with permission from the American Chemical Society. (d) Infinite chains of $[La(SO_4)_3]_n^{3n-}$ in **IX** running along the a-axis, redrawn from ref. 48, copyright (2003) with permission from Elsevier.

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chains are linked solely by hydrogen bonds as there are no interstitial cations whereas in organically templated compounds the chains are held together by the hydrogen bond assembly of the diprotonated amine molecules located in the inter-chain space to form the 3D assembly. The mineral uklonskovite consists of topologically identical $Mg(SO_4)(OH)(H_2O)_2$ chains, linked by 8-coordinated Na.

**Tancoite-type chain.** The tancoite chain is commonly found in open-framework materials. Tancoite is a phosphate mineral of the formula, $LiNa_2Hal(PO_4)_2(OH)$, possessing a one-dimensional chain structure.[41] The chain has the composition, $[M(TO_4)_2L]_n$ (M and T are cations of different coordination, usually octahedral and tetrahedral; L = anionic ligand, *e.g.* $O^{2-}$, $OH^-$ or $F^-$), and is found in vanadium and iron sulfates.[15,17] In $[FeF(SO_4)_2]^{3-}$, **VII**, the metal octahedra share vertices with similar neighbors to produce a linear zigzag chain, and the sulfate tetrahedra are grafted on to the chain in a symmetrical bridge. The *trans* orientation of the bridging OH/F group creates a {–M–(OH)/F–M–(OH)/F–M–} backbone in the linear chain and allows the sulfate moiety to bridge symmetrically to form a tancoite type topology as shown in Fig. 2b. Such a structure is also found in open-framework metal phosphates[42] as well as in several phosphate, sulfate and silicate minerals.[43] The 1-D tancoite type gallium phosphate chain has been shown to undergo facile transformation to 3-D open-framework structures under hydrothermal conditions.[44,45]

**α-Molybdena sulfate.** A sulfated α-molybdena, $[C_5H_{14}N_2][(MoO_3)_3(SO_4)].H_2O$, **VIII**, containing an organic amine has been reported.[46] It has three distinct $Mo^{6+}$ centers, each of which is coordinated to six oxygens in a distorted octahedral geometry. Three of the oxide ligands in each $MoO_6$ octahedron bridge between adjacent $Mo^{6+}$ centers in a $\mu^3$ fashion, exhibiting a structure analogous to that of α-molybdena (Fig. 2c). This chain topology has also been found in $Rb_2SMo_3O_{13}$.[47]

**Lanthanum and uranium sulfates.** Lanthanum forms a one-dimensional compound of the composition, $[C_4N_3H_{16}][La(SO_4)_3]\cdot H_2O$,[48] **IX**, where the edge linkage of the $LaO_{12}$ polyhedra and the $SO_4$ tetrahedra provides the building unit, the units being connected by the sharing of La atoms to give infinite chains of $[La(SO_4)_3]_n^{3-}$ along the *a*-axis. The $LaO_{12}$ polyhedra share faces *via* three-coordinated oxygens and the $SO_4$ tetrahedra are grafted on to the chains by sharing corners and edges (Fig. 2d). Several uranium sulfates are reported to occur in the presence of structurally related organic templating agents by O'Hare and coworkers.[49–56] One-dimensional chains are found in $[C_5N_2H_{14}][UO_2(H_2O)(SO_4)_2]$,[49] where the uranium ion is seven-coordinated in the pentagonal bipyramidal geometry. The two adjacent $[UO_7]$ pentagonal bipyramids are linked by the corner sharing sulfate tetrahedra. Adjacent $Ur\phi_5$ pentagonal bipyramids have their uranyl ions oriented approximately perpendicular to the chain length. The $Ur\phi_5$ polyhedra share corners with the sulfate tetrahedra in such a manner that each $Ur\phi_5$ pentaganal bipyramid is linked to four sulfate tetrahedra, the fifth equatorial ligand of the $Ur\phi_5$

pentaganal bipyramid being shared with an aqua ligand. This chain topology is analogous to the mineral $Mn[(UO_2)(SO_4)_2(H_2O)].4H_2O$ and $[(UO_2)(H_2PO_4)_2(H_2O)].(H_2O)_2$, and also occurs in arsenate and phosphate minerals such as brondtite, $Ca_2[Mn^{2+}(AsO_4)_2(H_2O)_2$, talmessite, $Ca_2[Mg(AsO_4)_2(H_2O)_2]$ and fairfieldite, $Ca_2[Mn^{2+}(PO_4)_2(H_2O)_2]$.

**Two-dimensional metal sulfates**

Organically templated metal sulfates possessing two-dimensional structures are not that common. One example is that of $[H_3N(CH_2)_2NH_3][Fe_2F_2(SO_4)_2(H_2O)_2]$, **X**, built up from $FeF_2O_4$, $FeF_2O_2(H_2O)_2$ octahedra and sulfate tetrahedra by sharing their vertices.[17] The $FeF_2O_4$ and $FeF_2O_2(H_2O)_2$ octahedra are alternately connected by their *trans*-fluorine vertexes to form an infinite {–F–Fe–F–Fe–} backbone analogous to the mineral butlerite[40] (Fig. 3a). The butlerite-type chains are fused together to form the layer architecture. This layer structure is similar to that of the iron fluorophosphates (ULM-10),[57] which consist of infinite chains of alternating corner-sharing $Fe^{3+}F_2O_4$ and $Fe^{2+}F_2O_2(H_2O)_2$ octahedra decorated by phosphate tetrahedra fused together to form the layered structure. ULM-11 and the mineral curetonite, $Ba_2[(Al, Ti)Al(PO_4)_2(OH, O_2)F]$, possess similar structures, being built up of the laucite motif.[58] Jacobson *et al.*[59] have reported two niobium phosphates and one titanium phosphate with similar structures.

In $[H_2N(CH_2)_4NH_2][Fe_2^{III}Fe_3^{II}F_{12}(SO_4)_2(H_2O)_2]$, **XI**, two iron octahedra are vertex-shared through *trans* –Fe–F–Fe– linkages to form an infinite chain along the *a*-axis.[60] These chains are connected by a trimer of edge-sharing octahedra along the <001> direction to form a layered network in the *ac*-plane. The triangular lattices formed by the trimers while connecting the chains are capped by the sulfate tetrahedra, thereby forming a 10-membered aperture within the layer (Fig. 3b). The layers are stacked one over the other along the *b*-axis in the AAA… fashion and are held together by hydrogen bonding interactions with the diprotonated amine molecules residing in the interlamellar space.

**Transition metal sulfates with the kagome lattice.** The most common iron sulfates with the kagome lattice are the jarosites which show magnetic frustration or low temperature antiferromagnetism.[61] The organically templated iron sulfate $[HN(CH_2)_6NH][Fe^{III}Fe_2^{II}F_6(SO_4)_2][H_3O]$, **XII**, is an unusual example of an iron compound with a perfect kagome structure.[60] The structure consists of anionic layers of vertex-sharing $Fe^{III}F_4O_2$ and $Fe^{II}F_4O_2$ octahedra and $SO_4$ tetrahedra units, which are fused together by $Fe^{III/II}$–F–$Fe^{III/II}$ and $Fe^{III/II}$–O–S moieties. Each $Fe^{III/II}F_4O_2$ unit shares four of its $Fe^{III/II}$–F vertices with similar neighbors with the $Fe^{III/II}$–O bonds roughly aligned in the *ab*-plane. The $Fe^{III/II}$–O bond is canted from the *ab*-plane and this $Fe^{III/II}$–O vertex effectively forces a three-ring trio of apical $Fe^{III/II}$–O bonds closer together to allow them to be capped by the $SO_4$ tetrahedra. The three- and six- rings of octahedra result from the in-plane connectivity and is typical of a kagome lattice with hexagonal tungsten bronze-type sheets (Fig. 3c). Simple calculations have been carried out to understand the properties of this mixed
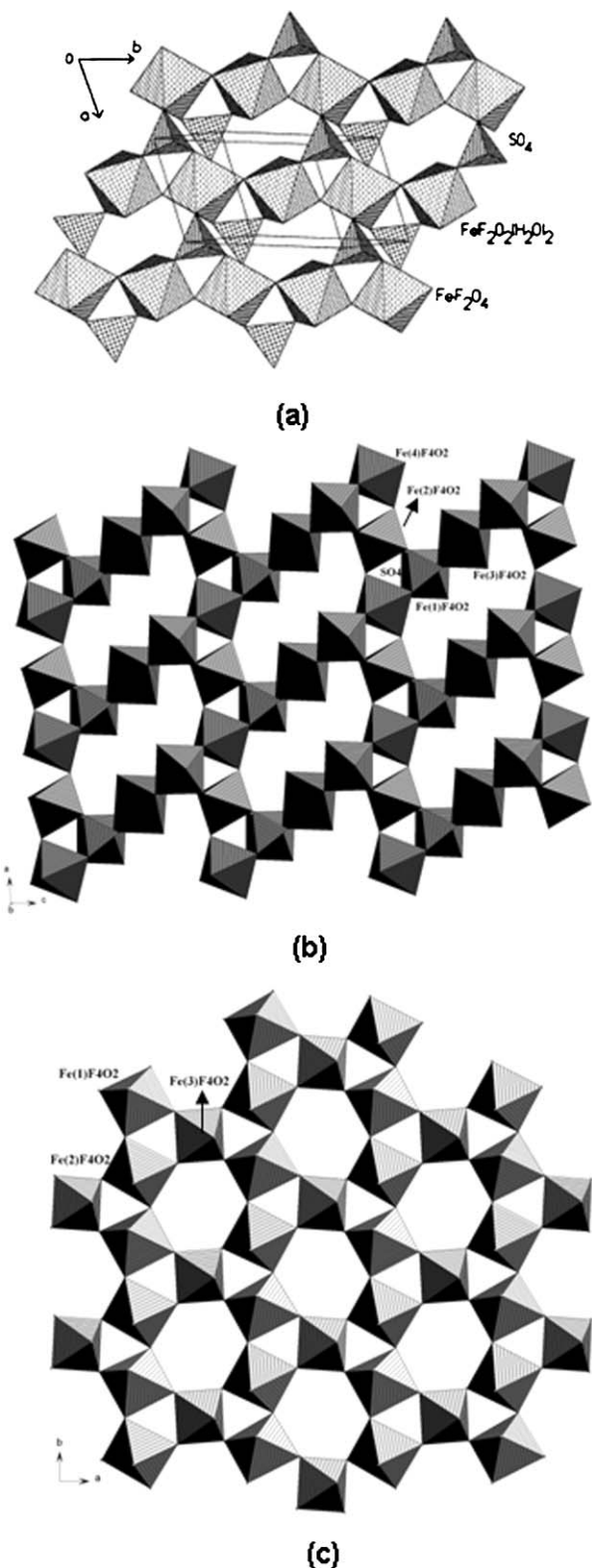
(a)



(b)



(c)

**Fig. 3** (a). Fusion of butlerite-type chains to form the layered structure in $[M_2F_2(SO_4)_2(H_2O)_2]_n^{2n-}$, **X**, (M = Fe, Mn) from ref. 17. (b) Layered in $[Fe_2^{III}Fe_3^{II}F_{12}(SO_4)_2(H_2O)_2]^{4-}$, **XI**, with symmetrical capping of the sulfate tetrahedra in the triangular lattice and the 10-membered aperture within it, redrawn from ref. 60. (c) Polyhedral view of the kagome layer in **XII**, from ref. 60.

valent kagome compound.[62] A layered iron sulfate with the kagome lattice with Fe in the +2 state has been reported.[63] An organically templated iron fluorosulfate $[H_3N(CH_2)_2NH_2-(CH_2)_2NH_2(CH_2)_2NH_3][Fe_3^{II}F_6(SO_4)_2]$ with a slightly distorted kagome lattice arising from the presence of the three edge-sharing $Fe^{II}$ octahedra instead of corner-sharing octahedra in the layered network has also been characterized.[64] Magnetic properties of the Fe(II) and the mixed valent Fe kagome compounds are distinctly different from those of the Fe(III) sulfates possessing the kagome lattice. Unlike the Fe(III) kagome compounds which show magnetic frustration or antiferromagnetism at low temperatures, the Fe(II) compound as well as the mixed-valent Fe compounds with kagome structures show ferromagnetic interactions at low temperatures. Similar features are shown by a Fe(III) compound with a distorted kagome lattice. An amine-templated cobalt(II) sulfate with the kagome lattice, is, however, found to exhibit magnetic properties comparable to those of the Fe(III) compound.[65] It appears that only those kagome compounds containing transition metal ions with integral spins (*e.g.*, Fe(II), V(III)) exhibit ferri/ferromagnetic interactions at low temperatures.

**Nickel sulfate.** The two-dimensional Ni sulfate, $[C_4N_2H_{12}][Ni_3F_2(SO_4)_3(H_2O)_2]$,[66] **XIII**, is built up of $Ni(1)F_2O_4$ and $Ni(2)F_2O_4$ octahedra and $SO_4$ tetrahedra sharing edges as M–μ-F–M bonds and vertices as Ni–O–S bonds. The $Ni(1)F_2O_4$ octahedra occur as dimers by sharing edges with two fluorines to form the $Ni_2F_2O_8$ unit. The $Ni(2)F_2O_4$ octahedra link to the anion at one end of the shared edges to form the trimeric $Ni_3F_3O_{12}$ units. The sulfate tetrahedra cap the trimers in such a way that they share three corners with three octahedra giving rise to the formation of a hexameric unit. These units are connected to one another through corner-sharing Ni–O–S linkages to form sinusoidal chains. The chains are covalently bonded to each other by the $SO_4$ group forming the layer structure with an eight-membered aperture in the *ab*-plane (Fig. 4a). The inorganic layers are stacked along the *c*-axis in the ABAB fashion and the interlayer space is occupied by the diprotonated amine molecules, which ensure the stability of the structure through extensive hydrogen bonding. This structure is obtained with different amines such as piperazine, 1,4-diazobicyclo-[2.2.2]octane (DABCO) and 1,3-diamonoprane (DAP). The structure of **XIII** can be compared to that of the mineral sulfoborite,[67] which is made up of complex sheets of $MgO_6$ and $SO_4$ units. In the mineral amarantite, octahedral tetramers are polymerized to form octahedral chains parallel to [100] and linked by $SO_4$ tetrahedra, with the linkage between the sheets being provided by $[B(OH)_4]$ tetrahedra.

**Cadmium sulfate.** In the two-dimensional cadmium sulfate $[H_3N(CH_2)_3][Cd_2(H_2O)_2(SO_4)_3]$,[35] **XIV**, one cadmium is octahedrally coordinated to six oxygens, of which four are from the corner-sharing sulfate ions and two are from the terminal water molecules. The second cadmium atom is coordinated to six sulfate ions of which four are from the corner-sharing sulfate ions and two are from the edge sharing sulfate ions. The inorganic layer is built up of four-membered rings formed by $CdO_6$ octahedra and two $SO_4$ tetrahedra linked through the
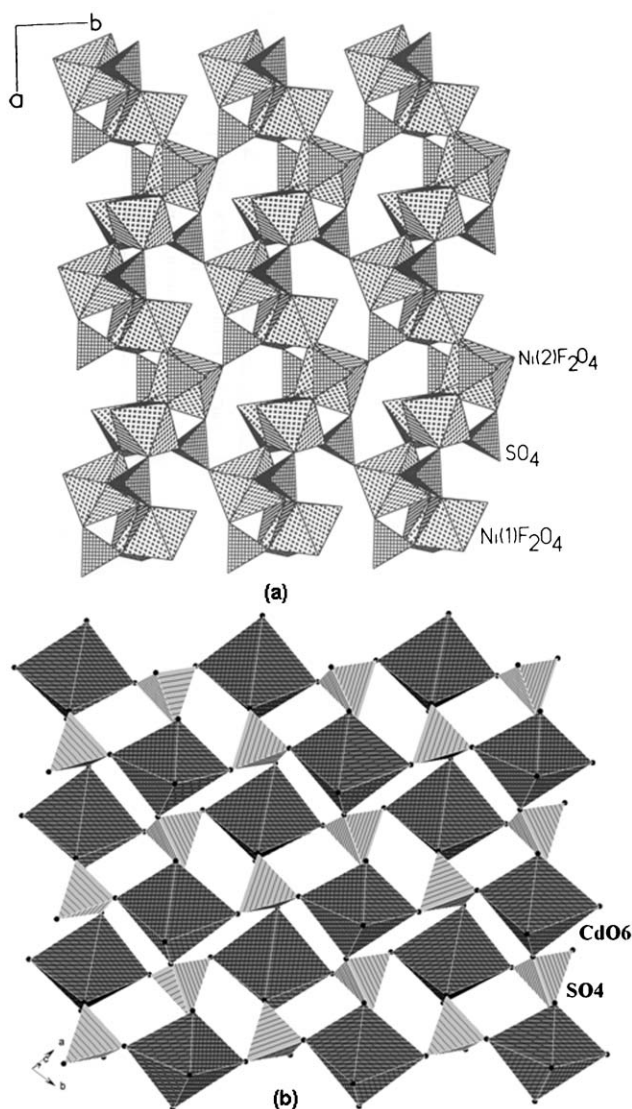
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**Fig. 4** (a). Two-dimensional $[Ni_3F_2(SO_4)_3(H_2O)_2]^{2-}$, **XIII**, formed by the sinusoidal chains which, in turn, consist of hexameric units from ref. 66. (b) (O–T) two-dimensional cadmium sulfate of $[Cd_2(SO_4)_3(H_2O)_2]^{2-}$ in **XIV**, redrawn from ref. 35. Note the fusion of the four-membered ring ladders to form the layered structures.

vertices. The connectivity between the four membered rings leads to the formation of a four-membered ladder with strictly alternating $CdO_6$ octahedra and $SO_4$ tetrahedra. The ladder is then fused in the *ab*-plane to form the two-dimensional framework of the inorganic layer (Fig. 4b). The four-membered rings surround both the cadmium atoms with direct linkage to four $SO_4$ tetrahedra.

**Rare-earth sulfates.** The 2D lanthanum sulfates adopt a corrugated layer structure with 8-membered ring apertures, wherein the lanthanum polyhedra get connected by the sulfate tetrahedra in bidentate or monodentate fashion. The coordination around the metal centre is then completed by either coordinating to water, as observed in $[C_6N_2H_{14}]_2[C_2N_2H_8]$-$[Ln_2(H_2O)_4(SO_4)_4][SO_4]\cdot3H_2O$, **XV**,[68] or by coordinating to other terminal sulfate tetrahedra by sharing edges or

corners.[69,70] The sulfate tetrahedra bonded to the Ln centres in the layers can get further bonded to other Ln atoms forming 4-membered ring ladders grafted onto the layers comprising 8-membered rings, as observed in $[C_2N_2H_{10}][La_2(H_2O)_4$-$(SO_4)_4]\cdot2H_2O$.[71] A layer with an eight-membered aperture formed by the joining of $NdO_9$ polyhedra and $SO_4$ tetrahedra is shown in Fig. 5a. The corrugated layer structure of the amine-templated lanthanum sulfates can be compared to that of β-$(NH_4)La(SO_4)_2$[72] or $(N_2H_5)Nd(H_2O)(SO_4)_2$,[73] except that in the latter hydrazinium groups are connected to the Nd atom. The interlamellar spacing depends on the size and orientation of the guest species, with the distance between the planes increasing with the increase in the size of the guest amine molecules.

The other structures of layered lanthanum sulfates are based on $LnO_3$ layers with (6, 3) nets as in $[C_3N_2H_{12}][La_2(SO_4)_4]$, **XVI**, (Fig. 5b). Here, the La centres are bridged by the sulfate tetrahedra to form 4-membered rings, which then join together by sharing of edges or corners. These chains or ladders of 4-membered rings fuse together through the three-coordinated oxygen atoms of the sulfate groups to form layers having infinite Ln–O–Ln linkages in two dimensions. The network formed by the linking of the Ln centres by the three-coordinated oxygens has the composition $LnO_3$ and can be described as (6, 3) nets with each Ln centre acting as a node.[68] An organically templated layered cerium phosphate sulfate, $[C_2N_2H_{10}][Ce^{III}(PO_4)(HSO_4)(H_2O)]$, has been reported.[74] Lanthanide compounds along with a few open-framework sulfates have been described in a review by Wickleder.[75]

**Uranium sulfates.** In contrast to the 2D-lanthanum sulfates, the uranium sulfates are made up of 4-membered uranium sulfate rings connected by the sulfate tetrahedra, giving rise to layers of different topologies. Depending on the mode of connectivity of the 4-membered rings, the layers comprise entirely of 4-membered rings as in $[C_3N_2H_5][(UO_2)_2(SO_4)_3]$, USO-8,[49] **XVII**, (Fig. 5c), contain 6-membered rings along with 4-membered rings as in $[C_3N_2H_{12}][(UO_2)_2(H_2O)(SO_4)_3]$, USO-2,[56] or 12-membered rings along with 4-membered rings as in $[C_6N_2H_{14}][UO_2(H_2O)(SO_4)_2]$, USO-5.[55] The inorganic layers in USO-2 and USO-5 contain bound water molecules which form additional hydrogen bonds. Two new layered actinide sulfates prepared recently by the amine-sulfate route, have structures similar to those of the lanthanum sulfates, wherein the uranium centres are bridged by the sulfate tetrahedra by the sharing of edges or corners to form layers with 8-membered ring apertures.[76] By employing hydrofluoric acid in the hydrothermal synthesis, six-layered uranium sulfates have been prepared.[51] The fluoride ligands join adjacent uranium centers through U–F–U linkages either by sharing an edge to form the dimer as in USFO-3 or corners to form a chain, which is then linked by the $SO_4$ tetrahedra to form layers as in USFO-5.

**Thorium sulfate.** In $[HN(CH_2)_6NH_2]_2[Th_2(SO_4)_6(H_2O)_2]\cdot$ $2H_2O$, **XVIII**,[13] two crystallographically distinct metal–oxygen polyhedra are capped by four sulfate ions in $Q_2$ connectivity to form the $Th_2S_4$ unit. The $Th(2)O_9$ polyhedra share edges with the $S(2)O_4$ tetrahedra to form a sinusoidal chain along the
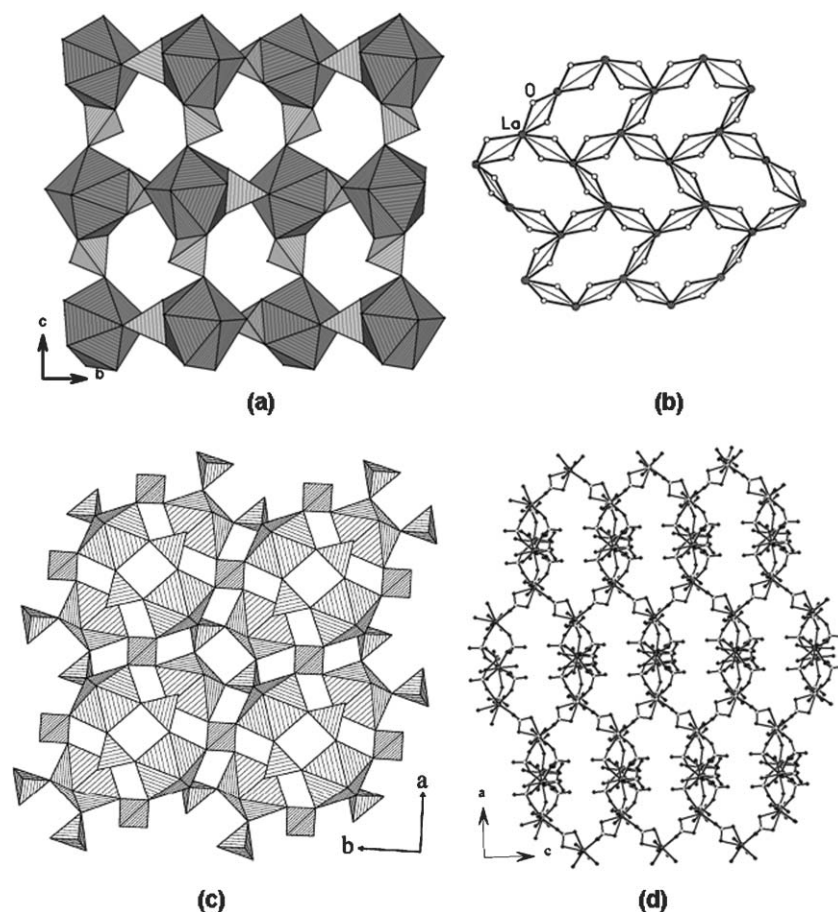
**Fig. 5** (a). Polyhedral view of the inorganic layer in $[Ln_2(SO_4)_4(H_2O)_4]^{4-}$ **XV** (Ln = La, Pr or Nd), formed by joining the $NdO_9$ polyhedra and $SO_4$ tetrahedra, redrawn from ref. 68. (b) The infinite two-dimensional La–O–La linkages in $[La_2(SO_4)_4]^{2-}$ in **XVI**, from ref. 68. (c) Two-dimensional uranium sulfate in $[UO_2(SO_4)_3]^{2-}$, **XVII**, formed by $[UO_7]$ and $[SO_4]$ units from ref. 49, copyright (2003) from the Royal Society of Chemistry. (d) Two-dimensional sheet of $[HN(CH_2)_6NH]_2[Th_2(SO_4)_6(H_2O)_2].2H_2O$, **XVIII** consist of cages along the *ac*-plane from ref. 13.

*c*-axis. Two such adjacent chains arranged in the ABAB… fashion connect the $Th(1)_2S_4$ unit at both their crests and troughs to form cages. The cages are extended in the *ac*-plane to generate a two-dimensional sheet as shown in Fig. 5d. The cages are occupied by amine and water molecules which form extensive hydrogen bonds with the framework oxygens.

**Three-dimensional metal sulfates**

**Nickel sulfate.** The prominent feature of the three-dimensional nickel sulfate, $[C_4N_2H_{12}][Ni_2F_4(SO_4) H_2O]$,[66] **XIX**, is a dimer of edge-sharing octahedra. The Ni(1) and Ni(2) octahedral units share edges through fluorine (Ni(1)–F(1), F(2) and Ni(2)–F(3), F(4) ) to form the dimer units $Ni_2(1)F_6O_2(H_2O)_2$ and $Ni_2(2)F_6O_4$. The dimers are linked by sharing octahedral edges to form two distinct infinite sinusoidal chains along the [001] direction. These chains are alternately stacked one over the other along the [100] direction and are interlinked by sharing corners with the tetrahedral corners of the $SO_4$ groups to form a layer with an 11-membered aperture in the [101] plane. **XIX** seems to be the first example of an 11-membered aperture in open-framework compounds. In the layer, each sulfate shares three corners with three octahedra of the adjacent chains. It is connected to the

Ni(1) octahedral chain by sharing one oxygen atom, whereas it shares two oxygen atoms with two neighboring octahedra of the Ni(2) chain. The layers are cross-linked by $SO_4$ tetrahedra along the *b*-axis through corner-sharing S–O–Ni linkages to form the three-dimensional structure. The cross inking of the layers gives rise to an elliptical channel along the *c*-axis as shown in Fig. 6a. The channels are filled by the amine molecules, which interact with the framework oxygen and fluorine atoms through F–H⋯O and C–H⋯O hydrogen bonds. This structure is somewhat related to the mineral phosphopherite,[77] which contains layers of sinusoidal chains made up of edge-shared octahedral trimers cross-linked by tetrahedral $PO_4$ units.

**Zinc sulfate.** $[(CN_3H_6)_2][Zn(SO_4)_2]$,[78] **XX**, is built up of alternating $ZnO_4$ and $SO_4$ tetrahedra, sharing vertices. The polyhedral connectivity of the $ZnO_4$ and $SO_4$ results in an infinite three-dimensional network. This gives a 12-ring system, built up of six $ZnO_4$ and six $SO_4$ units. The network possesses two-dimensional intersecting channels propagating along the <100> and <010> directions, with no channels apparent in the <001> direction. Well-ordered guanidinium cations occupy all the 12-ring windows (Fig. 6b) and interact with the zinc sulfate framework through N–H⋯O hydrogen
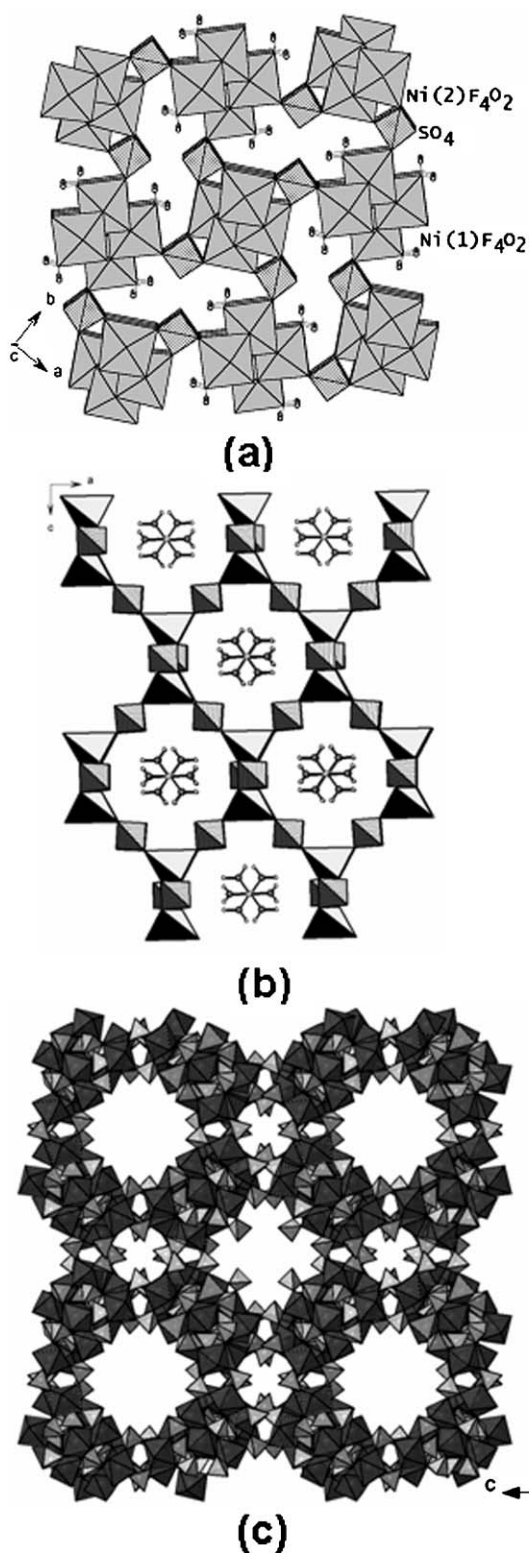
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**Fig. 6** (a). Three-dimensional Ni(II) sulfate in [C4N2H12][Ni2F4(SO4)H2O], **XIX**, showing 10-membered elliptical channels from ref. 66. (b) Polyhedral view of three-dimensional zinc sulfate comprising ZnO4 and SO4 tetrahedra in [(CN3H6)2][Zn(SO4)2], **XX**, redrawn from ref. 78. Note the presence of 12-membered channels. (c) Three-dimensional structure of scandium with mixed sulfate and phosphate tetrahedra in **XXI**, redrawn from ref. 81, copyright (2002) from the Royal Society of Chemistry.

bonds. The structure of **XX** resembles that of diamond and is akin to that of a three-dimensional zinc phosphite[79] and of a guanidinium-templated zinc phosphate.[80]

**Scandium sulfate.** A three-dimensional scandium sulfate in which secondary building units of the formula $Sc_7(S,P)_{12}O_{48}$, **XXI**, templated with azamacrocycles has been synthesized hydrothermally.[81] The structure is made up of $ScO_6$ octahedra that share corners with the sulfate tetrahedra. The main feature of the framework is that supercages are formed at the corners and at the centre of the cubic unit cell. Each supercage is connected to six other supercages *via* smaller cages, in which protonated cyclen molecules are present. Each small cage links two supercages in such a way that in a unit cell there are two supercages and six smaller cages (Fig. 6c).

**Rare-earth sulfates.** Compared to the number of 2D rare-earth sulfates, very few 3D rare-earth sulfates are known. The three-dimensional lanthanum sulfates reported hitherto contain 8-membered ring units, which are connected by the sulfate tetrahedra or by the three-coordinating oxygens of the $SO_4$ unit to form the 3D framework. In $[C_4N_2H_{12}]_2[La_2(H_2O)_2(SO_4)_4]$, the 8-membered rings join together by sharing edges to form the 3D framework, giving rise to 8-ring apertures down the *b*-axis.[70] $[C_2N_2H_{10}]_2[Ln_2(H_2O)_2(SO_4)_5]$ possesses a α-Po structure wherein the 8-membered rings are bridged by the sulfate tetrahedra along the three directions, resulting in the formation of a network of interconnected 8-membered ring channels. Such a connectivity also results in the formation of 16-membered ring channels down the *a*-axis of the unit cell.[68] In $[C_4N_2H_{12}][Nd_2(H_2O)_2(SO_4)_4]$, (**XXII**), the 8-membered rings get connected by the sulfate tetrahedra in one direction and three-coordinated oxygen atoms in another direction, thereby resulting in the formation of channels with 12-ring apertures around the 8-ring channels[68] (Fig. 7a). In all the three 3D lanthanum sulfates, the protonated amine molecules reside in the channels and form hydrogen bonds with the framework oxygens.

Organically templated 3d–4f mixed metal sulfates of the formula $[C_2N_2H_{10}][La_2M(H_2O)_2(SO_4)_6]$ (M = Co, Ni), have been recently synthesized by Clearfield *et al.*[82] The three-dimensional anionic framework is formed by the bridging of La(III) and divalent transition metal ions by the sulfate anions. 8-Membered ring tunnels run along the *c*-axis, which are occupied by the protonated organic cations.

There is one report of a three-dimensional actinide sulfate, $[C_4NH_{12}]_2[(UO_2)_6(H_2O)_2(SO_4)_7]$, MUS-1 **XXIII**,[83] formed by the bridging of the uranium centres by the sulfate tetrahedra. Each sulfate tetrahedron binds to four different uranium atoms to form the three-dimensional network (Fig. 7b). MUS-1 is structurally similar to $Mg(UO_2)_6(MoO_4)_7(H_2O)_{15}$ and $Sr-(UO_2)_6(MoO_4)_7(H_2O)_{19}$.[84] Channels run along the *c*-axis of the unit cell and are occupied by the tetramethylammonium cations.

### Open-framework metal selenites

Selenite-based frameworks are of interest due to the possible role of the lone pair of electrons as an invisible
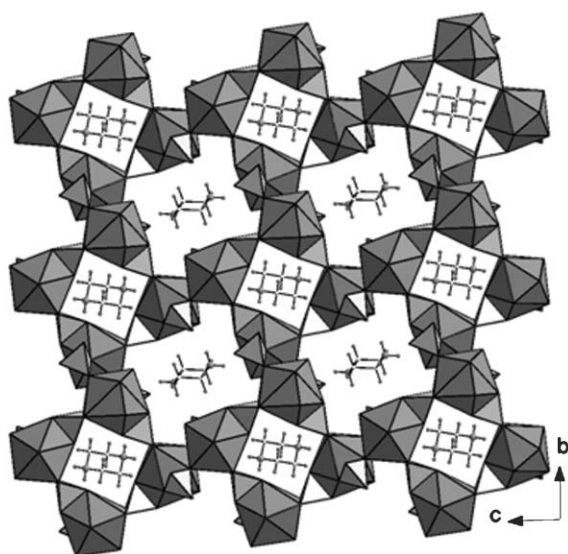
**(a)**
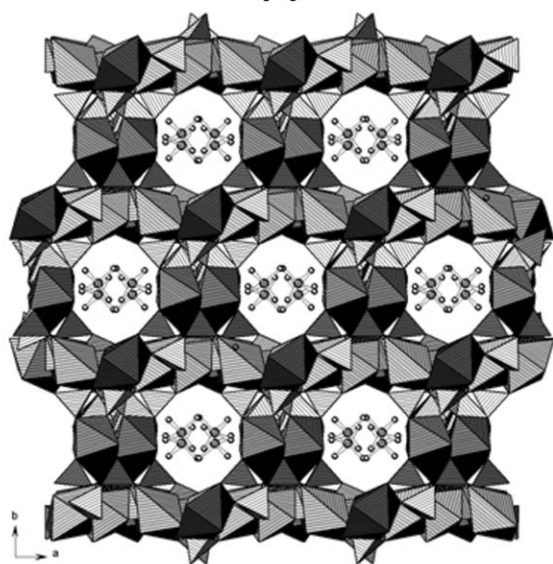


**(b)**

**Fig. 7** (a). The three-dimensional framework of neodymium sulfate with eight and 12-membered channels in $[C_4N_2H_{12}][Nd_2(H_2O)_2(SO_4)_4]$, **XXII**, redrawn from ref. 68. (b) Three-dimensional structure of MUS-1 in $[C_4NH_{12}]_2[(UO_2)_6(H_2O)_2(SO_4)_7]$, **XXIII**, as viewed along the [001] direction, redrawn from ref. 83, copyright (2002) from the Royal Society of Chemistry.

structure-directing agent. The stereochemically active lone pair of electrons in Se(IV) leads to a pyramidal coordination for the selenite species. Due to the presence of lone pair, metal selenites tend to crystallize in non-centrosymmetric structures giving rise to interesting physical properties, such as non-linear optical second harmonic generation (SHG).[85,86] The low reduction potential of the $Se^{IV}/Se^0$ couple, which under hydrothermal conditions may cause reduction to metallic Se, renders the synthesis of amine-templated open-framework metal selenites rather difficult. The first organically templated metal selenite with a layered structure was reported by Harrison *et al.*[87] Rao *et al.*[88,89] reported the first

three-dimensional organically templated iron(III) and zinc selenites. Since then, there have been a few other reports of 2D and 3D metal selenites

**One-dimensional zinc selenite.** $[C_3N_2H_{12}]_4[Zn_4(SeO_3)_8]$ is formed by the connectivity of the strictly alternating $ZnO_4$ and $SeO_3$ units which results in the formation of corner sharing 4-membered ring chains, similar to that observed in metal phosphates and sulfates.[90]

**Two-dimensional selenites.** Depending on the mode of connectivity between the selenite units and the different metal atoms, the two-dimensional metal selenites show a rich variety of architectures. The connectivity of the metal centres by the selenite units wherein the selenite oxygens occupy the equatorial positions around the metal atom results in the formation of layers with 8-membered ring apertures (Fig. 8a). The coordination around the metal atom is completed by bonding to halo or oxo groups, as in $[C_2N_2H_{10}]$-$[CdCl_2(HSeO_3)_2]$ and $[C_2N_2H_{10}][(VO)(SeO_3)_2]$, **XXIV**.[91,92] Such a layered topology is found in a copper hydrogen selenite,[93] which is not an open-framework and in a few open-framework layered phosphates such as the layered tin(II) phosphate and phosphatoantimonate.[94,95] The metal centres can also be connected by the selenite groups to form
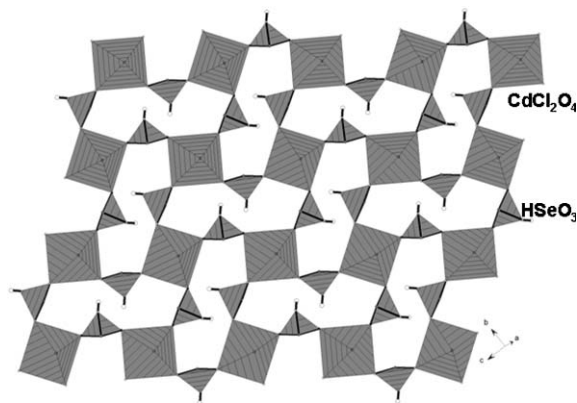


**(a)**
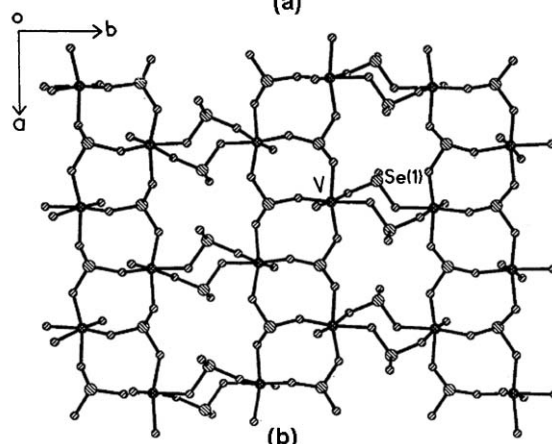


**(b)**

**Fig. 8** (a) The layer structure of $[C_2N_2H_{10}][CdCl_2(HSeO_3)_2]$, **XXIV**, with 8-membered ring aperture, redrawn from ref. 91. (b) Layer formed in $[C_6N_2H_{14}][(VO)_2(HSeO_3)_2(SeO_3)_2].2H_2O$, **XXV**, by the joining of the 4-membered ring ladders by $HSeO_3$ units from ref. 96.

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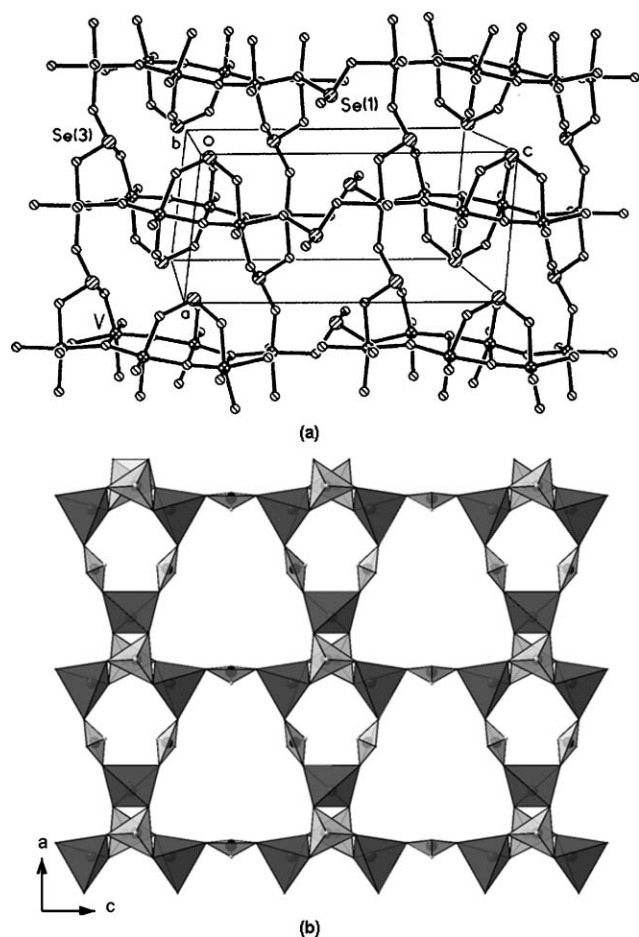
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**Fig. 9** (a) Layer structure formed by the joining of vanadium–oxygen metal clusters, which act as the secondary building units in $[C_2N_2H_{10}][(V^{iv}O)_2(V^vO)O_2(SeO_3)_3]\cdot1.25H_2O$, **XXVI**, from ref. 96. (b) Polyhedral view of the sheet topology of $[CN_3H_6]_4[Zn_3(SeO_3)_5]$ in **XXVII**, redrawn from ref. 87, copyright (2000) with permission from Wiley-VCH.





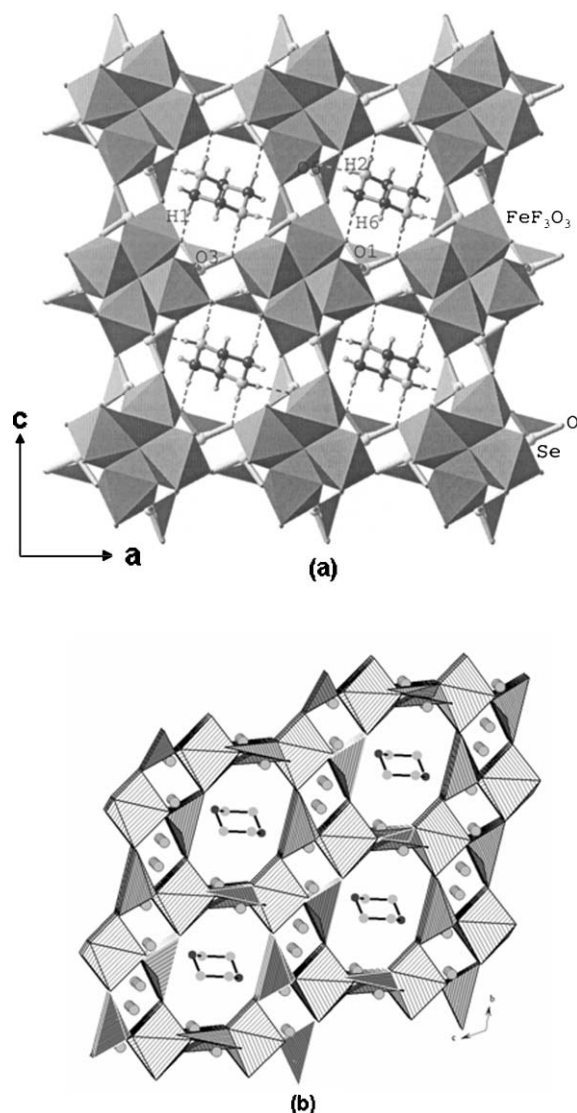**Fig. 10** (a) Polyhedral view of the inorganic framework of $[A][Fe_4F_6(SeO_3)_4]$, **XXVIII**, showing one-dimensional 8-ring channels from ref. 88. (b) Three-dimensional framework structure of $[C_4N_2H_{12}][M_2(HSeO_3)_2(Se_2O_5)_2]$, **XXIX**, showing 10-membered channels, redrawn from ref. 89.

4-membered ring units which get joined to form layers with 4- and 8-membered ring apertures (Fig. 8b) as in $[C_6N_2H_{14}][(VO)_2(HSeO_3)_2(SeO_3)_2]\cdot2H_2O$, **(XXV)**,[96] Thus, the structure can be described as being formed by the joining of the four-membered ring ladders by the $HSeO_3$ groups. The importance of the ladder structure as a possible precursor of the 3D metal phosphates has been pointed out.[19] The layer structure in the metal selenite is comparable to that of the indium phosphate, $[C_5NH_6][In(HPO_4)_2]$.[97] The metal atoms and the selenite groups can join together to form clusters, which then get connected to form layers, as in the vanadium selenite, $[C_2N_2H_{10}][(V^{iv}O)_2(V^vO)O_2(SeO_3)_3]\cdot1.25H_2O$, **XXVI**. In this compound, the clusters are joined by the selenite groups to form layers with 8-membered apertures[96] (Fig. 9a). Similarly, in $[CN_3H_6]_4[Zn_3(SeO_3)_5]$, **XXVII**, the layer is formed by the linking of $Zn_3Se_2O_{12}$ clusters by the selenite groups (Fig. 9b).[87]

**Three-dimensional selenites.** In the 3D selenites of the formula, $[A][Fe_4F_6(SeO_3)_4]$, **XXVIII**, obtained with different amines,[88] the Fe centres join together through bridging

fluorine atoms to form tetrameric $Fe_4F_6O_{12}$ clusters, which then get connected by the selenite groups to form the three-dimensional architecture. Such a connectivity results in the formation of 3-, 4-, 5- and 6-membered rings in the structure. There is also a 8-ring 1D channel along the *b*-axis of the unit cell (Fig. 10a). The presence of the near-tetrahedral $Fe_4F_6O_{12}$ cluster makes it an interesting geometrically frustrated magnetic material.

A three-dimensional open-framework metal selenite of the formula $[C_4N_2H_{12}][M_2(HSeO_3)_2(Se_2O_5)_2]$, **XXIX**, (M = Zn, Co or Ni), containing both the selenite and the diselenite units has been reported.[89] The structure possesses a diamondoid network and has intersecting two-dimensional 10-membered channels. The three-dimensional framework is formed by the connectivity of the zinc-diselenite layers by the selenite groups acting as pillars. This connectivity results in the formation of

4- and 6-membered rings in the structure. In both the three-dimensional metal selenite frameworks, protonated amine molecules reside in the channels and forming extensive hydrogen bonds with the framework atoms (Fig. 10b).

Three-dimensional inorganic–organic hybrid metal selenites, wherein the metal selenite layers get crosslinked by the organic moiety to form the 3D architecture have been reported. In $[C_2N_2H_8][Zn_2(SeO_3)_2]$, the zinc selenite layers get connected by the pillaring ethylene diamine molecules in an end-to-end fashion resulting in the formation of channels along the $a$- and $c$-axes.[88] An allotropic form of $[C_2N_2H_8][Zn_2(SeO_3)_2]$, reported by Ferey et al.,[90] differs only in the topology of the zinc selenite layers. In $[M(C_{10}N_2H_{10})(H_2O)V_2Se_2O_{10}]$, M = Co, Ni, the Co/Ni–V–SeO$_3$ layers get crosslinked by the 4,4′-bipyridyl units to form the three-dimensional architecture.[98]

### Open-framework metal selenates

It is only recently that it has been possible to prepare open-framework metal selenates. The difficulty in the synthesis of these compounds lies in the instability of Se(VI) in the basic medium. It, therefore, becomes necessary to prepare them in an acidic medium.

**One-dimensional selenates.** The framework structures in $[Cd(H_2O)_2(SeO_4)_2]^{2-}$ [99] and $[Zn(H_2O)_2(SeO_4)_2]^{2-}$, **XXX**,[100] has the kröhnkite-type topology. In this structure, a pair of selenate tetrahedra shares corners to form the one-dimensional chain structure bridging the neighboring metal octahedra as shown in Fig. 11a. Fleck et al.[101] have reviewed compounds with the kröhnkite-type topology. The structure of the kröhnkite-type infinite chain is composed of a distorted MO$_6$ octahedron corner-linked with the XO$_4$ tetrahedron, the remaining two opposite corners in the *trans* position being occupied by water molecules. Each tetrahedron connects the neighboring octahedra, forming infinite $[M(XO_4)_2(H_2O)_2]$ chains. The simplest chain of the formula $[Zn(SeO_4)(phen)(H_2O)]$, consisting of strictly alternating zinc octahedra and selenate tetrahedra similar to that of zinc sulfate $[Zn(SO_4)(H_2O)_2(2,2-bpy)]$, **I**, has been reported.[100]

**Two-dimensional selenates.** The structure of $[C_4N_2H_{14}]$ $[La_2(SeO_4)_4].H_2O$, **XXXI**,[102] involves LaO sheets formed by La–μ-O–La linkages forming chains running parallel to the $b$-axis with the alternate La atoms of the chains being bridged by La–μ-O–La linkages along the perpendicular direction which forms a hexanuclear lanthanide ring. The hexanuclear lanthanide rings are surrounded by six similar rings resulting in the formation of a (6,3) net. Along the chain, two LaO$_9$ polyhedra are capped on either side by the Se(2)O$_4$ units which are connected to two La atoms in the neighboring chains through a three-coordinate oxygen (O8). In the perpendicular direction, the bridging La-atoms are capped by two Se(1)O$_4$ units which share an edge with a LaO$_9$ polyhedron of the neighboring chain. Accordingly, the SeO$_4$ units are involved in both capping and bridging the La atoms in the LaO sheets. Such a dual connectivity of the SeO$_4$ units produces corner-shared four-membered rings propagating along the $a$-direction
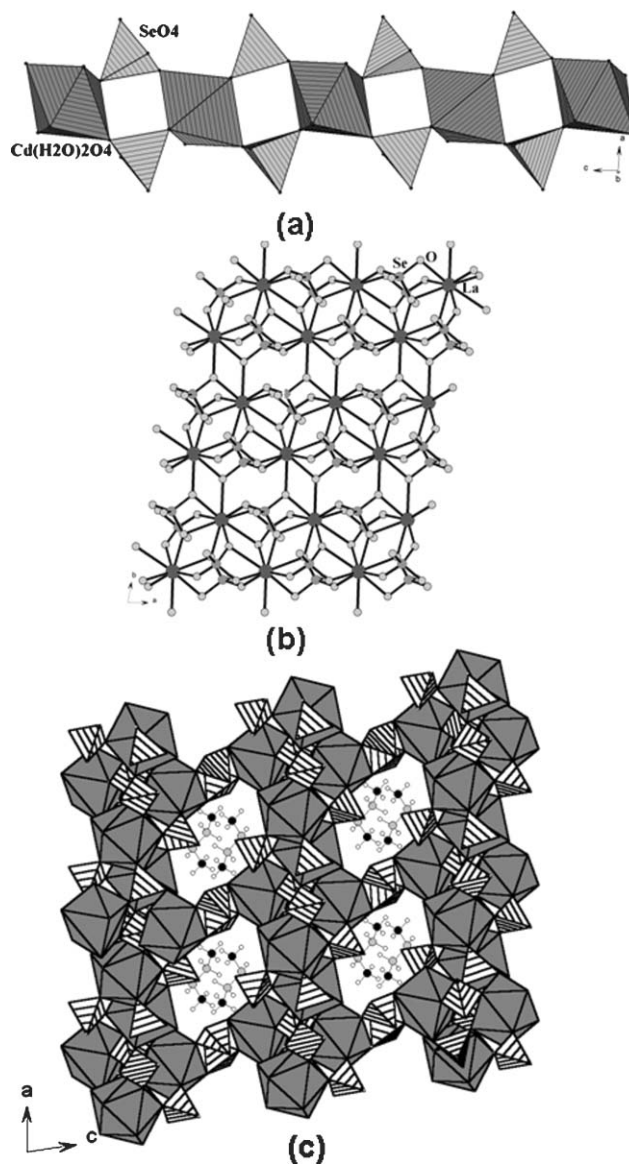


**Fig. 11** (a) Polyhedral structure of the $[Cd(SeO_4)_2(H_2O)_2]^{2-}$ chain in **XXX** along the $c$-axis from ref. 99. (b) The inorganic layer of $[La_2(SeO_4)_4]^{2-}$, in **XXXI** with the capping and bridging of the LaO$_9$ dimers by two selenate units, resulting in corner-shares four-membered rings along the $a$-axis from ref. 102. (c) Polyhedral view of three-dimensional lanthanum selenate comprising of La$_2$Se$_4$ building units in $[C_2N_2H_{10}][La_2(SeO_4)_4(H_2O)_3].H_2O$, **XXXII**, from ref. 103. Note the presence of 12-membered channels.

as shown in Fig. 11b. $[C_2N_2H_{10}][Ln_2(SeO_4)_4(H_2O)_4]$, constructed by capping two edge-shared LaO$_9$ polyhedra by SeO$_4$ groups has also been described.[102]

**Three-dimensional selenate.** A three-dimensional selenate of the formula, $[C_2N_2H_{10}][La_2(SeO_4)_4(H_2O)_3]\cdot H_2O$, **XXXII**, comprising La$_2$Se$_4$ building units and possessing 12-membered channels, has been prepared in an acidic medium under hydrothermal conditions.[103] The complex network of LaO$_8$, LaO$_9$ and SeO$_4$ moieties gives rise to a three-dimensional structure possessing channels along all the three axes. Connectivity between two building units with the La$_2$Se$_4$

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stoichiometry through La–O–Se–O–La linkages gives rise to infinite chains along the <100> direction, which are connected through a bridging Se(2)O$_4$ to form a two-dimensional layer in the *ab*-plane, with 4- and 8-membered apertures. The layers are stacked one over the other along the *c*-axis and connected by the Se(4)O$_4$ tetrahedra which share corners with the La(1)–O polyhedra from the adjacent layers forming the 3-dimensional network. The 3D structure has 12-membered channels along the *a*-and *b*-axes, and 8-membered channels along the *c*-axis. Amine molecules reside in the 12-membered channels forming hydrogen bonds with the framework oxygens (Fig. 11c).

## Conclusions

The discussion in the earlier sections should suffice to demonstrate how oxyanions such as, sulfate, selenite and selenate could be used to design novel inorganic open-framework materials. The structures of many of the sulfates and selenates are close to those of the phosphates. Although several open-framework metal sulfates have been synthesized and characterized, there is need for further work to investigate the effects of various reaction parameters and solvents on the formation of these materials. Great effort is necessary to synthesize 3D metal selenates since we have one organically templated metal selenate to-date. To our knowledge, no organically-templated metal sulfite has been reported hitherto. It would be worth exploring reactions of organic amine sulfites with metal ions. It should be possible to make use combinations of these oxyanions with other anions such as the phosphate and the silicate to produce novel architectures. There is also need for efforts to obtain open-framework metal sulfates, selenites and selenates with empty channels, in order to study sorption and other properties. An important aspect that is worthy of study relates to the possible transformation of chain sulfates to 2D and 3D structures. It would be of interest to know if there is a secondary building unit for the sulfates similar to the 4-membered ring structures in the case of open-framework phosphates. The synthesis and transformation of such a 4-membered ring sulfate should be examined.

## Acknowledgements

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