

An approach to the synthesis of organically templated open-framework metal sulfates by the amine–sulfate route

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The first organically templated cadmium sulfates, $[\text{C}_4\text{N}_2\text{H}_{12}][\text{CdCl}_2\text{SO}_4]\cdot\text{H}_2\text{O}$ and $[\text{C}_4\text{N}_2\text{H}_{12}]_4[\text{Cd}_3\text{Cl}_{10}(\text{SO}_4)_2(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$, consisting of infinite linear chains and a quasi-2D layer formed by strip-like units respectively, have been synthesized and characterized.

Amongst the variety of open-framework inorganic materials, the metal phosphates constitute one of the largest families.¹ In these materials, the phosphate tetrahedra share corners with the metal–oxygen polyhedra to build networks. Besides the phosphates, open framework 3D metal arsenates,² phosphites³ and germanates⁴ have been reported in the literature. Recently, an organically templated zinc selenite with a layered structure has also been reported.⁵ One would expect the sulfate tetrahedra to be able to play a role similar to the phosphate tetrahedra, but no open-framework sulfates are known hitherto. We were, therefore, interested in exploring whether open-framework metal sulfates can be synthesized by employing an appropriate strategy. Since the reactions carried out under standard hydrothermal conditions in the presence of amines were not effective, we attempted to synthesize sulfate-based networks by reacting organoammonium sulfates with metal ions. In adopting this approach, we were guided by the significant success achieved in the synthesis of open-framework metal phosphates^{6,7} and oxalates⁸ by the reaction of metal ions with organoammonium phosphates and oxalates, respectively. In this communication, we report the first success we have had in synthesizing two cadmium sulfates, with chain and layer structures, by the reaction of piperazinium sulfate with cadmium chloride. The results suggest that it may indeed be possible to obtain sulfate-based open-framework structures by this route.

Piperazine sulfate, $[\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2]\text{SO}_4\cdot\text{H}_2\text{O}$ (PIPS), prepared by the reaction of the amine with H_2SO_4 ,[†] was characterized by IR spectroscopy and single crystal X-ray diffraction. The structure of PIPS can be described as a 3-D supramolecular network formed by strong N–H \cdots O, O–H \cdots O and C–H \cdots O hydrogen bonds between the diprotonated piperazine, SO_4^{2-} anion and water molecules. Compounds $[\text{C}_4\text{N}_2\text{H}_{12}][\text{CdCl}_2\text{SO}_4]\cdot\text{H}_2\text{O}$ **I** and $[\text{C}_4\text{N}_2\text{H}_{12}]_4[\text{Cd}_3\text{Cl}_{10}(\text{SO}_4)_2(\text{H}_2\text{O})]\cdot 3\text{H}_2\text{O}$ **II**, synthesized by the reaction of PIPS with Cd^{2+} ions in butan-2-ol–water under hydrothermal conditions,[‡] were characterized by single-crystal X-ray diffraction,[‡] powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), IR spectroscopy and CHN analysis.

The asymmetric unit of **I** contains 15 non-hydrogen atoms with one crystallographically distinct Cd and S atom each in the asymmetric unit. The Cd atom is six-coordinated by four Cl and two O neighbors, the structure being built up of isolated infinite chains of $[\text{CdCl}_2\text{SO}_4]^{2-n}$ running along the *b*-axis. In the $[\text{CdCl}_2\text{SO}_4]^{2-n}$ -chain, CdCl_4O_2 octahedra share edges in *trans*-fashion via their Cl atoms, and the SO_4 tetrahedra are grafted on to the chain in a symmetrical bridge. The two Cd– μ -Cl–Cd linkages between the adjacent Cd atoms lead to infinite linear chains of *trans*-edge-sharing CdCl_4O_2 octahedra. The *trans* orientation of the bridging Cl atom creates a zigzag $\{-\text{Cd}-\mu\text{-Cl}-$

$\text{Cd}-\mu\text{-Cl}-\text{Cd}-\}$ backbone to the linear chain of CdCl_2O_4 octahedra. The pairwise canting of the Cd–O bonds gives rise to a helical arrangement responsible for the chirality of the structure. Two of the sulfate oxygens bond to two adjacent Cd sites of the edge-shared CdCl_4O_2 in the common symmetrical bridging mode as shown in Fig. 1(a), thus forming a synthetic analogue of the linarite chain.¹¹ The 1-D chains along the *b*-axis are arranged parallel to one another in the *bc*-plane to form a layer-like arrangement. Such layers are stacked one over the other along the *a*-axis, with the diprotonated amine molecules and the water molecules located in the inter-layer space. The amine and water molecules interact strongly with the inorganic framework through N–H \cdots O and O–H \cdots O hydrogen bonding to stabilize the 3-D structure shown in Fig. 1(b).

The asymmetric unit of **II** contains 33 non-hydrogen atoms with four amine fragments, each corresponding to half-units of piperazine and three water molecules as extra-framework moieties. Two of the four amine fragments and one water molecule are disordered. The structure can be visualized as two parallel chains made up of CdCl_3O_3 , CdCl_3O_2 and SO_4 units, running along the [010] direction. These chains are connected by CdCl_6 octahedra, giving rise to an anionic quasi 2-D layer. The structure contains three crystallographically distinct cadmium atoms and one sulfur atom. Cd(1) exists as CdCl_3O_3 , Cd(2) is penta-coordinated as CdCl_3O_2 and Cd(3) is hexa-coordinated as CdCl_6 . Cd(1) forms two Cd–O–S, and two Cd–Cl bonds besides one Cd–Cl–Cd bond with the neighboring S(1) and Cd(3) atoms. Hexa-coordination is satisfied by bonding to a H_2O molecule. Cd(2) forms a similar connectivity with the

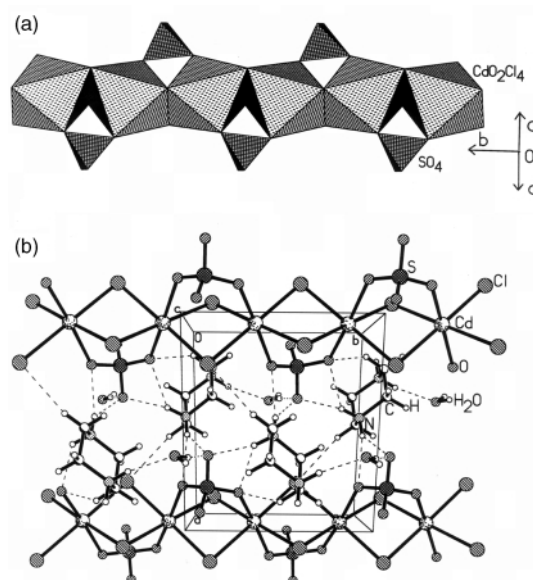


Fig. 1 (a) The inorganic part of **I**, $[\text{CdCl}_2\text{SO}_4]^{2-n}$, showing the linarite-type chain along the *b*-axis. (b) Illustration of the chain arrangement and the amine molecules along the *c*-axis in **I**. Dotted lines represent hydrogen bonding.

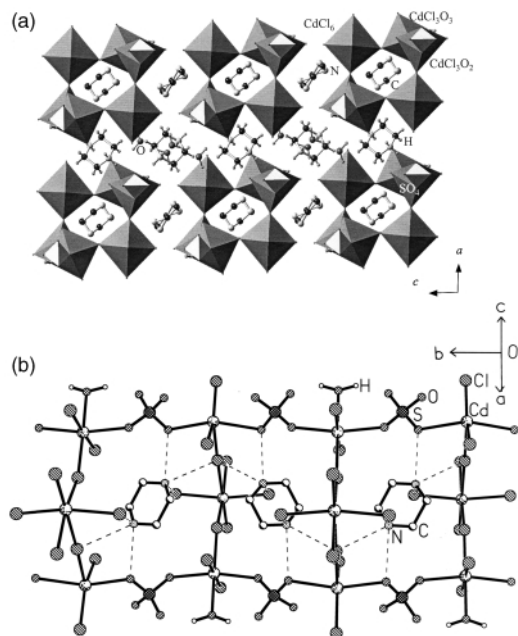


Fig. 2 (a) The quasi 2-D layer of $[C_4N_2H_{12}]_4[Cd_3Cl_{10}(SO_4)_2(H_2O)] \cdot 3H_2O$, **II** with the amine molecules sitting in the middle of the eight-membered aperture. (b) The arrangement of strips in **II** viewed along the b -axis.

neighbouring Cd(3) and S(1) but has a distorted trigonal bipyramidal coordination due to absence of a water molecule. Cd(3) on the other hand forms two Cd–Cl–Cd bonds with the two *cis* Cl atoms neighbouring Cd(1) and Cd(2) in addition to four Cd–Cl terminal bonds. The connectivity between Cd(1)Cl₃O₂(H₂O) and Cd(2)Cl₃O₂ polyhedra is brought about by the SO₄ tetrahedron *via* corner sharing to form a chain along the b -axis. Two such chains are linked by Cd(3)Cl₆ octahedron *via* corner sharing between Cd(1)Cl₃O₂(H₂O) and Cd(2)Cl₃O₂ polyhedra to form a strip-like quasi 2-D layer. Since the two Cl atoms of the bridging Cd(3)Cl₆ octahedra connecting the two chains are in *cis* orientation, the Cd(3)Cl₆ octahedra project themselves above and below the plane of the two chains alternately. Such a linkage creates eight-membered apertures within the *strip* in which heavily disordered piperazine moieties reside as shown in Fig. 2(a). These *strips* are held together by N–H⋯O and C–H⋯O hydrogen bonds in the bc -plane to form a layer-like arrangement. Protonated piperazine and water molecules present between the layers stabilise the 3-D structure [Fig. 2(b)].

To our knowledge the linarite-type chain **I** and the *strip*-like quasi-2D layer **II**, are the first members of the organically templated open-framework metal sulfate family. While there are a few piperazinium templated inorganic hosts, there is only one report of piperazine templated sulfate, comprising a dimer of VO₆ octahedra and SO₄ tetrahedra but this compound does not possess an extended structure.¹¹ Infinite chains of $[M(T\phi_4)\phi_2]$ stoichiometry in the linarite group minerals¹² are rather rare and generally occur in layered structures such as in iron phosphates¹³ and gallium phosphates¹⁴ and in the minerals tsumcorite and bermanite. Such a chain, not known in the metal phosphates, could act as the building block to form higher dimensional structures. It has been shown recently^{15,16} that 1-D zinc phosphate ladders and 1-D tancoite type gallium phosphate chains undergo facile transformations to form 3-D open-framework structures. The strip structure of the compound formed in **II**, forming a quasi 2-D layer is unusual and has been found in an open-framework cobalt phosphate.⁷

Notes and references

† *Synthesis*: $[H_2N(CH_2)_4NH_2]SO_4 \cdot H_2O$ (PIPS), was prepared by mixing a 1 M aqueous solution of piperazine with 1 M H₂SO₄. (CCDC reference number 170834).

In order to synthesize **I**, 0.1835 g of CdCl₂·H₂O was dissolved in a butan-2-ol–H₂O mixture (2.5 ml/0.49 ml) under constant stirring. To this solution was added 0.5031 g of PIPS and the stirring continued for several hours to obtain a homogeneous mixture. The final mixture with a molar ratio of 1 CdCl₂·H₂O : 2.73 PIPS : 30 butan-2-ol : 30 H₂O was transferred into a 7-ml PTFE-lined acid digestion bomb and heated at 423 K for 48 h. **II** was synthesized at a slightly higher temperature (453 K) starting with a reaction mixture of the composition 1 CdCl₂·H₂O : 2.75 PIPS : 28.32 butan-2-ol : 36 H₂O. The products contained colorless rod-shaped crystals, suitable for single crystal X-ray diffraction. TGA revealed that both **I** and **II** lose the water molecules in the range 100–150 °C range, with a sharp weight loss around 300 °C due to the loss of amine molecules and HCl (calc. 41.25%, obs. 47.58% for **I**; calc. 48.64%, obs. 42.52% for **II**). The dense cadmium sulfate in the case of **I** and chlorosulfate for **II** decompose to CdO at 600 °C. CHN analysis confirmed the amount of organic amine present in both the compounds (Found: C, 12.93; H, 3.79; N, 7.54. Calc.: C, 12.46; H, 3.66; N, 7.26% for **I**. Found: C, 14.72; H, 4.36; N, 8.62%. Calc.: C, 14.68; H, 4.31; N, 8.56% for **II**).

‡ *Crystal data*: $[C_4N_2H_{12}]_4[Cd_3Cl_{10}(SO_4)_2(H_2O)] \cdot 3H_2O$, **I**: $M_r = 385.54$, monoclinic, space group $P2_1$ (no. 4), $a = 9.3500(4)$, $b = 7.4689(3)$, $c = 9.4289(4)$ Å, $\beta = 116.134(10)^\circ$, $V = 591.14(4)$ Å³, $Z = 4$, $\mu = 2.478$ mm⁻¹, $D_c = 2.166$ g cm⁻³. A total of 2509 reflections were collected in the θ range 2.41–23.24 and merged to give 1582 unique data ($R_{int} = 0.021$) of which 1539 with $I > 2\sigma(I)$ were considered to be observed. Final $R = 0.022$, $R_w = 0.054$ and $S = 1.06$ were obtained for 144 parameters.

$[C_4N_2H_{12}]_4[Cd_3Cl_{10}(SO_4)_2(H_2O)] \cdot 3H_2O$, **II**: $M_r = 1308.54$, monoclinic, space group $P2_1/m$ (no. 11), $a = 12.578(2)$, $b = 13.093(4)$, $c = 13.006(3)$ Å, $\beta = 94.58(2)^\circ$, $V = 2135.0(9)$ Å³, $Z = 4$, $\mu = 2.261$ mm⁻¹, $D_c = 1.995$ g cm⁻³. A total of 8916 reflections were collected in the θ range 1.57–23.28 and merged to give 3216 unique data ($R_{int} = 0.052$) of which 2467 with $I > 2\sigma(I)$ were considered to be observed. Final $R = 0.058$, $R_w = 0.095$ and $S = 1.05$ were obtained for 246 parameters.

The structures were solved by direct methods using SHELXS-86⁹ and full-matrix-least-squares structure refinement against $|F^2|$ was carried out using SHELXL-PLUS¹⁰ package of programs. Two amine molecules and one water molecule in **II** being disordered were refined isotropically. CCDC reference numbers 171678 and 171679. See <http://www.rsc.org/suppdata/cc/b1/b107820h/> for crystallographic data in CIF or other electronic format.

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