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The first organically templated 1D lithioberyllofluoride chain, $[LiBe_2F_7][C_4N_2H_{12}][H_2O]_{1.5}$†

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Using a combination of hydrothermal and slow evaporation experimental techniques a 1D lithium-beryllium-fluoride chain has been synthesised. In this material a 3D hydrogen bonded network exists between solvent water, a doubly protonated organic piperazinium template and the inorganic chain.

Aluminosilicate and phosphate (oxo) framework materials exist with a large range of structural topologies.[1,2] These compounds are of considerable interest due to practical properties including ion exchange,[3] shape selectivity in catalysis[4] and porosity.[5] The majority of such materials are constructed through linked oxo-tetrahedral MO_4 units that are assembled with a variety of templating species. Using various organoamine structure directing agents many other novel structures, containing varying dimensionality, have been synthesised; these include 1D chains[6] 2D sheets[7] as well as the 3D networks.[8] Expanding the area of tetrahedral framework systems has led to studies of other linking anions such as fluoride, chloride and nitride. Fluoride ions have both comparable size and binding properties to oxide which can lead to similarities in the final structural topologies. Due to the decreased charge on the fluoride anion, a lowering of the charges on the cations is required to assist in reaching charge neutrality. Therefore in order to maintain the tetrahedral units, small-sized, low-charged metallic species such as Li, Be and B are required. We describe here the first organically templated 1D lithioberyllofluoride chain compound. The title material was synthesised using a combination of hydrothermal and ambient slow evaporation processes which yielded large rod-like colourless single crystals.‡

In the title compound each metal forms slightly distorted tetrahedra, beryllium to fluorine bond lengths range from 1.531(2)–1.611(2) Å and lithium to fluorine bond lengths are 1.831(3)–1.869(3) Å. Each BeF_4 unit is connected to two Li and one Be tetrahedra, through three doubly bridging fluorides which leaves two terminal fluorides per asymmetric unit. These two fluorides, if viewed down the *a* axis, lie at the four corners of the chain and point into the surrounding voids therefore playing a part in the hydrogen bonding to the water and piperazinium moieties.

The connectivity of the tetrahedral units produces a corner sharing, double-unit 1D chain which runs parallel to the *a* axis. The chain can be viewed as two linked strands with the repeating unit –[Be–Be–Li–Be–Be–Li–Be–Be]–, with each metal bonded through doubly bridging fluorides. Each strand is connected to another, exactly the same, but shifted by *a*/2 so that each Be–F–Be unit opposes a Li on the other side of the chain, Fig. 1.

The chains run parallel to each other and are encircled by doubly protonated piperazinium and solvent water molecules. Four stacks of each molecule surround the chain, if viewed down the *a* axis. The inorganic chain H-bonds to all four organoamine molecules but only to half of the waters. In the doubly protonated organoamine bond lengths, C–N (1.491(2)–1.497(2) Å) and C–C (1.513(2)–1.515(2) Å) are all in good agreement with the average distances reported for this molecule.

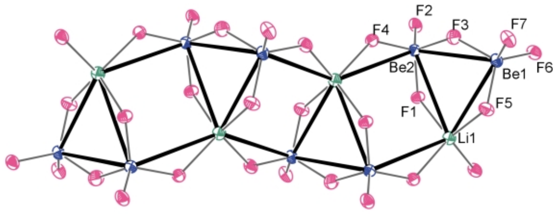

Fig. 1 Thermal ellipsoid, 50% probability, plot of a segment of the 1D Lithioberyllofluoride chain viewed perpendicular to the *ac* plane. Heavier lines represent metal–metal linkages through fluoride bridges.

If a view of the water molecules alone is taken then adjacent chains are linked though H-bonds diagonally across the *bc* plane, to two other chains, producing psuedo 2D sheets, Fig. 2. These sheets pack parallel to each other with the waters hydrogen bonding to the non-terminal fluorides, F3 and F6, at lengths of 2.849(3) and 2.721(2) respectively, with good agreement for known distances.[9]

Disorder, over two sites, is observed for one of the water molecules, O1a. A 50 : 50 split produces, for one position, hydrogen bonding to F3, 2.849(3) Å on one chain and to an adjacent O2, 2.635(3) Å;[9] for the other partially occupied site the hydrogen bonding is to symmetry related O2 and F3 in an adjacent chain. Overall this produces a 1D system of H-bonded water molecules running parallel to the *a* axis, with O…O of 2.635(3) Å and 2.760(3) Å. The complete scheme is represented pictorially in Fig. 3.

The other four hydrogen bonding sites are occupied by two types of symmetry related piperazinium molecules. As in the 2D Be/Li compounds, *vide infra*, H-bonding is observed between the protonated amine functionalities to terminal fluorides, F2 and F7. The lengths of these are very short giving 2.622(2) Å

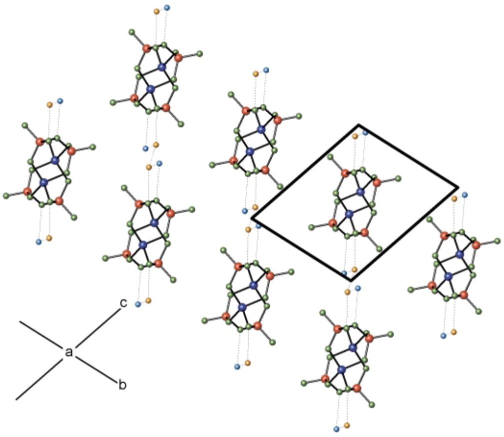

Fig. 2 Hydrogen bonding through just solvent water molecules onto non-terminal bridging fluoride ions, F(3) and F(6), viewed down the *a* axis. Atom colour sequence Be—red, Li—blue, F—green, O (solvent waters)—light blue and orange.

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† Electronic supplementary information (ESI) available: synthetic details and analytical data, TGA, IR, metal–metal and hydrogen bonding distances. See http://www.rsc.org/suppdata/cc/b2/b210894a/

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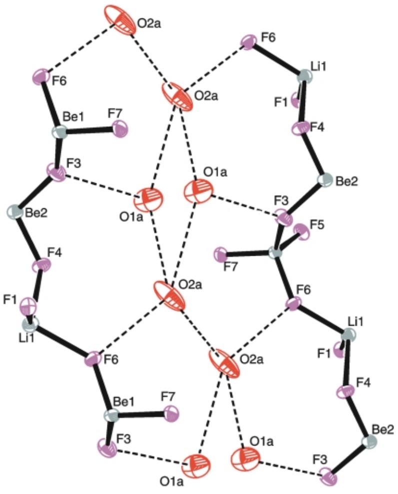

Fig. 3 Pictorial representation of the H-bonds interconnecting adjacent inorganic chains. Disorder exists for O1a over the two sites, each half occupied.

and 2.630(1) Å for N…F distances.[9] A hydrogen bonding representation of the doubly protonated piperazine and the negatively charged chain forms a square grid if viewed down the *a* axis, Fig. 4. Each amine functionality hydrogen bonds to two fluoride ions through each hydrogen with the two remaining H-bonds having lengths of 2.766(3) and 2.774(3) Å.[9]

The main structural motif in oxo transition metal phosphate or silicate materials forming 1D chains is the 4-net arrangement.[10] Examples of these 1D 4-nets, which are not as abundant as their 2D[11] and 3D counterparts,[12] include spiral chains of alternating PO_4 and ZnO_4 tetrahedra connected pairwise through the zinc in $Rb_2Zn_2(HPO_4)$[13] and a unidimensional cobalt hydrogen phosphate which contains edge sharing 4-membered rings of CoO_4 and HPO_4 tetrahedra found in $[H_3N(CH_2)_3NH_3]$ $[Co(HPO_4)_2]$.[14] Topologies of 1D silicate materials, the inosilicates, show either single chains, as $(Si_2O_6)^{4-}$, or double chains, as $(Si_4O_{11})^{6-}$.[15]

A view of the metal–metal connectivity in the title compound shows alternating 4- and 3-nets producing a zig-zag ladder, unique to Be/Li/F materials. As far as we are aware there is no other 1D chain composed of both 4- and 3-nets. In lithioberyllofluoride materials, similarities exist between the title compound and two organo-templated 2D compounds[16] recently synthesised in the group. These compounds consist of infinite rows of the 1D chains reported here but interconnected through more highly bridging fluorides into sheets.

Further work is in progress to determine if lithioberyllofluoride chains with other, new topologies can be synthesised by using different organo-templating moieties. The availability of extra functional groups may influence the growth of these chains with the possible formation of higher connectivity giving rise to 2D and 3D networks.

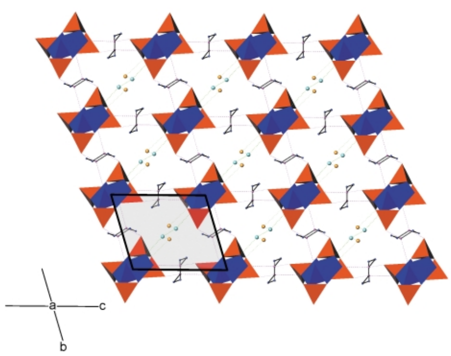

Fig. 4 Packing diagram to show the hydrogen bonding interactions between the three species forming a 3D network. Polyhedra colour sequence BeF_4—red, LiF_4—blue, O (solvent waters)—light blue and orange.

Caution: Toxicity of beryllium is a chronic problem. Appropriate precautions should be taken whilst both handling and disposing of all beryllium-containing materials.

Notes and references

‡ *Crystal data*: A suitable crystal, dimensions 0.12 × 0.04 × 0.02 mm, was selected for collection on a Nonius Kappa CCD area detector diffractometer (Mo K_α radiation) at 120(2) K. The frames were collected and processed using COLLECT, HKL DENZO and SCALEPACK.

The structure was solved and refined by least squares method using SHELXS/L-97. All calculations were performed using the WINGX system (Ver 1.64.03).

$LiBe_2F_7C_4N_2H_{15}O_{1.5}$, $M = 237.14$, triclinic, $P\bar{1}$ (No 2), $a = 7.3176(1)$ Å, $b = 8.1377(2)$ Å, $c = 10.0070(2)$ Å, $\alpha = 71.9104(10)$ °, $\beta = 76.8326(9)$ °, $\gamma = 81.8158(13)$ °, $V = 549.90(2)$ Å^3, $Z = 2$, $D_c = 1.65$ g cm^{-3}, 11909 reflections measured of which 2493 were unique and 2163 were observed ($R_{int} = 0.055$) [$I > 3\sigma(I)$]. The final anisotropic values $R = 0.0372$ and $R_w = 0.0979$.

CCDC 197150. See http://www.rsc.org/suppdata/cc/b2/b210894a/ for crystallographic data in CIF or other electronic format.

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