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Synthesis and crystal structure of the first scandium-containing open framework solid†

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A novel open framework scandium sulfate phosphate is prepared hydrothermally in the presence of the azamacrocycle cyclen (1,4,7,10-tetraazacyclododecane) in which secondary building units of formula $Sc_7(S,P)_{12}O_{48}$ are linked to give a structure with supercages.

The study of structurally and chemically diverse open framework solids is flourishing. The realisation that most of the elements in the Periodic Table can be incorporated in solids of this type, particularly in the presence of organic amines as templates, has stimulated the preparation of many new structures.[1] One promising area for the discovery of structures with novel topologies and properties is the synthesis of frameworks from combinations of tetrahedrally and octahedrally coordinated cations. Examples include titanium, yttrium and rare earth silicates[2,3] and a range of metal phosphates in which the metals are octahedrally coordinated (such as iron and nickel phosphates).[4,5] Fewer sulfate frameworks have been reported, although natural sulfate minerals of this type are known,[6,7] and open framework cadmium sulfates have been prepared recently[8] *via* the hydrothermal 'amine-sulfate' route, by which a pre-formed amine sulfate is reacted to give network cadmium sulfates.

A very wide range of metal cations have been incorporated into frameworks through hydrothermal routes, but to our knowledge no studies exist on scandium-containing solids. This is surprising, given that it possesses suitable solubility. The lack of work on scandium probably results from its high cost from typical commercial suppliers. In this communication we report the synthesis of a scandium sulfate phosphate (cyclen-ScSPO) templated by the azamacrocycle, cyclen, with a very open framework structure. Azamacrocycles, both metallated and protonated, have recently been found to be very effective structure directing agents for metal phosphates.[9–14]

The novel scandium compound was synthesised by hydrothermal treatment of scandium sulfate and scandium sulfate/phosphate gels.‡ X-Ray powder diffraction of the products indicate that the sulfate-only version of the compound is formed, but the scandium sulfate- and phosphate-containing preparation gave a monophasic product of cubic crystals suitable for laboratory-based single crystal diffraction so we report the characterisation of the mixed anion compound. The powder diffraction pattern can be fitted closely by the crystallographic data from the single crystal experiment, indicating that the bulk material is phase pure.

Elemental analysis of carbon, hydrogen and nitrogen gives a C : N ratio of 2 : 1, suggesting that the cyclen template remains intact. This is supported by single crystal diffraction, from which the position of the cyclen may be obtained, and solid state NMR. ^{13}C CP MAS NMR spectrum gives two peaks of equal intensity, taken to be the two crystallographically-distinct carbon environments of tetraprotonated cyclen within the structure, and ^{15}N CP MAS NMR gives a single resonance. Analysis of single crystals in the electron microscope gives a Sc : S : P ratio of 1 : 1.85 : 0.41. TGA coupled with mass spectrometrt1y shows that the compound loses mass in four episodes: physically adsorbed water up to 523 K, water and SO_2 between 523 and 673 K; SO_2 and fragments of cyclen (amu 44) between 673 and 873 K; at ~1050 K SO_2 and O_2 are lost (total weight loss 62.5%). Taken together, and given the crystallographically-determined structure, this gives a unit cell composition $Sc_{56}(SO_4)_{98}(PO_4)_{22}\cdot[(C_8N_4H_{24})^{4+}]_{15}\cdot 34H^+\cdot 57H_2O$. This calculated cyclen content is higher than that observed crystallographically. This would arise if disordered cyclen is present within the pores.

The structure is novel, and has a three-dimensionally-connected framework made up of ScO_6 octahedra that corner-share oxygens with sulfate (or phosphate) tetrahedra. The crystal structure analysis and ^{31}P MAS NMR suggest that phosphates occupy the same sites as sulfates in the structure—the tetrahedral oxyanions of the structure will be referred to as sulfates in the following description, but include substituting phosphates. The main features of the framework are an arrangement of supercages at the corners and the centre of the cubic unit cell. Each is connected to six other supercages *via* smaller cages, in which protonated cyclen molecules stand as 'gatekeepers' at the windows. Each smaller cage links two supercages in this way, so that in a unit cell there are two supercages and six smaller cages, as shown in Fig. 1.

The entire framework structure can be thought of as being constructed of secondary building units, formula $Sc_7S_{12}O_{48}$, illustrated in Fig. 2. Each building unit consists of one central

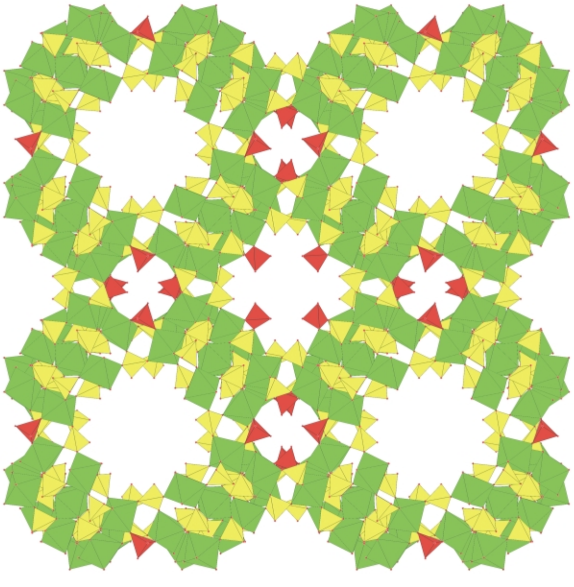

Fig. 1 Representation of the framework structure of cyclen-ScSPO, viewed along [100], showing the ScO_6 octahedra (green) and the mixed sulfate/phosphate tetrahedra (yellow, for tetrahedra with one dangling oxygen, red for tetrahedra with two dangling oxygens). The cyclen molecules are omitted for clarity.

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† Electronic supplementary information (ESI) available: crystallographic tables, TGA and TG-MS, le Bail plot and Rietveld fit. See http://www.rsc.org/suppdata/cc/b2/b202500k/

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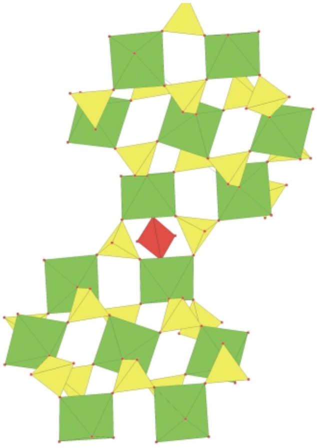

Fig. 2 A representation of two building units of ScSPO, showing the way they are attached. In the structure, each building unit is attached to six others in this way. The colour scheme is the same as for Fig. 1.

scandium, which is connected to six scandiums on the outside of the building unit *via* sulfate groups. Each external scandium of this kind is connected to three scandiums of the same building unit *via* sulfate groups within the unit. In addition, each external scandium is linked to an external scandium in a different building unit *via* three bridging sulfates, including one sulfate group which is not in either building unit, but possesses two 'dangling' oxygens (rather than one, which is the case with all the other sulfate groups). In this way, each 'Sc_7S_{12}' building unit is connected to six others, with the only other polyhedra unaccounted for being the SO_4 tetrahedra with two dangling bonds that link between building units.

The building units are arranged to give a framework that contains two types of cage. Two tetraprotonated cyclen molecules are located within the smaller cages, and form strong H-bonding with the sulfate groups. The larger cages, which have a free diameter of around 13 Å and possess six windows blocked by cyclen molecules, are filled with physically adsorbed water. The framework has a net negative charge of around −34 per unit cell, which must be balanced by protons within hydroxonium ions (or on sulfate or phosphate oxygens as terminal hydroxy groups). The framework structure is stable upon heating to 473 K, but decomposes at higher temperatures. After heating at 973 K for 2 h, X-ray powder diffraction shows that the material has decomposed to a mixture including Sc_2O_3 and $Sc_2(SO_4)_3$.

The demonstration of scandium as a framework-forming element is promising for the preparation of a range of novel open framework solids. In particular, the title compound is characterised by the clearly defined building units that link together to form the framework. Parallels may be drawn with the studies of Férey on iron phosphate systems.[4] The structural rigidity of these units, together with the structure directing action of the cyclen molecule, result in the cage structure in a similar way to rigid units in the structure of vanadyl phosphates[15] and nickel phosphates.

We acknowledge the assistance of Dr Alex Slawin in collecting the single crystal X-ray diffraction data and the EPSRC solid state NMR facility at Durham for the NMR data.§

Notes and references

‡ The title compound was prepared by hydrothermal treatment of a homogeneous gel of composition $0.5Sc_2O_32.3\ H_2SO_4:H_3PO_4:0.4$cyclen$:4H_2O:HF$, prepared by mixing 0.39 g of scandium sulfate pentahydrate, 0.19 g phosphoric acid (80 wt%) and 0.24 g cyclen sulfate (all from Aldrich), 0.045 g distilled water and 0.03 g HF. After ageing for one hour the resultant paste was transferred to a PTFE-lined acid digestion bomb (23 ml, Parr) and heated at 463 K for 4 days.

Characterisation: elemental carbon, hydrogen and nitrogen analysis gave 8.04 wt%C, 4.63 wt%N and 2.74 wt%H. The Sc : S : P ratio was measured on a JEOL JEM-2010 electron microscope using an Oxford Instruments EDX attachment. TG-MS was measured in a flow of helium. All NMR spectra were measured on a Varian 300 MHz instrument. ^{13}C CP MASNMR was measured using the following conditions: contact time 1 ms, acquisition time 30 ms, recycle delay 2 s, spinning speed 4 kHz, reference TMS. The ^{13}C spectrum contained two peaks of similar intensity (δ 40.3, 46.0) attributed to two cyclen carbons in different crystallographic environments. ^{15}N CP MASNMR (contact time 1.0 ms, acquisition time 15 ms, recycle delay 1.0 s, spinning speed 4650 Hz) gave a single peak (δ −343). DP ^{31}P was measured on the same spectrometer using an acquisition time of 20 ms, relaxation delay 120 s and a spin rate of 7.5 kHz; referenced to an 85wt% solution of H_3PO_4. The ^{31}P spectrum gave two strong peaks (δ −18.9 (strong), −2.3 (very strong)), attributed to phosphate replacing sulfate at the framework sulfate positions with one dangling oxygen, and a weak peak (δ 0.6).

Crystallography: single crystal_structure analysis: $M = 17722$, $T = 293$ K, $\lambda = 0.71073$ Å, cubic $Pn3n$ (no. 222), $a = 25.2469(3)$ Å, $V = 16092.5(3)$ Å^3, D_c (including disordered water) = 1.829 g cm^{-3}, R_1 [$I > 2\sigma(I)$] = 12.2%, wR_2 [$I > 2\sigma(I)$] = 34%. SO_4 and PO_4 units are distributed throughout the structure and the anions were all refined as sulfate groups. Hydrogen atoms were placed on the C and N atoms. Details of the le Bail fitting and the Rietveld refinement of the X-ray powder diffraction data are given in the ESI.†

CCDC reference number 181653. See http://www.rsc.org/suppdata/cc/b2/b202500k/ for crystallographic data in CIF or other electonic format.

§ *Note added in proof*: We note with interest the work of Riou *et al.*[16] describing $Sc(HPO_4)_2{\cdot}0.5(N_2C_2H_{10})$, the organically templated scandium analogue of $In(HPO_4)_2{\cdot}(N_2C_2H_{10})$.[17]

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