

# Hydrothermal synthesis and structure of organically templated chain, layered and framework scandium phosphates

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## Abstract

Four scandium phosphate-based structures have been prepared hydrothermally in the presence of the primary diamines ethylenediamine and diaminobutane and the primary amine cyclohexylamine and characterised by single crystal and powder X-ray diffraction,  $^{31}\text{P}$  and  $^{45}\text{Sc}$  solid-state MAS NMR and chemical analysis. Charge balancing protons in the structures are located using bond valence sum calculations and postulated hydrogen bonding networks. Compound **1**,  $[(\text{H}_3\text{NC}_2\text{H}_4\text{NH}_3)_3][\text{Sc}_3(\text{OH})_2(\text{PO}_4)_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)]$ ,  $P\bar{1}$ ,  $a = 5.4334(6)$ ,  $b = 8.5731(9)$ ,  $c = 16.3022(18)$  Å,  $\alpha = 79.732(4)$ ,  $\beta = 83.544(4)$ ,  $\gamma = 80.891(5)^\circ$ ,  $Z = 2$ , is built up of scandium phosphate ribbons, based on trimers of  $\text{ScO}_6$  octahedra linked by OH groups. These trimers are joined through phosphate groups bound through three oxygens, and are decorated by phosphate groups linked by a single oxygen atom. The ribbons are arranged parallel to the  $a$ -axis and linked one to another by fully protonated ethylenediammonium ions. Compounds **2**,  $[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_3][(\text{Sc}(\text{OH}_2))_6\text{Sc}_2(\text{HPO}_4)_{12}(\text{PO}_4)_2]$ ,  $P\bar{3}$ ,  $a = 13.8724(3)$ ,  $c = 9.4351(11)$  Å,  $Z = 1$ , and **3**,  $[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_2(\text{H}_3\text{O})][\text{Sc}_3\text{F}_4(\text{HPO}_4)_8]$ ,  $C2/m$ ,  $a = 12.8538(4)$ ,  $b = 14.9106(4)$ ,  $c = 10.1906(3)$  Å,  $\beta = 101.17(9)^\circ$ ,  $Z = 2$ , were prepared using diaminobutane as the organic template in the absence and presence, respectively, of fluoride ions in the gel. Compound **2** has a pillared layered structure, in which  $\text{ScO}_6$  octahedra are linked by three vertices of hydrogenphosphate groups into sheets and the sheets pillared by  $\text{ScO}_6$  octahedra to give a three-dimensionally connected framework isostructural with a previously reported iron(III) hydrogenphosphate. The protonated diaminobutane molecules occupy cavities between the layers. Compound **3** has a layered structure in which isolated  $\text{ScO}_6$  octahedra and tetrameric arrangements of  $\text{ScO}_4\text{F}_2$  octahedra, the latter linked in squares through fluoride ions, are connected by phosphate tetrahedra that share two or three oxygens with scandium atoms. In this structure, the protonated diaminobutane molecules connect the layers, the  $-\text{NH}_3^+$  groups fitting into recesses in the layers. Compound **4**,  $[(\text{C}_6\text{H}_{11}\text{NH}_3)][\text{ScF}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$ ,  $Pbca$ ,  $a = 7.650(3)$ ,  $b = 12.867(5)$ ,  $c = 26.339(11)$  Å,  $Z = 8$ , the first scandium phosphate to be prepared with a monoamine, is also a layered solid. In this case, the layers contain single chains of  $\text{ScO}_4\text{F}_2$  octahedra which share fluoride ions in trans positions. Phosphate tetrahedra bridge across scandiums via two of their four oxygens, both within the same chain and also to neighbouring chains to make up the layer. The protonated amine groups of the cyclohexylamine molecules achieve close contact with phosphates of the layer, while the cyclohexyl moieties, which are in the chair configuration, project into the interlayer space.

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## 1. Introduction

Since the discovery of aluminophosphate molecular sieves consisting primarily of tetrahedrally linked frame-

works [1], metal phosphates have been synthesised hydrothermally with increasing diversity, in terms of both their chemical composition and structural motifs [2]. In particular, families of gallium [3–6], iron(III) [7] and indium [8] phosphates and fluorophosphates have been reported. Scandium is among the metals most recently investigated as a structural element of open

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framework solids, partly in response to its increasing availability at reasonable expense as the oxide. The acid–base chemistry of scandium is similar to that of aluminium, but the ionic radius is significantly larger (0.745 Å cf. 0.535 Å) [9]. It is expected that scandium will form a rich variety of phosphates, as aluminium does, and that the scandium sites will be available for substitution by trivalent transition metals ions such as  $\text{Cr}^{3+}$  (radius 0.80 Å) and  $\text{Fe}^{3+}$  (radius 0.78 Å), which could impart novel adsorptive or catalytic properties. A scandium sulphate/phosphate templated by the azamacrocyclic 1,4,7,10-tetraazacyclododecane (cyclen) and possessing giant cages, indicated the feasibility of preparing novel scandium-containing frameworks [10]. Riou et al. [11] reported an open framework scandium phosphate, prepared using ethylenediamine as an organic template, isostructural with an indium phosphate, and commented that there should be a family of scandium phosphates. Subsequent works of Bull et al. [12] and most recently Park et al. [13] and Ewald et al. [14] have confirmed that octahedral scandium can form other phosphate structures templated by ethylenediamine and diazabicyclooctane. We are continuing our own program to investigate the crystal chemistry of scandium-containing solids prepared hydrothermally. Here we report the synthesis of chain, layered and framework scandium phosphates prepared in the presence of primary amines. In all cases, the amines interact strongly with oxygens of the phosphate groups via well-defined hydrogen bonding networks.

## 2. Experimental section

### 2.1. Synthesis and characterisation

All reactions were carried out by hydrothermal crystallisation from aqueous gels in 25 ml Teflon-lined steel autoclaves (Parr type). Gels were prepared by thorough (1 h) mixing before heating. Once removed from the oven, products were filtered and washed with distilled water and dried at 100 °C. The products were then sonicated in water to remove any unreacted  $\text{Sc}_2\text{O}_3$  with the coarse fraction yielding crystalline powders. The resulting powders were routinely examined by X-ray powder diffraction using a STOE Stadi/p diffract-

ometer operating with monochromated Cu  $K\alpha_1$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ).

The content of carbon, hydrogen and nitrogen in the samples was measured by a Carlo Erba elemental analyser. The inorganic composition (Sc, P, O, F) was examined semi-quantitatively by EDX on a JEOL-5600 SEM with an Oxford INCA energy 200 EDX system. Thermogravimetric analysis was conducted on a TA Instruments SDT 2960 thermogravimetric analyser. Approximately 10 mg of sample was loaded in an alumina crucible and data collected from room temperature to 1200 °C at 5 °C  $\text{min}^{-1}$  in a flow of  $\text{O}_2$ , with calcined alumina as a reference sample.

Solid-state NMR spectroscopy experiments were carried out on the as-prepared materials at room temperature using either a triple channel Varian infinityplus 500 MHz spectrometer with a T<sub>3</sub> Chemagnetics 4-mm probe at resonance frequencies of 121.480 and 202.466 for  $^{45}\text{Sc}$  and  $^{31}\text{P}$ , respectively, or a Varian unityplus 300 MHz spectrometer with a Chemagnetic apex 7-mm probe at a resonance frequency of 121.371 for  $^{31}\text{P}$ . A 1 M aqueous solution of  $\text{ScCl}_3$  and solid references of  $\text{CaHPO}_4 \cdot \text{H}_2\text{O}$  (Brushite) and adamantane were used as reference materials for  $^{45}\text{Sc}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$ , respectively. Samples were spun at the magic angle at a spinning speed of 12, 7.5 and 5 kHz with pulse durations of 1.5, 4 and 4  $\mu\text{s}$ , and pulse delays of 0.2, 30 and 2 s for  $^{45}\text{Sc}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$ , respectively.

Details of the syntheses of the four new compounds reported in this work are given in Table 1. In each case, the volume of water in the preparation was around 20 ml. The sources of the reagents were  $\text{Sc}_2\text{O}_3$  (Stanford Materials, 99.999%),  $\text{H}_3\text{PO}_4$  (Porlabo, 85% aqueous solution), ethylenediamine (Avocado), 1,4-diaminobutane (Aldrich), cyclohexylamine (Acros) and HF (Aldrich, 48 wt% aqueous solution). A series of gel compositions were attempted for each amine. The reported values give the phase pure product or, for compound 4, the sample with the least impurity. The sample from this preparations included small spherulites of an impurity phase,  $\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$  [12]. In addition to the primary amines incorporated into structures 1–4, secondary and tertiary amines were also included in synthetic preparations. Alternative organic directing agents included tetramethylammonium hydroxide, tetraethylammonium hydroxide, isopropylamine,

Table 1

Synthesis conditions for compounds 1–4, including gel compositions and crystallisation temperatures and times

	Formula	Amine (R)	$\text{Sc}_2\text{O}_3:\text{H}_3\text{PO}_4:\text{R}:\text{HF}:\text{H}_2\text{O}$	T/K	t/h	pH <sub>0</sub>
1	$[(\text{H}_3\text{NC}_2\text{H}_4\text{NH}_3)_3][\text{Sc}_3(\text{OH})_2(\text{PO}_4)_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)]$	Ethylenediamine	1 : 1.7 : 2.2 : 0.48 : 200	453	48	2
2	$[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_3][(\text{Sc}(\text{OH})_2)_6\text{Sc}_2(\text{HPO}_4)_{12}(\text{PO}_4)_2]$	1,4-Diaminobutane	0.5 : 3 : 1 : 0 : 200	463	72	3
3	$[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_2(\text{H}_3\text{O})][\text{Sc}_5\text{F}_4(\text{HPO}_4)_8]$	1,4-Diaminobutane	0.5 : 3.5 : 1.5 : 2 : 200	463	72	2
4	$[\text{C}_6\text{H}_{11}\text{NH}_3][\text{ScF}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$	Cyclohexylamine	1 : 3.4 : 2 : 1 : 200	463	72	2

dicyclohexylamine and 2,2,6,6-tetramethylpiperidine but no crystalline solids other than the known inorganic  $\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$  were obtained.

### 3. X-ray crystallography

Details of the single crystal X-ray data collections for all structures are summarised in Table 1. Structure **1** was determined using a Rigaku MM007RA (confocal optics, Cu radiation) and a Rigaku Mercury CCD detector, whilst structures **2** and **3** used a Mo X-ray source and a Rigaku Saturn 70 CCD detector. Due to the small crystal size of **4**, single crystal X-ray diffraction was carried out on station 9.8 at the CCLRC synchrotron radiation source at Daresbury using a Bruker SMART 1K CCD diffractometer. In addition, high-resolution X-ray powder diffraction data were collected for structure **1** on station ID-31 at the European Synchrotron Radiation Facility. In this case, data collection was carried out at room temperature in Debye-Scherrer geometry, with the sample in a sealed quartz glass capillary, with  $2\theta$  of  $2\text{--}35^\circ$  using monochromated radiation with a wavelength of  $0.63248 \text{ \AA}$ . The structure was observed to change gradually in the intense X-ray beam, so five data collections over 2 min were performed

on freshly exposed portions of the sample and the data sets were summed. During the short data collection time (2 min) no changes occurred.

### 4. Structure solution and discussion

#### 4.1. $[(\text{H}_3\text{NC}_2\text{H}_4\text{NH}_3)_3][\text{Sc}_3(\text{OH})_2(\text{PO}_4)_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)]$ , **1**

Structure **1** was solved by direct methods and Fourier syntheses from laboratory single crystal X-ray data collected on a small crystal as described in Table 2. Structure details are given in Tables 3 and 4 and the structure is illustrated in Figs. 1 and 2. A Rietveld refinement of high-resolution X-ray powder data collected at the ESRF was performed with the GSAS suite of programs [15] using the atomic coordinates determined by the single crystal structure solution as a starting point to confirm phase purity. Instrumental parameters (background, zero-point, peak profile coefficients) and structural parameters (unit cell, atomic coordinates, thermal parameters) were refined, keeping constraints on the bond distances and angles. A close final fit to the observed data was achieved ( $R_{\text{wp}} = 10.0\%$ ) with atomic positions refining to

Table 2  
Data collection and refinement parameters for structures **1–4**

Compound	Structure 1	Structure 2	Structure 3	Structure 4
Chemical formula	$[(\text{NH}_3\text{C}_2\text{H}_4\text{NH}_3)_3][\text{Sc}_3(\text{OH})_2(\text{PO}_4)_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)]$	$[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_3][\text{Sc}(\text{OH}_2)_6\text{Sc}_2(\text{PO}_4)_{12}(\text{PO}_4)_2]$	$[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_2(\text{H}_3\text{O})][\text{Sc}_3\text{F}_4(\text{PO}_4\text{H})_8]$	$[(\text{C}_6\text{H}_{11}\text{NH}_3)][\text{ScF}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$
Formula wt	930.1	2080.0	1300.8	358.11
Crystal system	Triclinic	Trigonal	Monoclinic	Orthorhombic
Space group	$P\bar{1}(2)$	$P\bar{3}(147)$	$C2/m(12)$	$Pbca(61)$
Z	2	1	2	8
$a(\text{Å})$	5.4534(6)	13.8724(3)	12.8538(4)	7.650(3)
$b(\text{Å})$	8.5731(9)	13.8724(4)	14.9106(4)	12.867(5)
$c(\text{Å})$	16.3022(18)	9.4351(11)	10.1906(3)	26.339(11)
$\alpha(^\circ)$	79.732(4)	—	—	—
$\beta(^\circ)$	83.544(4)	—	101.17(9)	—
$\gamma(^\circ)$	80.891(5)	—	—	—
$V(\text{Å}^3)$	775.0(14)	1572.5(7)	1916.14(10)	2592.6(14)
Diffractometer	Saturn	Mercury	Saturn	Daresbury, 9.8
Temperature (K)	173	93	93	120
$\lambda(\text{Å})$	1.54178	0.71073	0.71073	0.68920
No. reflections	7973	8635	5862	19,254
No. unique reflections	2033	1881	1756	19,481
$2\theta$ range	8.26–67.76	1.70–25.34	2.71–25.35	2.99–25.70
Variables	218	154	93	169
R1 ( $I > 2\sigma I$ )	0.0701	0.0536	0.0518	0.1552
R1 (all data)	0.0796	0.0686	0.0557	0.2754
Max., min. diff. e. density ( $\text{eÅ}^{-3}$ )	0.743, $-0.565$	0.656, $-0.751$	2.33, $-1.10$	2.21, $-1.35$

Note: Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 261857–261860. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

Table 3  
Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[(\text{H}_3\text{NC}_2\text{H}_4\text{NH}_3)_3][\text{Sc}_3(\text{OH})_2(\text{PO}_4)_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)]$ , (1)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Sc(1)	0.7134(2)	0.1143(1)	0.2923(1)	13(1)
Sc(2)	0.0	0.0	0.5	13(1)
P(1)	0.2538(3)	-0.1323(2)	0.3189(1)	12(1)
P(2)	0.1562(3)	0.3147(2)	0.3474(1)	12(1)
P(3)	0.5508(3)	0.2507(2)	0.920(1)	18(1)
O(1)	0.0152(8)	-0.0682(5)	0.2757(3)	17(1)
O(2)	0.2045(8)	-0.1377(6)	0.4139(3)	20(1)
O(3)	0.3466(8)	-0.3057(5)	0.3017(3)	16(1)
O(4)	0.4618(8)	-0.0370(6)	0.2838(3)	17(1)
O(5)	0.9841(8)	0.2697(5)	0.2898(3)	18(1)
O(6)	0.1319(8)	0.2090(5)	0.4341(3)	19(1)
O(7)	0.0749(8)	0.4923(5)	0.3581(3)	20(1)
O(8)	0.4262(7)	0.2983(5)	0.3104(3)	16(1)
O(9)	0.7080(8)	0.1966(5)	0.1648(3)	19(1)
O(10)	0.5148(9)	0.4362(6)	0.0733(3)	26(1)
O(11)	0.2809(8)	0.1987(6)	0.1186(3)	27(1)
O(12)	0.6522(9)	0.1761(6)	0.173(3)	25(1)
O(13)	0.7149(7)	0.0435(5)	0.4218(2)	9(1)
C(1)	0.8138(13)	-0.1900(9)	0.1165(4)	24(2)
C(2)	0.9221(12)	-0.3547(8)	0.1583(4)	23(2)
C(3)	0.6165(11)	0.4965(8)	0.4692(4)	19(1)
N(1)	0.0025(11)	-0.0814(7)	0.1022(3)	21(1)
N(2)	0.7286(10)	-0.4514(7)	0.1942(4)	20(1)
N(3)	0.6861(10)	0.6608(7)	0.4454(4)	22(1)
H(13A)	0.5927	0.1240	0.4451	0.013
H(13B)	0.6401	-0.0553	0.4331	0.013
H(N1A)	0.0652	-0.0763	0.1555	0.030
H(N1B)	0.9286	0.0257	0.0771	0.030
H(N1C)	0.1413	-0.1216	0.0641	0.020
H(C1A)	0.7539	-0.1977	0.0624	0.029
H(C1B)	0.6695	-0.1465	0.1524	0.029
H(C2A)	0.0303	-0.4101	0.1169	0.028
H(C2B)	0.0236	-0.3440	0.2033	0.028
H(N2A)	0.8036	-0.5509	0.2273	0.033
H(N2B)	0.6445	-0.4764	0.1493	0.033
H(N2C)	0.7972	0.6664	0.3937	0.033
H(C2A)	0.7548	0.4228	0.4955	0.023
H(C2B)	0.5826	0.4567	0.4189	0.023

positions very close to the values determined from single crystal diffraction (for profile fit and structural data see Supplementary information). The positions of hydrogen atoms in the structure were interpreted from measured bond lengths, bond valence sum (b.v.s.) calculations [16] and consideration of the distances of oxygens from nitrogens of the ethylene diamine molecules, which were taken to be protonated, and from other oxygens in a potential H-bonding network. The oxygen O(13) that bridges scandium atoms Sc(1) and Sc(2) (b.v.s. = 1.08) is protonated. Oxygens O(3) and O(7) (b.v.s. 1.18 and 1.20, respectively) of phosphate groups that link the scandium trimers are part of POH groups that share protons  $\text{O}(3)\text{--O}(7) = 2.45 \text{ \AA}$ . The terminal (P(3)) phosphate tetrahedra possess three oxygens that have b.v.s. values less than 2, O(10), O(11) and O(12) (b.v.s. values

Table 4  
Selected bond distances and probable hydrogen bonding scheme for  $[(\text{H}_3\text{NC}_2\text{H}_4\text{NH}_3)_3][\text{Sc}_3(\text{OH})_2(\text{PO}_4)_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)]$  (1)

Bond	Distance ( $\text{\AA}$ )	Bond	Distance ( $\text{\AA}$ )
Sc(1)–O(4)	2.063(5)	P(1)–O(3)	1.557(4)
Sc(1)–O(8)	2.075(4)	P(1)–O(4)	1.504(5)
Sc(1)–O(9)	2.076(5)		
Sc(1)–O(13)	2.090(4)	P(2)–O(5)	1.544(5)
Sc(1)–O(1)	2.113(4)	P(2)–O(6)	1.551(5)
Sc(1)–O(5)	2.132(5)	P(2)–O(7)	1.535(5)
Sc(2)–O(13) × 2	2.068(4)	P(2)–O(8)	1.522(4)
Sc(2)–O(6) × 2	2.101(5)		
Sc(2)–O(2) × 2	2.105(4)	P(3)–O(9)	1.505(5)
		P(3)–O(10)	1.550(5)
P(1)–O(1)	1.527(4)	P(3)–O(11)	1.596(5)
P(1)–O(2)	1.535(5)	P(3)–O(12)	1.484(5)
D–H...A	<i>d</i> (D...A) ( $\text{\AA}$ )	D–H...A	<i>d</i> (D...A) ( $\text{\AA}$ )
O(10)–H...O(10)	2.499	N(2)–H...O(5)	2.90
O(3)–H...O(7)	2.521	N(2)–H...O(3)	2.967
O(7)–H...O(3)	2.521	N(3)–H...O(7)	2.781
N(1)–H...O(12)	2.749	N(3)–H...O(6)	2.824
N(2)–H...O(10)	2.779		

Hydroxyl groups have been assigned using valence bond calculations.

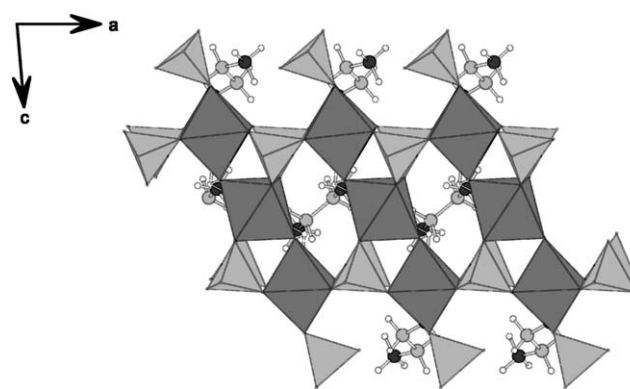


Fig. 1. Projection down [010] of  $[(\text{H}_3\text{NC}_2\text{H}_4\text{NH}_3)_3][\text{Sc}_3(\text{OH})_2(\text{PO}_4)_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)]$  (1), showing ribbons extending parallel to the *a*-axis. Representation: Dark octahedra,  $\text{ScO}_4(\text{OH})_2$ ; light tetrahedra,  $\text{PO}_4$ ; dark grey, mid-grey; and white spheres, N, C and Hs of protonated ethylenediamine. O(3), O(7), O(10) and O(11) are assigned to hydroxyl groups.

1.2, 1.06 and 1.43). The O(10)–O(10) distance of  $2.45 \text{ \AA}$  suggests that these share a proton. O(11) is too far from other oxygens to be involved in hydrogen bonding and is taken to be protonated and O(12) is H-bonded to the organic nitrogen. The final charge-balanced structural formula is therefore  $[(\text{H}_3\text{NC}_2\text{H}_4\text{NH}_3)_3][\text{Sc}_3(\text{OH})_2(\text{PO}_4)_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)]$ . For the CHN analysis in wt%, calculated: C, 7.75%; H, 4.01%; N, 9.08%; measured: C, 6.78%; H, 3.63%; N, 8.62%, suggesting some amorphous inorganic impurity is present.

The main structural unit of compound 1 is a ribbon-like chain running parallel to the *a*-axis (Fig. 1). Each

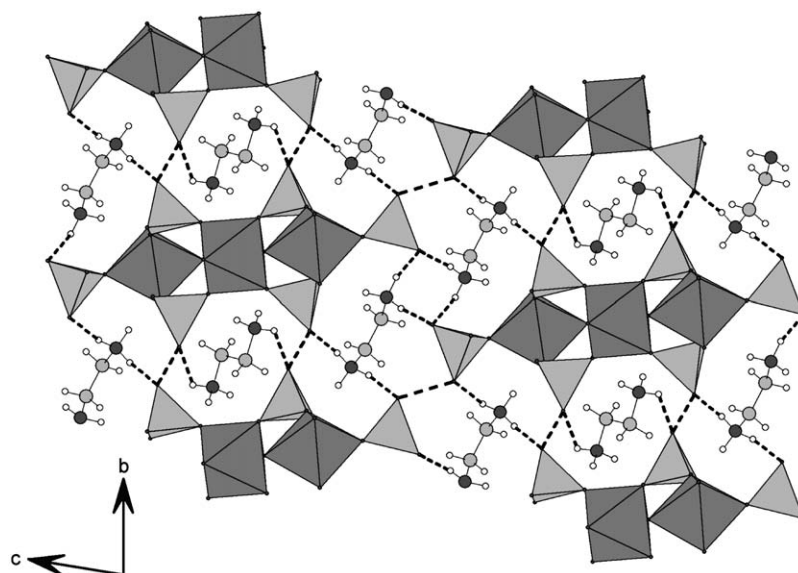


Fig. 2. Projection down [010] of  $[(\text{H}_3\text{NC}_2\text{H}_4\text{NH}_3)_3][\text{Sc}_3(\text{OH})_2(\text{PO}_4)_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)]$  (1), showing the hydrogen bonding network. Representation as for Fig. 1.

chain is made up of trimers of corner-sharing  $\text{ScO}_6$  octahedra, the two shared oxygens of each trimer being part of a hydroxyl group. Adjacent  $\text{Sc}_3(\text{OH})_2$  trimers are linked along  $a$  by three apices of phosphate ( $\text{PO}_3\text{OH}$ ) groups that share protons, the POH group of each of which points away from the ribbon. Two phosphate tetrahedra are attached by one corner to the  $\text{Sc}_3(\text{OH})_2$  trimers at the edges of the ribbons to make up the structure. Adjacent ribbons are stacked along the  $b$ -axis and these stacks are arranged in a staggered way along  $c$  (Fig. 1). The protonated ethylenediamine molecules occupy space between the ribbons and between stacks of ribbons, holding them together through hydrogen bonding with oxygens of the terminal phosphate groups, as shown in Fig. 2. The interatomic distances and bond angles in the inorganic ribbons are as expected: Sc–O bond distances are between 2.084(7) and 2.190(8) Å and P–O distances are from 1.499(9) to 1.616(8) Å.

Solid-state  $^{31}\text{P}$  DP MAS NMR (Fig. 3a) gives a single broad peak at  $\delta -9.7$  ppm of 960 Hz, so that the different crystallographic sites are not resolved.  $^{45}\text{Sc}$  MAS NMR (Fig. 4a) shows two broad peaks at 35.4 and 8.8 ppm, consistent with two different scandium sites in the structure.  $^{45}\text{Sc}$  is a quadrupolar nucleus, and quadrupolar interactions results in broad resonances.  $^{13}\text{C}$  CP MAS NMR (not shown) shows a broad peak at 37 ppm indicating that the template is still intact within the structure. Thermogravimetric analysis shows a total weight loss of 23.3% occurring between 250 and 600 °C due to combustion of the organic and dehydroxylation (theoretical, 21.9%).

The synthetic conditions for this phase were adapted from previous experiments that report the formation of scandium phosphates using ethylenediamine as the

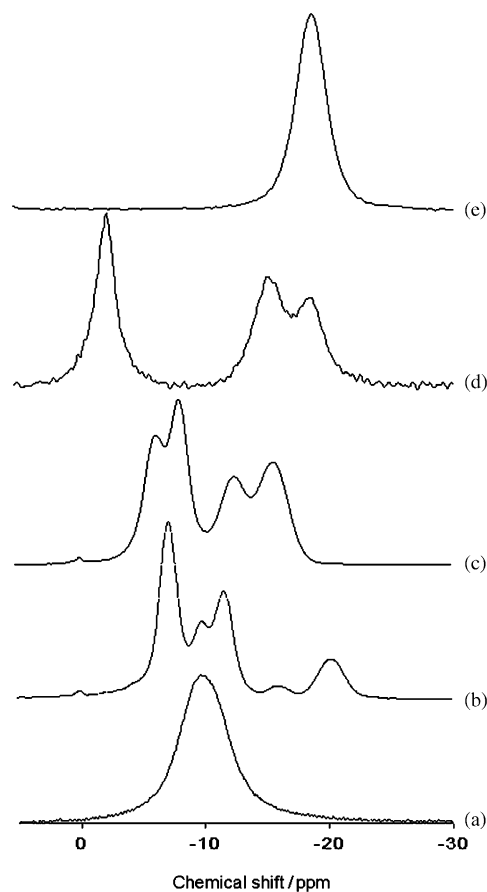


Fig. 3.  $^{31}\text{P}$  MAS NMR spectra of (a) compound 1,  $[(\text{H}_3\text{NC}_2\text{H}_4\text{NH}_3)_3][\text{Sc}_3(\text{OH})_2(\text{PO}_4)_2(\text{HPO}_4)_3(\text{H}_2\text{PO}_4)]$ , (b) compound 2,  $[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_3][(\text{Sc}(\text{OH})_2)_6\text{Sc}_2(\text{HPO}_4)_{12}(\text{PO}_4)_2]$ , (c) compound 3,  $[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_4(\text{H}_3\text{O})_2][\text{Sc}_{10}\text{F}_8(\text{HPO}_4)_{16}]$ , (d) a mixture of compound 4  $[\text{C}_6\text{H}_{11}\text{NH}_3][\text{ScF}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$  and  $\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$  and (e) synthetic  $\text{ScPO}_4 \cdot 2\text{H}_2\text{O}$ .

organic structure directing agent. It is instructive to compare the chain structure of **1** with the framework structures obtained previously with ethylenediamine. Table 5 compares the reaction stoichiometry used for structure **1** with those for phosphates prepared previously with those for structure **1**. Structure **1** is the first chain scandium phosphate structure observed with ethylenediamine.

## 5. Syntheses with diaminobutane

### 5.1. Structures **2**, $[(H_3NC_4H_8NH_3)_3]$ $[(Sc(OH_2))_6Sc_2(HPO_4)_{12}(PO_4)_2]$ and **3**, $[(H_3NC_4H_8NH_3)_2(H_3O)][Sc_5F_4(HPO_4)_8]$

Diaminobutane was chosen as a primary diamine similar to ethylenediamine. Syntheses were attempted in

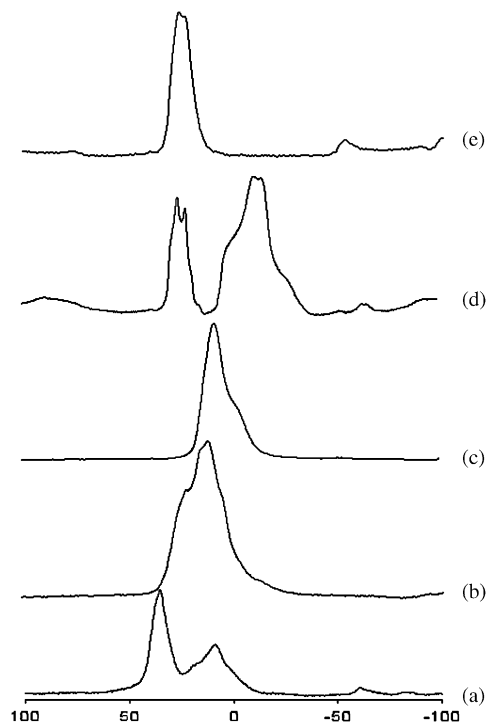


Fig. 4.  $^{45}Sc$  MAS NMR of samples (a)–(e), as described for Fig. 4.

the presence and absence of HF, because fluoride is known to act as a mineralising agent in similar preparations [11–14].

Without fluoride, the preparation resulted in the crystallisation of structure **2** as pseudohexagonal prisms of suitable quality for laboratory single crystal diffraction. The scandium, phosphorus and oxygen of the framework and the carbon and nitrogen atoms of the organic were readily located from the diffraction data (Figs. 5 and 6, Tables 6 and 7). Comparison of observed and simulated powder diffraction patterns indicates that the phase is pure. Hydrogen atoms were assigned to the framework by b.v.s. calculations. Accordingly, O(11) (b.v.s. 0.47) belongs to a water molecule coordinated to scandium. Also, the terminal oxygens of O(4), O(6) and O(10) (b.v.s. values of 1.22, 1.07 and 1.03) are expected to be protonated or involved in H-bonding. O(4), O(6) and O(10) are the only non-bridging oxygens on the three different phosphorus atoms, P(1), P(2) and P(3). Postulating a proton on each of these  $PO_4$  tetrahedra, and considering the diaminobutane molecules to be fully protonated more than balances the negative charge on the framework. Of the oxygens with b.v.s. values close to 1, O(4) shows the closest approaches to the nitrogen of the organic template. We therefore assume a disordered arrangement of protons between O(4) and the diaminobutane. For convenience the overall unit cell formula is written  $[(H_3NC_4H_8NH_3)_3 \cdot (Sc(OH_2))_6Sc_2(HPO_4)_{12}(PO_4)_2]$ , where the amine is fully protonated. CHN analysis, wt%, calculated: C, 6.11%; H, 3.04%; N, 3.62%; measured: C, 6.98%; H, 2.54%; N, 4.09%.

Within structure **2** there are no Sc–O–Sc linkages, and therefore there is strict alternation between Sc and P in the framework. The structure can best be thought of as being made up of gently undulating sheets of  $ScO_6$  octahedra and  $PO_4$  tetrahedra, arranged in four-membered and six-membered rings, with the phosphate groups pointing away from the centre of the sheet and into the cavities between sheets (Fig. 5). Adjacent sheets are then pillared by  $ScO_6$  octahedra, the oxygens of which are the vertices of phosphate groups directed away from the sheets (Fig. 6). The gallery space between the layers is connected at its narrowest point through highly irregular, flattened windows comprising six  $ScO_6$

Table 5  
Reaction stoichiometries used in the preparation of scandium phosphates templated with ethylenediamine (en)

Structure	Molar ratio of reactants						<i>t</i> (h)	<i>T</i> (°C)	Structure type
	$Sc_2O_3$	$H_3PO_4$	HF	en	$H_2O$	$H_3BO_3$			
$[(C_2N_2H_{10})_8][Sc_8(ScO_2)_4(PO_4)_4(HPO_4)_{12}] \cdot 12H_2O$ [11]	1	1.8	2	2	100	—	72	190	Framework
$[N_2C_2H_{10}][Sc_2(HPO_4)_4]$ [10]	1	2	1	1	200	—	48	190	Framework
$[(C_2N_2H_{10})_2][Sc_2F_6(HPO_4)_2]$ [13]	1	4	40	2	230	2	336	170	Framework
$[(H_3NC_2H_4NH_3)_3][Sc_3(OH)_2(PO_4)_2(HPO_4)_3(H_2PO_4)]$	1	1.7	0.5	2.2	200	—	48	190	Ribbons

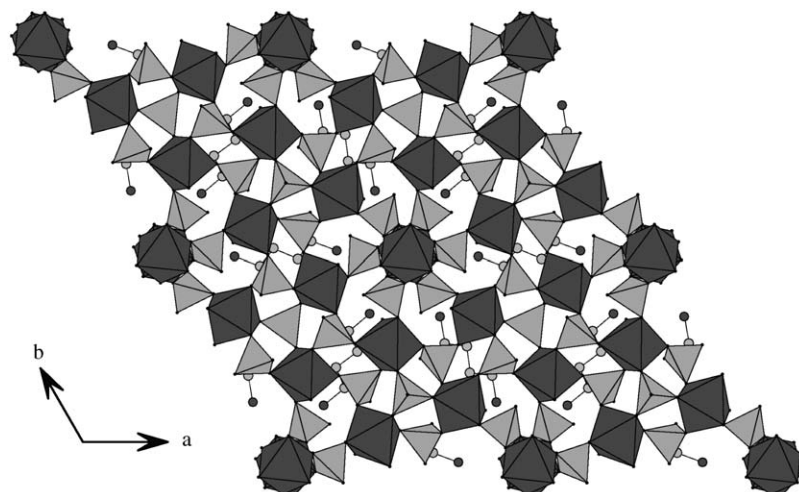


Fig. 5. The structure of **2**,  $[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_3][(\text{Sc}(\text{OH}_2)_6)\text{Sc}_2(\text{HPO}_4)_{12}(\text{PO}_4)_2]$ , projected down the  $c$ -axis. Representations as for Fig. 1.

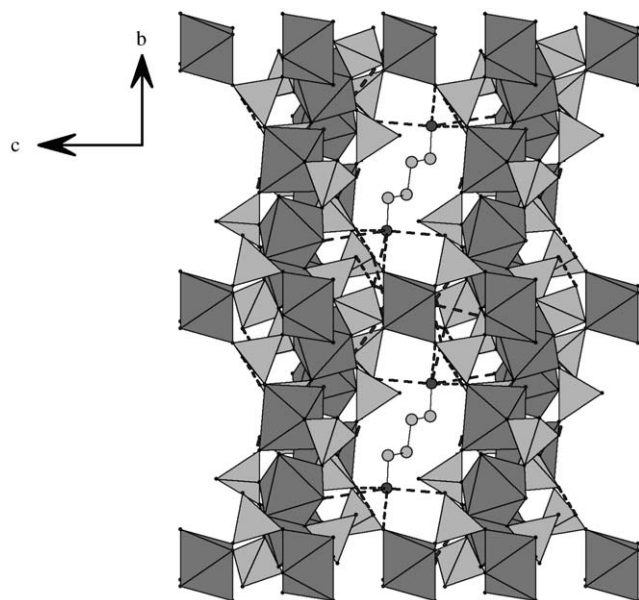


Fig. 6. Projection down  $[100]$  of  $[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_3][(\text{Sc}(\text{OH}_2)_6)\text{Sc}_2(\text{HPO}_4)_{12}(\text{PO}_4)_2]$  showing hydrogen bonding within the structure. A single orientation of two symmetry related positions for the diaminobutane, each refined with 50% occupancy, is shown. Values for the hydrogen bonding distances are given in Table 5.

octahedra (two of which are pillaring units) and six phosphate groups. The minimum and maximum O–O distances across the rings are 5.5 and 11.6 Å. The protonated template molecules occupy space between the layers, and interact with phosphate groups projecting into the interlayer space via hydrogen bonding. The interatomic distances are as expected. Sc–O bond distances are from 2.023(4) to 2.098(4) Å with the exception of Sc(1)–O(1), which corresponds to coordi-

Table 6

Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for  $[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_3][(\text{Sc}(\text{OH}_2)_6)\text{Sc}_2(\text{HPO}_4)_{12}(\text{PO}_4)_2]$  (**2**)

	$x$	$y$	$z$	$U(\text{eq})$
Sc(1)	−0.43850(9)	−0.14470(9)	0.40794(12)	10.5(4)
Sc(2)	0	0	0	8.4(6)
Sc(3)	0	0	0.5	8.4(6)
P(1)	−0.18379(12)	−0.01516(12)	0.24528(16)	11.3(4)
P(2)	−0.36825(12)	0.12651(12)	0.39689(16)	10.9(4)
P(3)	−0.6667	−0.3333	0.2157(3)	10.3(6)
O(1)	−0.2998(3)	−0.1091(3)	0.2862(4)	14.3(9)
O(2)	−0.1389(3)	−0.566(3)	0.1284(4)	10.8(9)
O(3)	−0.1072(3)	0.0306(3)	0.3757(4)	10.6(9)
O(4)	−0.1942(3)	0.0838(3)	0.1770(4)	15.9(9)
O(5)	−0.4237(4)	0.0065(3)	0.3553(5)	26.5(1)
O(6)	−0.3012(3)	0.1953(4)	0.2625(5)	24.7(11)
O(7)	−0.4506(3)	0.1647(4)	0.4318(5)	25.9(11)
O(8)	−0.2837(3)	0.1518(3)	0.5160(4)	14.2(9)
O(9)	−0.5552(3)	−0.2345(3)	0.2605(4)	13.6(9)
O(10)	−0.6667	−0.3333	0.0469(8)	23.4(18)
O(11)	−0.3101(3)	−0.0513(3)	0.5765(4)	14.3(9)
C(1A)	−0.3651(10)	0.0590(10)	0.8956(13)	17(3)
C(1B)	−0.4098(13)	−0.0551(13)	0.9329(17)	39(4)
C(2A)	−0.4622(10)	−0.0252(11)	0.9870(13)	10(3)
C(2B)	−0.4396(13)	0.0280(15)	0.9699(17)	34(4)
N(1A)	−0.2835(5)	0.0140(6)	0.8890(7)	40(2)
N(1B)	−0.2835(5)	0.0140(6)	0.8890(7)	40(2)

nated water, and displays a longer bond length (2.253(4) Å). P–O distances range from 1.495(4) to 1.593(8) Å. Solid-state  $^{31}\text{P}$  DP MAS NMR (Fig. 3b) gives four main peaks at  $\delta$  −7.2, −9.9, −11.5 and −20.4 ppm, in the ratio 6:2:4:2, rather than 6:6:2. No evidence for lower symmetry was observed from the X-ray diffraction, so the non-equivalence is attributed to the effects of proton disorder in the structure. It is

known that 12 protons are distributed over 14 sites, so it is suggested that phosphorus P(2) and P(3) all belong to HPO<sub>4</sub> groups, whereas P(1) is present both as HPO<sub>4</sub> and PO<sub>4</sub>. The unprotonated groups could be those at –20.4 ppm (with a shift similar to that observed for PO<sub>4</sub> groups in ScPO<sub>4</sub>·2H<sub>2</sub>O). <sup>45</sup>Sc NMR (Fig. 4b) gives a single broad peak, which, based on the crystallography, must include three overlapping signals from the sample. <sup>13</sup>C MAS CP NMR gives two peaks at 39.3 and 25.7 ppm which correspond to the two crystallographically unique carbon atoms.

Compound **2** is closely similar to indium [17,18] and iron(III) [19,20] phosphates prepared with imidazolium, diazabicyclooctane and sodium as structure directing agents, and isostructural with a ferric phosphate that, like **2**, is templated by diaminobutane (Table 8). The similarity in the ionic radii [9] of these trivalent cations (Fe(III), 0.645 Å; Sc, 0.745 Å; In, 0.80 Å) permit the same structure to crystallise. All of these structures are made up of similar layers, but whereas for **2** and the ferric phosphate prepared with diaminobutane each layer has an identical orientation, in the other structures there is an alternation between layers in one orientation

Table 7  
Selected bond distances and angles and probable hydrogen bonding for [(H<sub>3</sub>NC<sub>4</sub>H<sub>8</sub>NH<sub>3</sub>)<sub>3</sub>][(Sc(OH)<sub>2</sub>)<sub>6</sub>Sc<sub>2</sub>(PO<sub>4</sub>H)<sub>12</sub>(PO<sub>4</sub>)<sub>2</sub>] (**2**)

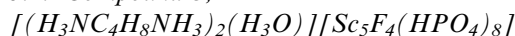
Bond	Distance (Å)	Bond	Distance (Å)
Sc(1)–O(1)	2.077(4)	P(1)–O(1)	1.530(4)
Sc(1)–O(5)	2.063(4)	P(1)–O(2)	1.514(4)
Sc(1)–O(7)	2.074(4)	P(1)–O(3)	1.540(4)
Sc(1)–O(8)	2.078(4)	P(1)–O(4)	1.587(4)
Sc(1)–O(9)	2.023(4)	P(2)–O(5)	1.495(4)
Sc(1)–O(11)	2.253(4)	P(2)–O(6)	1.578(4)
Sc(2)–O(2) × 6	2.070(4)	P(2)–O(7)	1.517(4)
Sc(3)–O(3) × 6	2.098(4)	P(2)–O(8)	1.534(4)
		P(3)–O(9) × 3	1.526(4)
		P(3)–O(10)	1.593(8)
D–H...A	d(D...A) (Å)	D–H...A	d(D...A) (Å)
O(4)–H...O(6)	2.746	N(1)–H...O(4)	2.942
O(6)–H...O(4)	2.746	N(1)–H...O(1)	2.943
N(1)–H...O(2)	2.802	N(1)–H...O(11)	3.052

Table 8  
Structures similar to compound **2** including indium and iron(III) phosphates prepared with imidazolium, diazabicyclooctane and sodium as structure directing agents, and isostructural with a ferric phosphate that, like **2**, is templated by diaminobutane

Compound	Template	Space group	<i>a</i> (Å)	<i>c</i> (Å)	Ref.
[(H <sub>3</sub> NC <sub>4</sub> H <sub>8</sub> NH <sub>3</sub> ) <sub>3</sub> ][(Sc(OH) <sub>2</sub> ) <sub>6</sub> Sc <sub>2</sub> (HPO <sub>4</sub> ) <sub>12</sub> (PO <sub>4</sub> ) <sub>2</sub> ]	1,4-Diaminobutane	<i>P</i> $\bar{3}$	13.8724	9.4351	
Na <sub>4</sub> [In <sub>8</sub> (HPO <sub>4</sub> ) <sub>14</sub> (H <sub>2</sub> O) <sub>6</sub> ].12(H <sub>2</sub> O)	Na <sup>+</sup>	<i>P</i> $\bar{3}c1$	13.85	18.43	[17]
[(C <sub>3</sub> N <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ][In <sub>8</sub> (HPO <sub>4</sub> ) <sub>14</sub> (H <sub>2</sub> O) <sub>6</sub> ](H <sub>2</sub> O) <sub>5</sub> (H <sub>3</sub> O)	Imidazole	<i>P</i> $\bar{3}$	13.859	19.186	[18]
[H <sub>3</sub> N(CH <sub>2</sub> ) <sub>4</sub> NH <sub>3</sub> ] <sub>3</sub> [Fe <sub>8</sub> (HPO <sub>4</sub> ) <sub>12</sub> (PO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ]	1,4-Diaminobutane	<i>P</i> $\bar{3}$	13.495	9.396	[19]
[H <sub>3</sub> N(C <sub>2</sub> H <sub>4</sub> ) <sub>3</sub> NH <sub>3</sub> ] <sub>3</sub> [Fe <sub>8</sub> (HPO <sub>4</sub> ) <sub>12</sub> (PO <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> ]	Dabco	<i>P</i> $\bar{3}c1$	13.5274	19.2645	[20]

and layers related by a *c* glide. This results in a doubling of the *c*-axis repeat and a change in the space group symmetry from *P* $\bar{3}$  to *P* $\bar{3}c1$  in those structures. The cause of this change in stacking is due to the different organic amine used as a structure directing agent. The H-bonding arrangement with diaminobutane favours the stacking sequence in which each of the layers is crystallographically identical. TGA shows a weight loss in a single step of 18.9% between 250 and 600 °C (theoretical loss from dehydration, 5.2%, from loss of organic, 13.0%). The product after heating is amorphous.

### 5.2. Compound **3**,



Adding HF to the synthesis gels that contain diaminobutane results in the crystallisation of a different phase, compound **3**. Statistical analysis of the diffraction data clearly indicates a centrosymmetric structure [mean  $|E^*E - 1| = 0.966$ ; expected values are 0.968 for centrosymmetric and 0.736 for non-centrosymmetric] and the structure was thus solved and refined in *C2/m*. Comparison of the simulated and measured X-ray powder diffraction patterns (not shown) indicated the material to be phase pure. Semi-quantitative energy dispersive X-ray analysis indicated the sample contained fluorine, and refinement of sites originally identified as oxygens gave a more satisfactory refinement, in terms of their thermal parameters, when refined as fluorine atoms. The diaminobutane molecules are taken to be fully protonated. Initially, structure solution gave layers, as shown in Figs. 7 and 8, with two crystallographically distinct scandium sites and three distinct phosphorus sites, the latter in the ratio P(3):P(2):P(1) = 2:1:1. However, solid-state <sup>31</sup>P DP NMR shows four peaks in the ratio 1:1:1:1 (Fig. 3c). Closer inspection of the structure indicated high thermal parameters associated with P(3) and O(9) and O(10), and improved refinement of the single crystal data was obtained by considering the structure to contain ScO<sub>4</sub>F<sub>2</sub> octahedra with two different orientations, or tilts, as shown in Fig. 9a and b. The differently tilted octahedra, which are associated with different positions of the attached phosphate



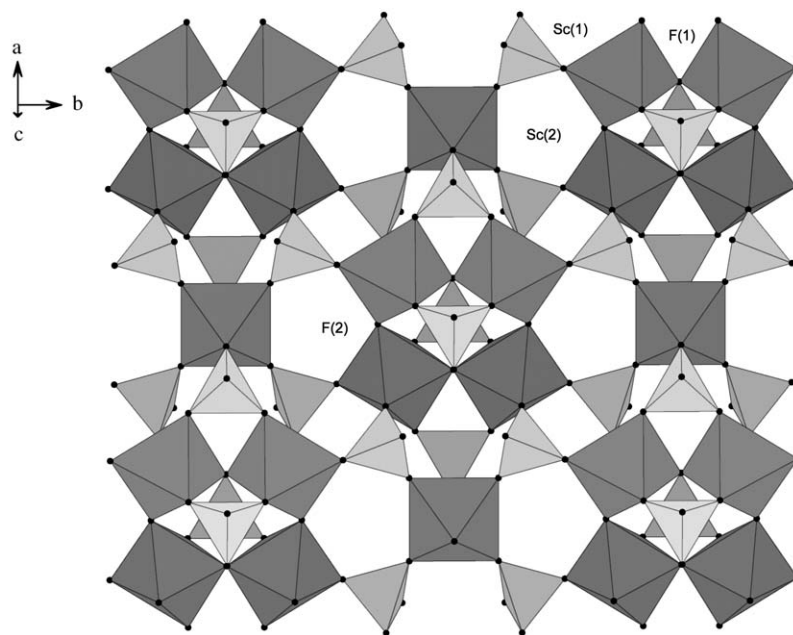


Fig. 7. A view of the 'average' structure of compound **3**,  $[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_2(\text{H}_3\text{O})][\text{Sc}_5\text{F}_4(\text{HPO}_4)_8]$ , viewed onto (001) plane. For the refined structure with tilted  $\text{Sc}(2)\text{O}_6$  octahedra, see Fig. 9.

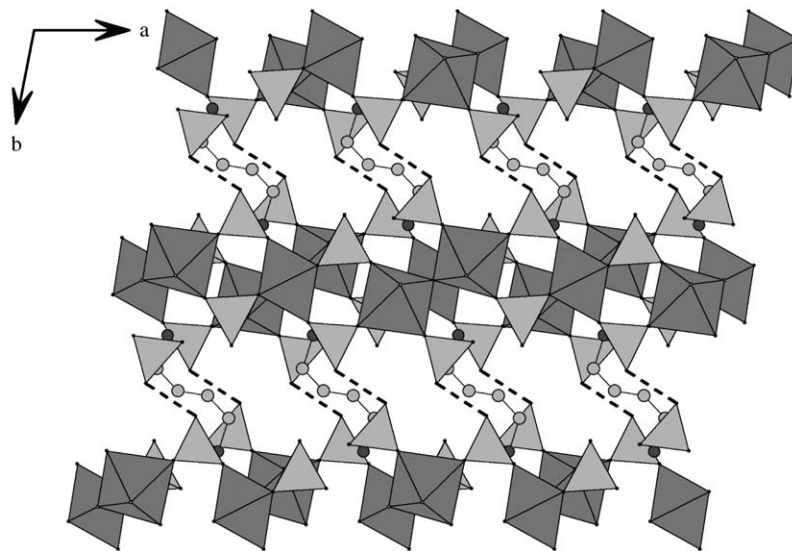


Fig. 8. Projection of the 'average' structure of compound **3** along [010], indicating how the layers are bridged by protonated diaminobutane molecules.

tetrahedra, are thought to be disordered within domains of crystals of **3**, and result in crystallographic non-equivalence of some phosphorus and oxygen atoms in the structure. Details of the crystal structure are given in Tables 9 and 10.  $^{45}\text{Sc}$  NMR (Fig. 4c) shows two broad overlapping peaks, consistent with the crystallography.  $^{13}\text{C}$  MAS CP NMR shows two peaks at 42.19 and 25.7 ppm corresponding to the two chemically distinct carbon atoms in the template. The b.v.s. calculations

were performed to locate protons on oxygen atoms of the framework. Oxygens O(2), O(3), O(6) and O(21), which do not bridge Sc and P, have b.v.s. values of 1.06, 1.24, 1.11 and 1.33, respectively. O(3) is close to O(6), 2.65 Å and is taken to H-bond to it, sharing a proton. All the phosphate tetrahedra are therefore thought to be of the form  $\text{PO}_4\text{H}$ . In addition, O(21), which is 50% occupied, is taken to belong to protonated water molecules, giving the unit cell formula

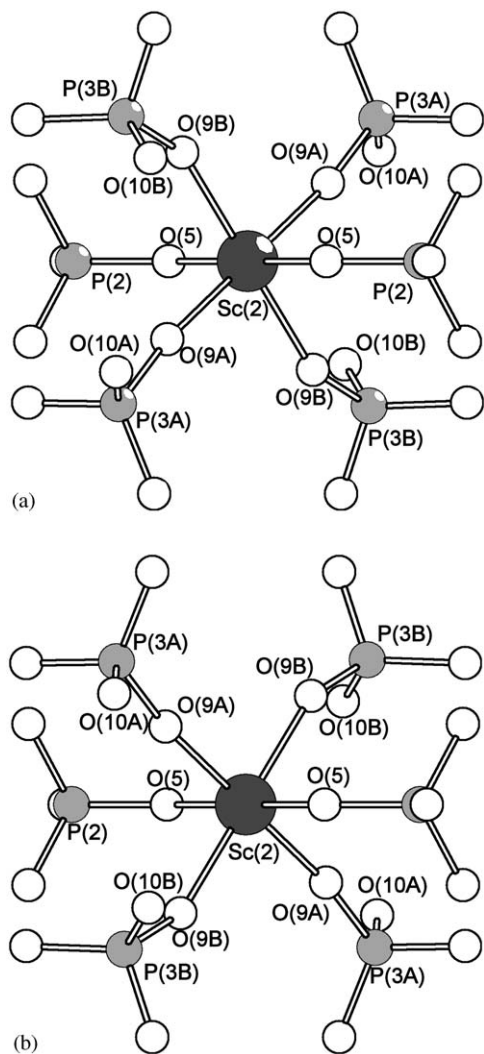


Fig. 9. Projection down [001] of structure 4,  $[\text{C}_6\text{H}_{11}\text{NH}_3][\text{ScF}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$ , showing both conformations which are possible due to tilts around P(3) and Sc(2).

$[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_4(\text{H}_3\text{O})_2][\text{Sc}_{10}\text{F}_8(\text{HPO}_4)_{16}]$ . CHN analysis, wt%, calculated: C, 7.57%; H, 3.10%; N, 4.42%; measured: C, 7.34%; H, 2.89%; N, 4.27%.

The structure is made up of scandium fluoride phosphate layers bridged by protonated diaminobutane molecules. The final refined structure is therefore a layered structure, each layer consisting of isolated  $\text{ScO}_6$  octahedra linked via phosphate groups to tetramers of corner-sharing  $\text{ScO}_4\text{F}_2$  octahedra, the latter themselves linked through fluoride ions. The isolated  $\text{ScO}_6$  octahedra are linked to the tetrameric squares through corner-sharing  $\text{PO}_4$  tetrahedra which bond to scandiums by three apical oxygens, the remaining oxygens projecting into the interlayer space. In addition, one phosphate group is attached to the tetramer of  $\text{ScO}_4\text{F}_2$  octahedra by two apical oxygens, the remaining two groups projecting into the interlayer space. The layers are

Table 9

Fractional atomic coordinates, occupancies and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_2(\text{H}_3\text{O})][\text{Sc}_5\text{F}_4(\text{HPO}_4)_8]$  (3)

	<i>x</i>	<i>y</i>	<i>z</i>	Occ.	<i>U</i> (eq)
Sc(1)	0.38292(10)	0.62566(9)	0.09594(12)	1	9.7(4)
Sc(2)	0	0.5	0	1	8.6(6)
P(1)	0.56194(19)	0.5	0.3025(2)	1	7.8(5)
P(2)	0.2166(2)	0.5	0.2433(3)	1	13.4(6)
P(3 <sup>a</sup> )	0.1609(4)	0.6504(4)	−0.1510(6)	0.5	5.8(18)
P(3 <sup>b</sup> )	0.1514(5)	0.6526(4)	−0.1322(6)	0.5	7.9(19)
O(1)	0.5070(4)	0.5853(3)	0.2460(5)	1	13.3(10)
O(2)	0.6791(6)	0.5	0.2731(7)	1	17.2(16)
O(3)	0.5814(5)	0.5	0.4561(6)	1	9.9(14)
O(4)	0.2702(4)	0.5850(4)	0.2039(5)	1	17.5(11)
O(5)	0.0984(6)	0.5	0.1885(7)	1	18.4(16)
O(6)	0.2251(5)	0.5	0.4002(7)	1	14.7(15)
O(7)	0.2729(5)	0.6492(4)	−0.0798(6)	1	26.5(13)
O(8)	0.1162(5)	0.7448(4)	−0.1653(6)	1	29.9(14)
O(9 <sup>a</sup> )	0.0998(8)	0.5822(8)	−0.0827(11)	0.5	16(2)
O(9 <sup>b</sup> )	0.0813(9)	0.6147(8)	−0.0472(11)	0.5	18(2)
O(10 <sup>a</sup> )	0.1634(9)	0.6166(7)	−0.2942(10)	0.5	13(2)
O(10 <sup>b</sup> )	0.1210(13)	0.6088(10)	−0.2783(15)	0.5	42(4)
O(21)	0.0013(19)	0.5	−0.432(2)	0.5	58(6)
F(1)	0.3886(4)	0.5	0.0196(5)	1	10.6(11)
F(2)	0.5	0.6669(4)	0	1	11.6(12)
C(1)	0.1103(7)	0.7272(6)	0.3906(9)	1	30(2)
C(2)	0.1978(8)	0.7758(7)	0.4895(10)	1	37(2)
N(1)	0.1241(5)	0.7258(5)	0.2442(7)	1	25.8(16)

<sup>a,b</sup>Refers to atoms associated with the two orientations of the P(3) phosphate tetrahedra.

Table 10

Selected bond distances and angles and probable hydrogen bonding scheme for  $[(\text{H}_3\text{NC}_4\text{H}_8\text{NH}_3)_2(\text{H}_3\text{O})][\text{Sc}_5\text{F}_4(\text{HPO}_4)_8]$  (3)

Bond	Distance (Å)	Bond	Distance (Å)
Sc(1)–F(1)	2.035(3)	P(2)–O(4) × 2	1.533(5)
Sc(1)–F(2)	2.042(2)	P(2)–O(5)	1.513(8)
Sc(1)–O(1)	2.074(5)	P(2)–O(6)	1.582(7)
Sc(1)–O(4)	2.073(5)	P(3A)–O(7)	1.543(8)
Sc(1)–O(7)	2.086(6)	P(3A)–O(8)	1.501(8)
Sc(1)–O(8)	2.156(6)	P(3A)–O(9A)	1.534(8)
Sc(2)–O(5) × 2	2.085(7)	P(3A)–O(10A)	1.552(9)
Sc(2)–O(9A) × 2	2.068(10)	P(3B)–O(7)	1.481(8)
Sc(2)–O(9B) × 2	2.108(11)	P(3B)–O(8)	1.517(8)
P(1)–O(1) × 2	1.514(4)	P(3B)–O(9B)	1.533(12)
P(1)–O(2)	1.591(8)	P(3B)–O(10B)	1.580(12)
P(1)–O(3)	1.537(7)		

bridged by protonated diaminobutane molecules, each  $-\text{NH}_3^+$  group of which fits into recesses between four phosphate tetrahedra that project out from the layers. As a result, layers are stacked along the *c*-axis. Protonated water molecules also occupy this space.

TGA shows a single weight loss of ca. 23% between 200 and 600 °C (theoretical, amine loss 14.2%, water loss 1.4%, HF loss 6.3%) and the product after heating is amorphous.

### 5.3. Structure 4, $[C_6H_{11}NH_3][ScF(HPO_4)(H_2PO_4)]$

Structure 4 was prepared using cyclohexylamine as the added primary amine from a synthesis gel including fluoride ions and illustrates how a primary amine can direct the scandium phosphate crystallisation. The crystals of 4 were small and could not be analysed on a laboratory diffractometer, so data were collected on a small crystal at station 9.8 at the Daresbury synchrotron. The structure was solved by direct methods and refined using the program SHELXTL. In addition to 4, the sample was also found to contain the known phase  $ScPO_4 \cdot 2H_2O$  by analysis of the X-ray powder diffraction pattern (not shown). Elemental analyses indicate a C:N ratio of 6:1, confirming that the amine is included intact into the layered scandium phosphate. Fluoride was identified as a constituent of the structure from EDX analysis and atoms linking the chain of scandium atoms were attributed as fluorine on the basis of their temperature factors. The final crystal structure is described in Tables 11 and 12. The b.v.s. calculations suggest that protons are associated with oxygens O(2) and O(4) on P(1) phosphate tetrahedra (b.v.s. 1.17 and 1.18), and with O(8) on P(2) phosphate tetrahedra (b.v.s. 1.08), giving the formula  $[C_6H_{11}NH_3][ScF(HPO_4)(H_2PO_4)]$ . Solid-state  $^{31}P$  NMR (Fig. 3d) of the compound 4/ $ScPO_4 \cdot 2H_2O$  mixture shows three peaks,

Table 11  
Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $[C_6H_{11}NH_3][ScF(HPO_4)(H_2PO_4)]$  (4)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Sc(1)	0.02949(7)	0.35299(5)	0.25071(3)	10.72(15)
P(1)	−0.22297(11)	0.36277(7)	0.35345(3)	10.9(2)
P(2)	−0.00874(11)	0.59964(7)	0.20458(3)	13.3(2)
O(1)	−0.0728(3)	0.39581(19)	0.32057(9)	14.2(6)
O(2)	−0.1648(3)	0.27809(18)	0.39226(8)	14.0(6)
O(3)	−0.3762(3)	0.32023(18)	0.32269(8)	12.7(6)
O(4)	−0.2838(3)	0.45325(19)	0.38852(9)	16.9(6)
O(5)	0.0715(3)	0.51085(19)	0.23471(8)	12.8(6)
O(6)	0.0033(3)	0.6999(2)	0.23493(9)	17.7(7)
O(7)	0.0682(3)	0.60839(19)	0.15195(9)	15.7(1)
O(8)	−0.2092(3)	0.57303(19)	0.19588(9)	20(7)
F(1)	−0.2197(2)	0.35457(16)	0.22396(7)	12.3(4)
N(1)	0.0022(4)	0.6282(2)	0.36060(11)	17(8)
C(1)	0.0672(4)	0.6373(3)	0.41435(14)	20.3(10)
C(2)	0.1592(5)	0.5363(3)	0.42908(2)	28.5(11)
C(3)	0.2377(5)	0.5438(4)	0.48171(15)	30(11)
C(4)	0.3631(5)	0.6338(3)	0.48499(14)	27(11)
C(5)	0.2757(5)	0.7350(4)	0.47055(14)	27.9(11)
C(6)	0.1926(5)	0.7308(3)	0.41729(14)	24.4(11)

Table 12  
Selected bond distances and angles for  $[C_6H_{11}NH_3][ScF(HPO_4)(H_2PO_4)]$  (4)

Bond	Distance (Å)	Bond	Distance (Å)
Sc(1)–O(6)	2.019(3)	P(1)–O(1)	1.504(2)
Sc(1)–F(1)	2.031(2)	P(1)–O(2)	1.558(2)
Sc(1)–F(1)	2.035(2)	P(1)–O(3)	1.526(2)
Sc(1)–O(1)	2.072(2)	P(1)–O(4)	1.557(2)
Sc(1)–O(5)	2.099(3)	P(2)–O(5)	1.523(3)
Sc(1)–O(3)	2.106(2)	P(2)–O(6)	1.524(3)
		P(2)–O(7)	1.508(2)
		P(2)–O(8)	1.586(3)

at −2.5, −15.4 and −18.6 ppm. The peak at −18.6 ppm can be attributed to the  $ScPO_4 \cdot 2H_2O$  impurity.  $^{45}Sc$  NMR (Fig. 4d) gives two peaks with quadrupolar line shapes, distributed around chemical shift values of 23.8 and −15.5 ppm. The first of these is from the  $ScPO_4 \cdot 2H_2O$  impurity.

Compound 4 is a layered structure. Each layer is built from corner-sharing chains of  $ScO_4F_2$  octahedra (the shared corners being the trans-fluoride ion) running parallel to the *a*-axis (Fig. 10). Adjacent chains are linked along *b* by phosphate tetrahedra, the remaining 2 oxygens of the phosphate group projecting into the interlayer space. In addition, adjacent  $ScO_4F_2$  octahedra along the chain are bridged by phosphate tetrahedra by sharing two apices. This results in undulating chains of  $ScO_4F_2$  octahedra. The remaining two unbound oxygens of these intrachain phosphate groups also project into the interlayer space. The cyclohexylamine molecules link via the protonated amine groups to the negatively charged layers (Fig. 11). The cyclohexyl groups are in the chair configuration, with the amine groups in equatorial positions: amine groups from adjacent layers project into the interlayer space.

## 6. Summary

The structures described here further demonstrate the structural versatility of scandium in organically templated scandium and scandium fluoro-phosphate/hydrogenphosphates. Scandium can exist as ‘isolated’  $ScO_6$  or  $ScO_4F_2$  octahedra, 2, 3, also structures in [12,13]; as corner-sharing trimers, 1; as tetramers in which the scandiums are bridged by fluoride ions; and as chains, bridged by fluoride ions, 4 (Fig. 12). Such geometries, or combinations of them, can be connected by one, two, three and four connected phosphate groups into chain, layer and framework structures. The solid-state NMR of scandium for these samples shows a typical range of quadrupolar peak shapes. Overlap between the resonances from crystallographically different sites make a

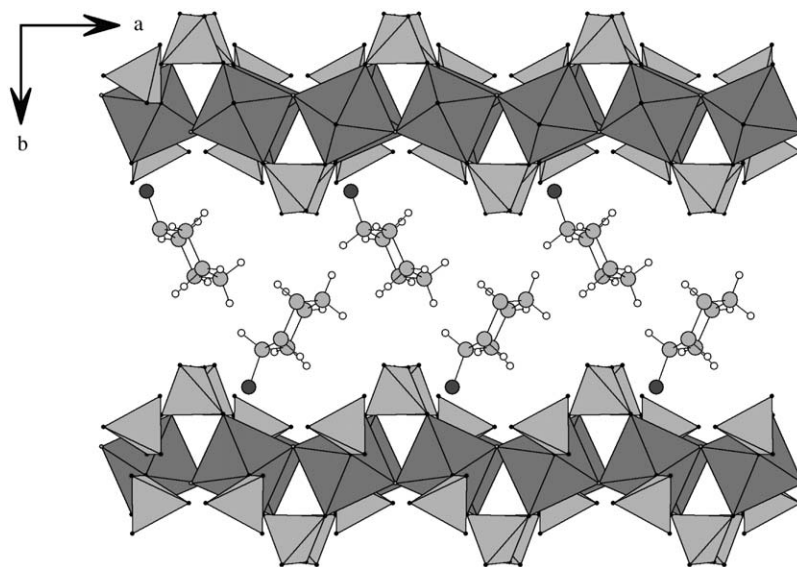


Fig. 10. Projection down [010] of structure 4,  $[\text{C}_6\text{H}_{11}\text{NH}_3][\text{ScF}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$ , showing undulating layers perpendicular to the  $c$ -axis separated by cyclohexylamine molecules. Symmetry related positions for statically disordered cyclohexylamine molecules have been omitted for clarity.

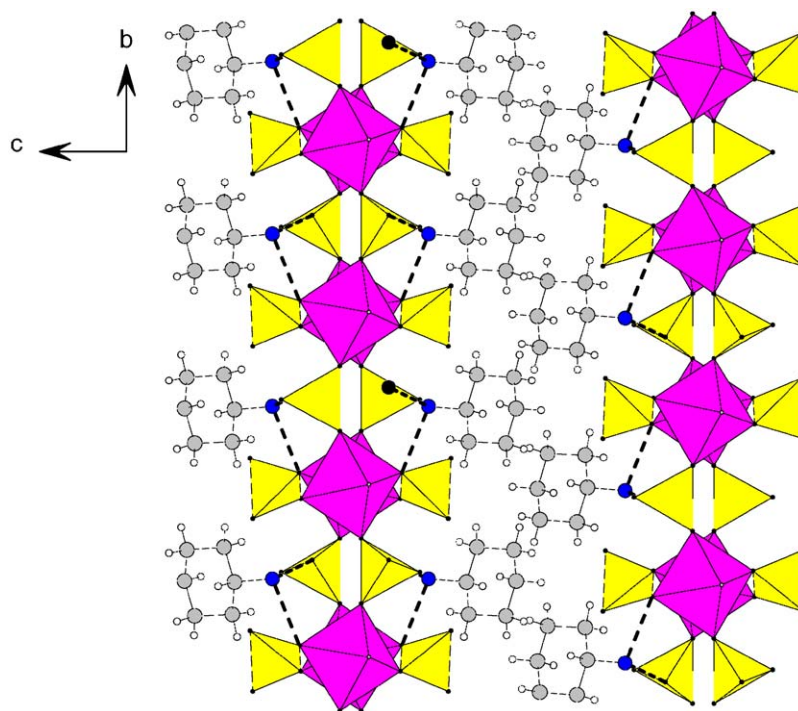


Fig. 11. Projection down [100] of  $[\text{C}_6\text{H}_{11}\text{NH}_3][\text{ScF}(\text{HPO}_4)(\text{H}_2\text{PO}_4)]$  (4), showing the sheet-like structure separated by cyclohexylamine molecules. Postulated hydrogen bonds shown.

full line shape analysis difficult and further two-dimensional studies are in progress to assign the peaks to the different scandium environments ( $\text{ScO}_6$ ,  $\text{ScO}_5\text{OH}$ ,  $\text{ScO}_4\text{F}_2$ ,  $\text{Sc}(\text{OH})_2\text{O}_4$ , etc.). The  $\text{ScO}_6$  or  $\text{ScO}_4\text{F}_2$  octahedra can be thought to be linked via phosphate groups to give secondary building units (SBUs) within

the structures. Key SBUs within the four structures are shown in Fig. 13. In structure 1, the scandium trimers are linked in ribbons; in structure 2 layers are attached through pillars to give central columns of octahedra strictly alternating with phosphate groups; tetramers and isolated scandium octahedra are linked by

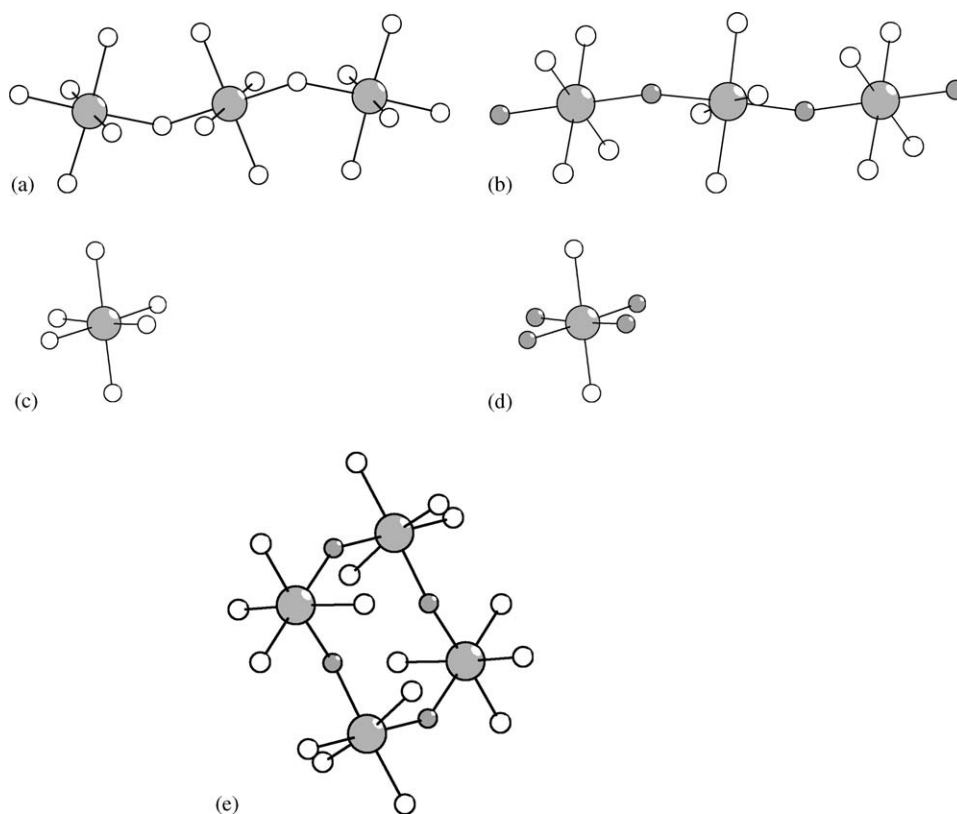


Fig. 12. Different scandium environments found in reported scandium phosphate structures: (a)  $\text{Sc}_3\text{O}_{16}$  trimers [structure 1], (b)  $-(\text{ScF}_2\text{O}_4)-$  chains [structure 4], (c)  $\text{ScO}_6$  [structure 2], (d)  $\text{ScF}_4\text{O}_2$  [14] and (e)  $\text{Sc}_4\text{F}_4\text{O}_{16}$  tetramers [structure 3].

phosphate groups into strips in **3** (these connect to give layers); structure **4** is built of chains of scandium octahedra cross-linked by phosphate groups.

Primary amines have been shown to be particularly effective in templating scandium phosphate structures. Almost all reported scandium phosphates have been prepared using primary amines, except for the framework structure prepared with diazabicyclooctane by Park et al. [13]. There are now five reported structures prepared using diaminoethane, with and without additional fluoride, which further increases the complexity of structures that can form. Under the conditions we employed for synthesis, secondary and tertiary amines and alkylammonium hydroxides did not give novel organically templated scandium phosphates. It is likely that the additional hydrogen bonding that is possible using primary amines favours their interactions with non-framework solids. The smaller primary amines will have more protons available for hydrogen bonding per nitrogen and are also sterically favoured to achieve a close approach to the phosphate groups.

While it is possible to prepare scandium phosphate-based frameworks, the presence of species such as fluoride, hydroxyl and water that make up additional scandium coordination sites on such solids renders the

materials so far prepared unstable to thermal treatment, probably because scandium becomes unstable with less than six-fold coordination.

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### Appendix A. Supplementary information

The online version of this article contains additional supplementary data. Please visit [doi:10.1016/j.jssc.2005.03.012](https://doi.org/10.1016/j.jssc.2005.03.012).

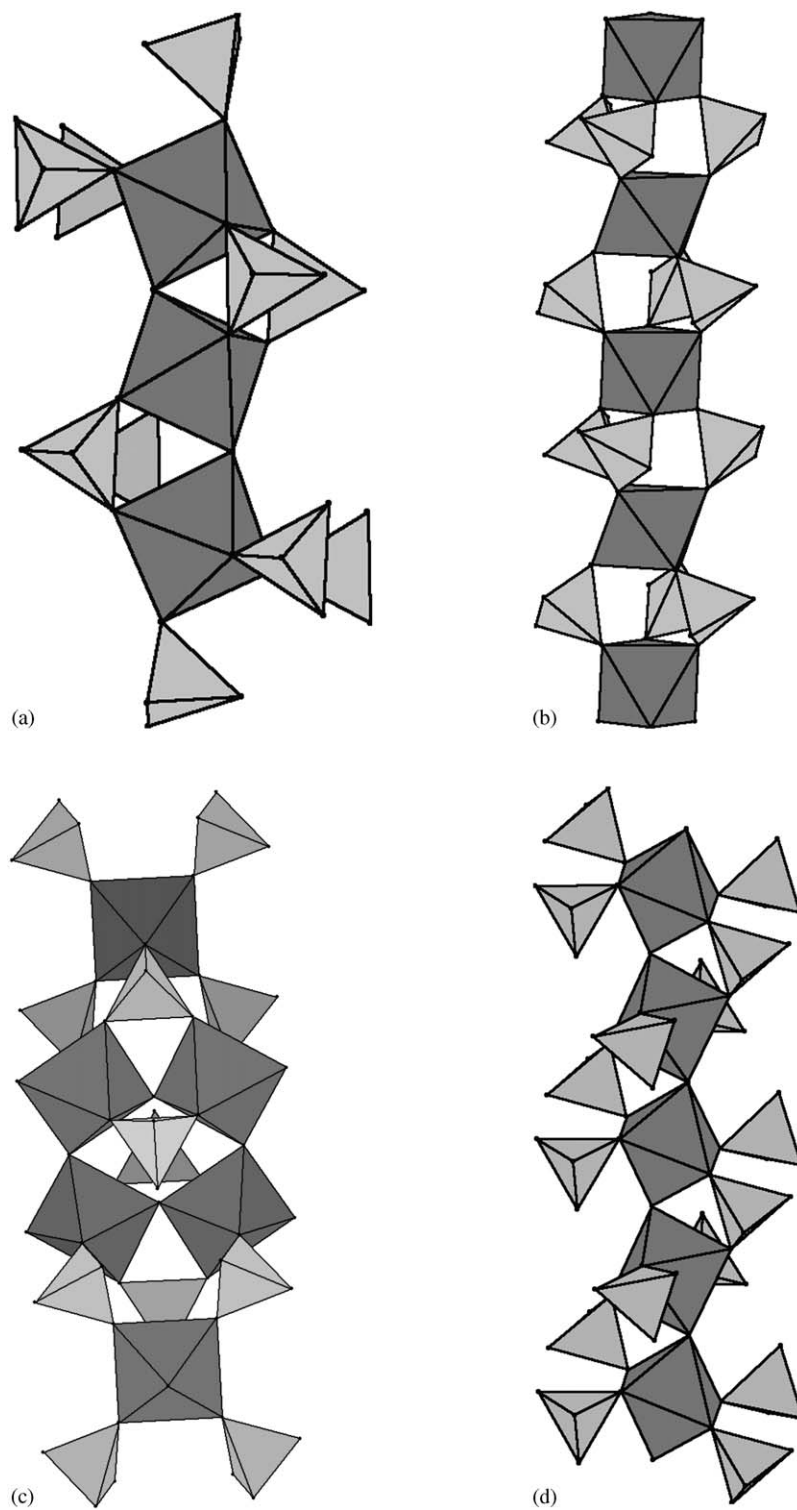


Fig. 13. Secondary building units comprising scandium-centred octahedra and phosphate tetrahedra in the structures 1–4 (a–d).

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