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Synthesis and crystal structure of MIL-14: a new layered fluoroaluminophosphate templated with tris(2-aminoethylamine): $Al_2(HPO_4)_3F_2{\cdot}H_2PO_4{\cdot}N_4C_6H_{21}$

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MIL-14, formulated $Al_2(HPO_4)_3F_2{\cdot}H_2PO_4{\cdot}N_4C_6H_{21}$, is a new layered fluoroaluminophosphate obtained by hydrothermal synthesis using tris(2-aminoethyl)amine as a template. It crystallizes in the monoclinic space group $P2_1/c$ with $a=13.154$, $b=9.518$, $c=17.889$ Å, $\beta=106.165°$ and $Z=4$. Its structure consists of an alternation along [100] direction of inorganic layers interleaved by amine phosphates. The structural unit of the inorganic layer contains five polyhedra: two aluminium octahedra and three HPO_4 tetrahedra. Strong hydrogen bonds ensured framework stability.

1 Introduction

The chemistry of the microporous solids has expanded during the last fifteen years. The first step was the discovery in 1982 by Wilson *et al.*[1] of a novel class of microporous aluminophosphate materials ($AlPO_4$-*n*). Subsequently, the addition of fluoride to the starting mixture by Guth *et al.*[2] allowed new syntheses in acidic media. Using this method, an overall series of fluorometallophosphates, initially labeled ULM-*n* (for Université Le Mans) and then MIL-*n* (for Materials of Institute Lavoisier), has been developed in the system M–P–F–amine–H_2O, with M = Al, Ga, Fe, Ti and V.[3–7] The wide range of the structures of microporous compounds discovered in the group demonstrates the influence of the templating agent as well as fluorine during the hydrothermal synthesis, allowing for the proposal of a mechanism of formation.[8] Here is presented the preparation and the structural characterization of a new fluoroaluminophosphate, $Al_2(HPO_4)_3F_2{\cdot}H_2PO_4{\cdot}N_4C_6H_{21}$ or MIL-14, formed with branched tris(2-aminoethyl)amine (tren). This phase is the third obtained with tren as a structure directing agent. Indeed, two fluorogallophosphates were discovered: ULM-8[9] with tren as a simple structure directing agent, and tren–GaPO[10] which uses a mixture of tren and pyridine as the template. Here, as for ULM-8, the exclusive use of tren leads to a two-dimensional compound, MIL-14.

2 Experimental

Synthesis

The title compound was obtained by hydrothermal synthesis in a 23 ml Teflon-lined Parr bomb under autogenous pressure at 180 °C for 48 h from a 2:2:2:0.15:80 (molar ratio) mixture of aluminium hydroxide [$Al(OH)_3$, Prolabo R.P. Normapur, 85%], phosphoric acid (H_3PO_4, Prolabo R.P. Normapur, 85%), hydrofluoric acid (HF, Prolabo R.P. Normapur, 48%), tris(2-aminoethyl)amine (Aldrich 99%) and distilled water. The initial pH was 1 and was raised to 3 in the final medium. The crystalline product was filtered off, washed with distilled water and dried at room temperature. The resulting mixture was observed by scanning electron microscope at 15 kV (JEOL 5800LV instrument) and revealed the presence of a powder (unknown phase), and plate-like crystals stacked in aggregates of *ca.* 1 mm diameter (Fig. 1) which corresponds to the title compound. Crystals of MIL-14 were easily isolated and therefore, the X-ray powder diffraction (XRD) data from crushed crystals were collected on a Siemens D5000 diffractometer with Cu-Kα radiation (Fig. 2).

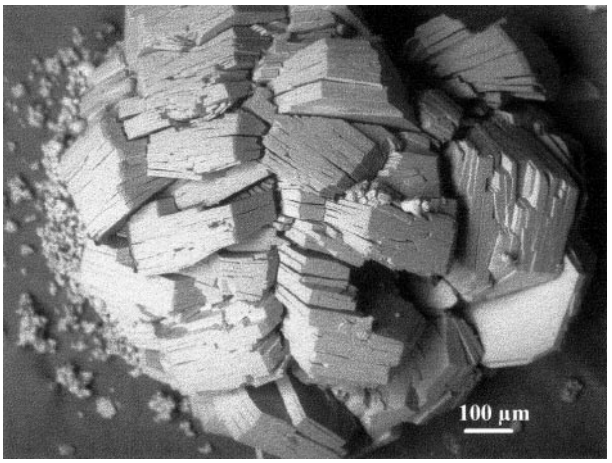

Fig. 1 Scanning electron micrograph of MIL-14.

Thermogravimetric analysis of MIL-14 was performed on a TA-Instrument type 2050 thermoanalyser under a nitrogen gas flow with a heating rate of 5 °C min^{-1} between 50 and 600 °C. The thermogram reveals a single weight loss of 25% (theoreti-

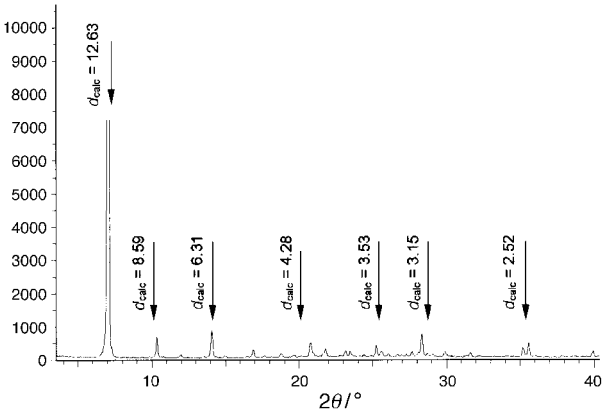

Fig. 2 X-Ray powder pattern of MIL-14 (*d*-spacings (Å) of the mean reflections are given in the figure).

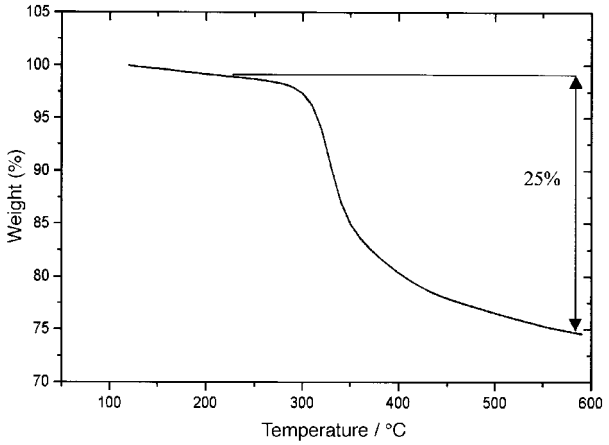

Fig. 3 Thermogravimetric analysis of MIL-14.

cal = 24%) above 250 °C, corresponding to the loss of amine (Fig. 3). The final residue at 600 °C is amorphous.

Structure determination

A suitable platelet shape single crystal was isolated for X-ray diffraction analysis. The intensity data were performed on a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector. The crystal-to-detector distance was 45 mm allowing for the data collection up to 60° (2θ). Slightly more than one hemisphere of data was recorded and the acquisition time per frame was 30 s. Crystal data and details of the data collection are given in Table 1. An empirical absorption correction was applied by using the SADABS program.[11] The structure was solved in the space group $P2_1/c$ by direct methods using the TREF option of the SHELX-TL program.[12] The heaviest atoms (Al and P) were easily located and all the non-hydrogen atoms were found from the difference Fourier map analysis. The location of fluorine atoms was deduced from considerations of the isotropic thermal parameters and is in good agreement with the chemical analysis ($\%F_{theoretical} = 2\%$, $\%F_{analysis} = 1.9$). The Fourier map analysis indicated five residues around terminal oxygens of PO_4 groups, three of them belonging to the three phosphates of the inorganic layer and the two others belonging to the isolated phosphate. The H atoms of the amine were refined with restraints applied to maintain the C–H and N–H geometries. The final refinement factors converged to $R_1 = 0.037$, $wR_2 = 0.096$ for 5530 reflections [$I > 2\sigma(I)$]. The resulting atomic coordinates, including isotropic temperature parameters, hydrogen coordinates and a selection of bond distances and angles, are given in Tables 2, 3 and 4 respectively.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/131.

Table 1 Crystal data and structure refinement for MIL-14

Identification code	MIL-14
Empirical formula	$C_6H_{26}Al_2F_2N_4O_{16}P_4$
M	626.15
T/K	293(2)
λ/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a/Å	13.1538(1)
b/Å	9.5185(1)
c/Å	17.8893(2)
β/°	106.165(1)
V/Å^3, Z	2151.27(3), 4
D_c/g cm^{-3}	1.933
μ/mm^{-1}	0.536
$F(000)$	1128
Crystal size/mm	$0.44 \times 0.140 \times 0.020$
θ range for data collection/°	1.61–29.64
Limiting indices	$-18 \leqslant h \leqslant 14$, $-13 \leqslant k \leqslant 11$, $-21 \leqslant l \leqslant 24$
Reflections collected	14168
Independent reflections (R_{int})	5530 (0.0256)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5530/0/331
Goodness-of-fit on F^2	0.672
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0373$, $wR2 = 0.0963$
R indices (all data)	$R1 = 0.0507$, $wR2 = 0.1124$
Extinction coefficient	0.0007(2)
Largest diff. peak and hole/e Å^{-3}	1.149 and −0.491

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for MIL-14

Atom	x	y	z	U_{eq}[a]
P(1)	4120(1)	1202(1)	548(1)	11(1)
P(2)	6341(1)	2862(1)	−592(1)	1(1)
P(3)	6532(1)	5148(1)	−2468(1)	9(1)
P(4)	9361(1)	6975(1)	−2827(1)	21(1)
Al(1)	4638(1)	1872(1)	−1039(1)	1(1)
Al(2)	5094(1)	2298(1)	−2842(1)	1(1)
F(1)	5375(1)	1994(2)	−1786(1)	13(1)
F(2)	5670(1)	2809(2)	−371(1)	20(1)
O(1)	7738(2)	5052(2)	−2001(1)	16(1)
O(2)	6218(1)	3616(2)	−2631(1)	15(1)
O(3)	6480(1)	5954(2)	−3223(1)	14(1)
O(4)	2997(2)	1103(2)	719(1)	21(1)
O(5)	7593(2)	−574(2)	−2528(1)	21(1)
O(6)	4659(2)	−192(2)	705(1)	20(1)
O(7)	6106(1)	970(2)	−2942(1)	13(1)
O(8)	8816(2)	7199(2)	−2194(1)	25(1)
O(9)	10158(2)	5716(3)	−2632(2)	38(1)
O(10)	8486(2)	6520(3)	−3593(2)	43(1)
O(11)	5942(1)	5884(2)	−1964(1)	14(1)
O(12)	4756(2)	2647(2)	−3923(1)	14(1)
O(13)	3845(1)	1633(2)	−309(1)	14(1)
O(14)	5908(1)	−1312(2)	−2252(1)	14(1)
O(15)	6038(2)	−1360(2)	−3639(1)	16(1)
O(16)	9983(2)	8197(2)	−2994(1)	28(1)
N(1)	8241(2)	3275(3)	230(1)	20(1)
N(2)	6517(2)	5409(3)	−93(2)	28(1)
N(3)	6879(2)	1500(3)	894(2)	25(1)
N(4)	8156(2)	2021(3)	−1735(2)	26(1)
C(1)	11341(2)	7763(3)	−844(2)	24(1)
C(2)	7926(2)	2951(3)	−3646(2)	24(1)
C(3)	8386(3)	10277(3)	−4475(2)	26(1)
C(4)	2356(3)	4254(3)	17(2)	31(1)
C(5)	8692(3)	3093(4)	−422(2)	33(1)
C(6)	1838(6)	−1893(6)	927(3)	83(2)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

3 Results

Description of the structure

MIL-14, formulated $Al_2(HPO_4)_3F_2{\cdot}H_2PO_4{\cdot}N_4C_6H_{19}$, presents a layered-structure with the alternation of inorganic layers, amine and isolated phosphates along the [100] direction (Fig. 4).

The inorganic layer (Fig. 5) is built up from dimers of aluminium octahedra linked together by sharing corners with HPO_4 tetrahedra forming *trans* Al(2)–Al(1)–HP(1)O_4 chains, running parallel to the c axis. Satellites composed by four HPO_4 tetrahedra are grafted onto the dimer (Fig. 6).

On both sides of the chain, one HPO_4 satellite bridges the two aluminium octahedra of the dimer and shares a third vertex with an aluminium octahedron of another dimer, while the other HPO_4 satellite shares one vertex with one octahedron of the dimer and two vertices with another dimer. The connection between the dimers *via* HPO_4 tetrahedra leads to

Table 3 Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for MIL-14

Atom	x	y	z	U_{eq}
H(1P)	7865(38)	−1274(54)	−2422(28)	51
H(2P)	8098(37)	5792(54)	−2064(27)	52
H(3P)	3087(35)	1106(50)	1194(27)	46
H(4P)	10020(43)	5078(58)	−2464(32)	60
H(5P)	7837(50)	6641(68)	−3589(36)	85
H(N2A)	6409(5)	4493(5)	−180(15)	41
H(N2B)	6104(2)	5890(21)	−490(10)	41
H(N2C)	6360(6)	5643(25)	344(6)	41
H(N3A)	6932(5)	585(6)	811(13)	38
H(N3B)	6677(10)	1947(19)	439(6)	38
H(N3C)	6403(5)	1642(24)	1155(7)	38
H(N4A)	8749(9)	2441(24)	−1763(2)	39
H(N4B)	7601(11)	2530(22)	−1990(4)	39
H(N4C)	8116(20)	1170(3)	−1948(4)	39
H(C1A)	11252(2)	8657(3)	−610(2)	29
H(C1B)	10652(2)	7460(3)	−1162(2)	29
H(C2D)	7830(2)	2056(3)	−3415(2)	28
H(C2E)	8240(2)	3601(3)	−3228(2)	28
H(C3D)	8260(3)	10243(3)	−3967(2)	32
H(C3E)	9112(3)	9991(3)	−4415(2)	32
H(C4D)	2232(3)	4288(3)	526(2)	38
H(C4E)	2206(3)	3307(3)	−184(2)	38
H(C5A)	9445(3)	2909(4)	−227(2)	40
H(C5B)	8599(3)	3949(4)	−728(2)	40
H(C6A)	2563(6)	−1823(6)	901(3)	99
H(C6B)	1479(6)	−1027(6)	719(3)	99

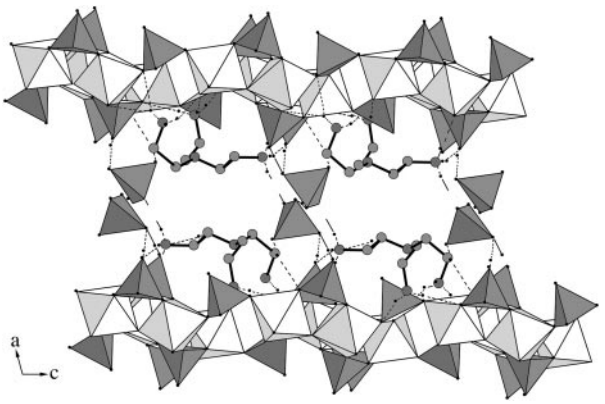

Fig. 4 Projection of MIL-14 along [010]. Hydrogen bonds are shown as dotted lines.

the formation of the two-dimensional framework of the inorganic layer.

The inorganic layer can also be described in terms of asymmetric units (Fig. 6) formed with three HPO_4 tetrahedra and two aluminium octahedra. The three HPO_4 tetrahedra share three of their vertices with aluminium octahedra and the fourth is a terminal hydroxy group. Al(1) is surrounded by four oxygen atoms of the phosphate group and two fluorine atoms, which are *cis* located within their octahedral surrounding. Furthermore, one of the fluorine atoms, [F(1)], links the

Table 4 Bond lengths (Å) and angles (°) for MIL-14[a]

P(1)–O(6)	1.494(2)	O(6)–P(1)–O(13)	113.21(11)
P(1)–O(13)	1.529(2)	O(6)–P(1)–O(12)#1	111.65(11)
P(1)–O(12)#1	1.535(2)	O(13)–P(1)–O(12)#1	111.32(10)
P(1)–O(4)	1.593(2)	O(6)–P(1)–O(4)	109.14(12)
		O(13)–P(1)–O(4)	103.60(11)
		O(12)#1–P(1)–O(4)	107.44(11)
P(2)–O(7)	1.517(2)	O(7)–P(2)–O(15)	112.90(11)
P(2)–O(15)	1.523(2)	O(7)–P(2)–O(14)	113.67(10)
P(2)–O(14)	1.526(2)	O(15)–P(2)–O(14)	112.45(10)
P(2)–O(5)	1.588(2)	O(7)–P(2)–O(5)	100.83(11)
		O(15)–P(2)–O(5)	109.17(11)
		O(14)–P(2)–O(5)	106.90(11)
P(3)–O(11)	1.515(2)	O(11)–P(3)–O(2)	113.59(10)
P(3)–O(2)	1.521(2)	O(11)–P(3)–O(3)	112.74(10)
P(3)–O(3)	1.538(2)	O(2)–P(3)–O(3)	111.46(11)
P(3)–O(1)	1.576(2)	O(11)–P(3)–O(1)	108.57(10)
		O(2)–P(3)–O(1)	103.07(11)
		O(3)–P(3)–O(1)	106.67(10)
P(4)–O(16)	1.498(2)	O(16)–P(4)–O(8)	115.93(13)
P(4)–O(8)	1.515(2)	O(16)–P(4)–O(9)	105.67(14)
P(4)–O(9)	1.566(2)	O(8)–P(4)–O(9)	111.60(14)
P(4)–O(10)	1.585(3)	O(16)–P(4)–O(10)	110.2(2)
		O(8)–P(4)–O(10)	107.73(14)
		O(9)–P(4)–O(10)	105.2(2)
Al(1)–F(2)	1.779(2)	F(2)–Al(1)–F(1)	89.96(8)
Al(1)–F(1)	1.859(2)	F(2)–Al(1)–O(6)#2	89.87(9)
Al(1)–O(6)#2	1.860(2)	F(1)–Al(1)–O(6)#2	88.47(8)
Al(1)–O(3)#3	1.895(2)	F(2)–Al(1)–O(3)#3	177.26(9)
Al(1)–O(13)	1.900(2)	F(1)–Al(1)–O(3)#3	89.23(7)
Al(1)–O(15)#4	1.916(2)	O(6)#2–Al(1)–O(3)#3	92.71(9)
		F(2)–Al(1)–O(13)	93.43(8)
		O(6)#2–Al(1)–O(13)	89.71(9)
		O(3)#3–Al(1)–O(13)	87.47(8)
		F(2)–Al(1)–O(15)#4	87.96(9)
		F(1)–Al(1)–O(15)#4	91.16(8)
		O(6)#2–Al(1)–O(15)#4	177.80(10)
		O(3)#3–Al(1)–O(15)#4	89.45(9)
		O(13)–Al(1)–O(15)#4	90.79(8)
Al(2)–F(1)	1.844(2)	F(1)–Al(2)–O(11)#3	90.28(7)
Al(2)–O(11)#3	1.877(2)	F(1)–Al(2)–O(7)	92.69(8)
Al(2)–O(7)	1.880(2)	O(11)#3–Al(2)–O(7)	89.84(8)
Al(2)–O(12)	1.889(2)	F(1)–Al(2)–O(12)	177.72(8)
Al(2)–O(2)	1.896(2)	O(11)#3–Al(2)–O(12)	89.17(8)
Al(2)–O(14)#4	1.908(2)	O(7)–Al(2)–O(12)	89.52(8)
		F(1)–Al(2)–O(2)	88.69(8)
		O(11)#3–Al(2)–O(2)	175.67(9)
		O(7)–Al(2)–O(2)	86.01(8)
		O(12)–Al(2)–O(2)	92.02(9)
		F(1)–Al(2)–O(14)#4	87.98(8)
		O(11)#3–Al(2)–O(14)#4	91.72(9)
		O(7)–Al(2)–O(14)#4	178.30(9)
		O(12)–Al(2)–O(14)#4	89.82(8)
		O(2)–Al(2)–O(14)#4	92.45(8)

O–H distances in the phosphate groups:[b]

H(1P)–O(5)	0.755(2)
H(2P)–O(1)	0.873(2)
H(3P)–O(4)	0.825(2)
H(4P)–O(9)	0.723(2)
H(5P)–O(10)	0.864(2)

Distances and angles in the amine:

N(1)–C(5)	1.459(4)	C(5)–N(1)–C(1)#6	111.6(3)
N(1)–C(1)#6	1.466(4)	C(5)–N(1)–C(3)#7	110.9(2)
N(1)–C(3)#7	1.469(4)	C(1)#6–N(1)–C(3)#7	112.3(2)
N(2)–C(4)#8	1.485(4)	N(1)#6–C(1)–C(2)#9	111.3(2)
N(3)–C(2)#1	1.488(4)	N(3)#5–C(2)–C(1)#10	110.8(2)
N(4)–C(6)#2	1.449(5)	N(1)#11–C(3)–C(4)#4	112.1(3)
C(1)–C(2)#9	1.512(4)	N(2)#8–C(4)–C(3)#3	111.6(3)
C(3)–C(4)#4	1.521(5)	N(1)–C(5)–C(6)#2	110.3(3)
C(5)–C(6)#2	1.502(5)	N(4)#2–C(6)–C(5)#2	114.1(3)

[a]Symmetry transformations used to generate equivalent atoms: #1 x, $-y+1/2$, $z+1/2$; #2 $-x+1$, $-y$, $-z$; #3 $-x+1$, $y-1/2$, $-z-1/2$; #4 $-x+1$, $y+1/2$, $-z-1/2$; #5 x, $-y+1/2$, $z-1/2$; #6 $-x+2$, $-y+1$, $-z$; #7 x, $-y+3/2$, $z+1/2$; #8 $-x+1$, $-y+1$, $-z$; #9 $-x+2$, $y+1/2$, $-z-1/2$; #10 $-x+2$, $y-1/2$, $-z-1/2$; #11 x, $-y+3/2$, $z-1/2$. [b]Owing to the use of X-rays, the accuracy of the location of hydrogen is very poor and the majority of the P–O–H distances, as usual, are shorter than the theoretical value (0.96 Å).

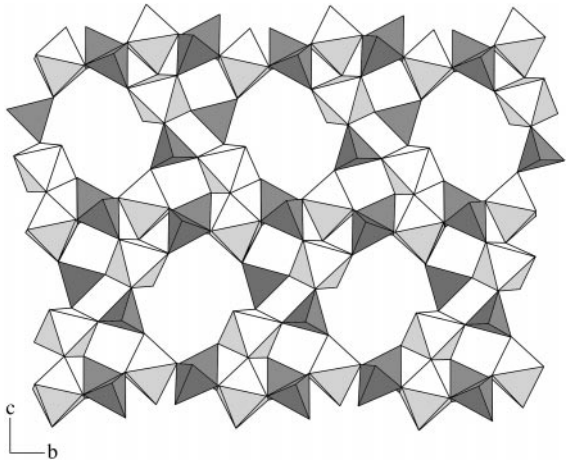

Fig. 5 View along *a* axis of the inorganic layer of MIL-14. The fluorine atoms are located at the shared vertex of the aluminium octahedra.

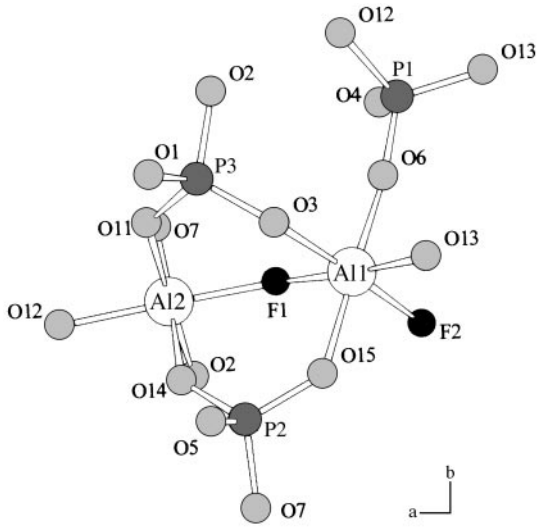

Fig. 6 Asymmetric unit of MIL-14.

two aluminium octahedra, while the other [F(2)], is in a terminal position. Al(2) shares all its vertices with the other polyhedra, five of them are oxygen atoms of PO_4 tetrahedra and the sixth is the bridging fluorine between the two aluminium octahedra. Finally, the structural unit can be formulated $[Al_2(HPO_4)_3F_2]^{2-}$ and the connection of these units generates a layer with 8-polyhedra rings along the *a* axis. In the aluminium octahedra, distances range from 1.779(2) to 1.916(2) Å for Al(1) and 1.844(2) to 1.908(2) Å for Al(2) (see Table 3). The mean values [1.86(5) Å for Al(1) and 1.88(2) Å for Al(2)] are in good agreement with those previously observed in similar compounds.[3,4] The P–O distances range from 1.494(2) to 1.593(2) Å with an average distance of 1.54(3) Å. Moreover each Al(2) octahedron is connected to four phosphate groups by sharing its vertices in the *trans* position and develops infinite chains along the *b* axis (Fig. 7).

The connectivity between inorganic layers is ensured by the organic molecules and the isolated H_2PO_4 groups *via* strong hydrogen bonds (see Fig. 4). The most probable hydrogen bonds are listed in Table 5. The three terminal ammoniums of tren interact with the oxygens of PO_4 groups and with the bridging fluorine of the inorganic layer [the shortest distance is N(3)–H(B)···F(2) 1.856 Å]. The isolated H_2PO_4 group interacts either with one of the ammonium groups of tren [N(4)–H(4A)···O(16) 1.973 Å] and with the inorganic sheet [the shortest distance is O(1)–H(2P)···O(8) 1.692 Å].

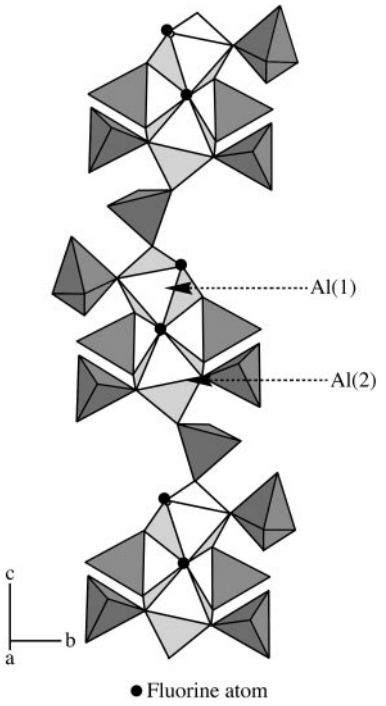

Fig. 7 *trans* chain Al(2)–Al(1)–HP(1)O_4 with its satellites.

Table 5 Most probable hydrogen bonds (*d*/Å) in MIL-14

Between the inorganic sheet and the isolated H_2PO_4 group	
O(5)–H(1P)···O(8)	1.887
O(1)–H(2P)···O(8)	1.692
Between the isolated H_2PO_4 group and the inorganic sheet	
O(10)–H(5P)···O(3)	2.167
Between the inorganic sheet and the protonated amine	
N(2)–H(2A)···F(2)	1.856
N(2)–H(2B)···O(12)	2.126
N(2)–H(2C)···O(15)	2.095
N(3)–H(3A)···O(13)	2.407
N(3)–H(3A)···O(3)	2.461
N(3)–H(3B)···F(2)	1.860
N(3)–H(3C)···O(12)	2.237
N(3)–H(3C)···O(2)	2.265
N(4)–H(4B)···O(2)	2.129
N(4)–H(4B)···O(1)	2.408
N(4)–H(4C)···O(5)	1.977
Between the isolated PO_4 group and the protonated amine	
N(4)–H(4A)···O(16)	1.973

4 Discussion

The MIL-14 phase exhibits a lamellar structure obtained from tris(2-aminoethyl)amine. This seems to confirm that the use of exclusively branched amine leads to the formation of oxyfluorinated two-dimensional materials instead of three-dimensional ones, as has already been observed for the synthesis of the layered gallium fluorophosphate ULM-8.[9]

The anionic inorganic layer with an Al:P ratio of 2:3 is another structural example of Al_2P_3 stoichiometry. Up to now, five other layered aluminophosphates with $Al_2P_3O_{12}$ formula [$(2\text{-}BuNH_3)_2HAl_2P_3O_{12}$, $(pyH)H_2Al_2P_3O_{12}$,[13] UT-3,[14] UT-4 and UT-5[15]] have been reported by using linear monoamines or cyclic amines in an alcoholic system under hydrothermal conditions. The structures of the layers are mainly based on the connection of hexagonal rings of P and Al centers. In some cases such as in $(pyH)H_2Al_2P_3O_{12}$ or UT-4, the connection of the six-membered rings generated 4- and 8-ring apertures within the layer. The aluminium can be found in four-fold (tetrahedron) or five-fold (trigonal bipyramid) coordination. The presence of fluorine in the reaction medium

drastically modifies the structure of the inorganic layer since the fluorine atom participates directly in the coordination sphere of aluminium, which is octahedral. Al–F–Al bridges occur within the layer resulting in the formation of three-membered rings connected with four-membered ones, generating 8-ring apertures.

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