Journal of Fluorine Chemistry 130 (2009) 1099–1105

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Evidence of 13 hybrid fluoroaluminates in the composition space diagram of the $Al(OH)_3$–*tren*–HF–ethanol system

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ARTICLE INFO

Article history:
Received 14 May 2009
Accepted 5 June 2009
Available online 16 June 2009

Keywords:
Fluoroaluminates
Hybrid fluorides
Hydrothermal synthesis
Microwave heating

ABSTRACT

Thirteen phases are now evidenced in the composition space diagram of the $Al(OH)_3$–*tren*–HF–ethanol system at 190 °C. Solvothermal syntheses are performed under microwave heating. Six new organic–inorganic fluorides crystallise and their structures are determined: $(H_3O)\cdot[H_4\textit{tren}]_2\cdot(AlF_6)_3\cdot 6H_2O$ (*P*-1, *Z* = 2), $[H_3\textit{tren}]_2\cdot(AlF_5(H_2O))_3\cdot 8H_2O$ (*C*2/*c*, *Z* = 8), $[H_3\textit{tren}]_4\cdot(AlF_6)_2\cdot(Al_2F_{11})\cdot(F)\cdot 10H_2O$ (*P*2_1/*n*, *Z* = 2), $[H_3\textit{tren}]_2\cdot(Al_4F_{18})\cdot 3.5H_2O$ (*P*6_3, *Z* = 2), $[H_3\textit{tren}]_2\cdot(Al_4F_{18})$ (*P*-1, *Z* = 1), and $[H_3\textit{tren}]_4\cdot(Al_8F_{35})\cdot(OH)\cdot H_2O$ (*P*-1, *Z* = 1). The existence domains are approximately located for all phases. *Tren* amine is tetraprotonated at high HF concentration, otherwise it is triprotonated. A protonated water cluster, $H_3O^+(H_2O)_6$, appears in $(H_3O)\cdot[H_4\textit{tren}]_2\cdot(AlF_6)_3\cdot 6H_2O$ while a new Al_4F_{18} unit, found in $[H_3\textit{tren}]_2\cdot(Al_4F_{18})$, is evidenced; it results from corner and edge sharing association of four AlF_6 octahedra. Finally, the structure of $[H_3\textit{tren}]_4\cdot(Al_8F_{35})\cdot(OH)\cdot H_2O$ revealed the largest known fluoroaluminate polyanion, built from eight vertex sharing AlF_6 octahedra, $(Al_8F_{35})^{11-}$.

1. Introduction

Our recent work was mainly devoted to the study of the reaction of metal salts with linear or cyclic organic amines in fluoride solutions under hydro(solvo)thermal conditions. Most often, however, the dimensionality of the inorganic entities was low. This trend was confirmed in the $Al(OH)_3$–*tren*–$HF_{aq.}$–EtOH system in which seven phases were evidenced: five phases were based on AlF_6 units, $[H_3\textit{tren}]\cdot(AlF_6)\cdot H_2O$, $[H_3\textit{tren}]\cdot(AlF_6)\cdot HF$, $[H_4\textit{tren}]\cdot(AlF_6)\cdot(F)$ [1] or condensed polyanions, $[H_4\textit{tren}]\cdot(Al_2F_{10})\cdot H_2O$ [2], $(H_3O)\cdot[H_4\textit{tren}]_2\cdot(Al_7F_{30})$ [3]. The last and most condensed phases were $[H_4\textit{tren}]_2\cdot(Al_7F_{29})\cdot 2H_2O$ [3] and $[H_4\textit{tren}]_{3/2}\cdot(Al_6F_{24})\cdot 3H_2O$ [4] with a 1D architecture. It was suggested that other phases could exist and a careful examination of the system was of interest. It is now found that more than 13 phases crystallise within the studied concentration domains. In this article, we report on the stability regions of these *tren* derived fluoroaluminates and the crystal structures of six new phases are described. The evolution of the compositions of the crystallised solids with the variation of the concentration of the starting materials is discussed.

It must be noted that crystals are frequently very small and numerous attempts to grow larger crystals failed; then, the quality of the X-ray diffraction data and of the resulting refinements is not always perfect. However, the exceptional number of phases that are found at various Al^{3+} concentrations in this $Al(OH)_3$–*tren*–$HF_{aq.}$–EtOH system justifies this review article.

2. Results and discussion

2.1. Composition space diagram

The 2D composition space diagram of the $Al(OH)_3$–*tren*–$HF_{aq.}$–EtOH system is established for several $[Al^{3+}]$ concentrations (0.1, 0.5, 1 mol L^{-1}) at 190 °C. In Fig. 1, the labels are associated with the composition of the solids and they are located at the figurative points of the starting compositions. The limits of the domains are roughly estimated. In addition to seven previously described phases, six new compounds are evidenced (Table 1).

At high amine concentrations, the solids are built up from isolated $(AlF_6)^{3-}$ anions associated with triprotonated $[H_3\textit{tren}]^{3+}$ cations and H_2O or HF molecules. At high HF concentrations, the tetraprotonation of the *tren* amine occurs to give fluoroaluminates with condensed $(Al_7F_{30})^{9-}$ or $(Al_2F_{10})^{4-}$ polyanions. For $[Al^{3+}]$ = 0.5 mol L^{-1}, both AlF_6 and Al_2F_{11} units are found in $[H_3\textit{tren}]_4\cdot(AlF_6)_2\cdot(Al_2F_{11})\cdot(F)\cdot 10H_2O$.

At low amine concentration and intermediate HF content, the largest known fluoride polyanion $(Al_8F_{35})^{11-}$ appears in $[H_3\textit{tren}]_4\cdot(Al_8F_{35})\cdot(OH)\cdot H_2O$. For a lower amine concentration, a chain-structure aluminum fluoride $[H_4\textit{tren}]_2\cdot(Al_7F_{29})\cdot 2H_2O$ crystallises. For $[Al^{3+}]$ = 1 mol L^{-1}, two different Al_4F_{18} units are encountered in $[H_3\textit{tren}]_2\cdot(Al_4F_{18})\cdot 3.5H_2O$ and $[H_3\textit{tren}]_2\cdot(Al_4F_{18})$.

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doi:10.1016/j.jfluchem.2009.06.006

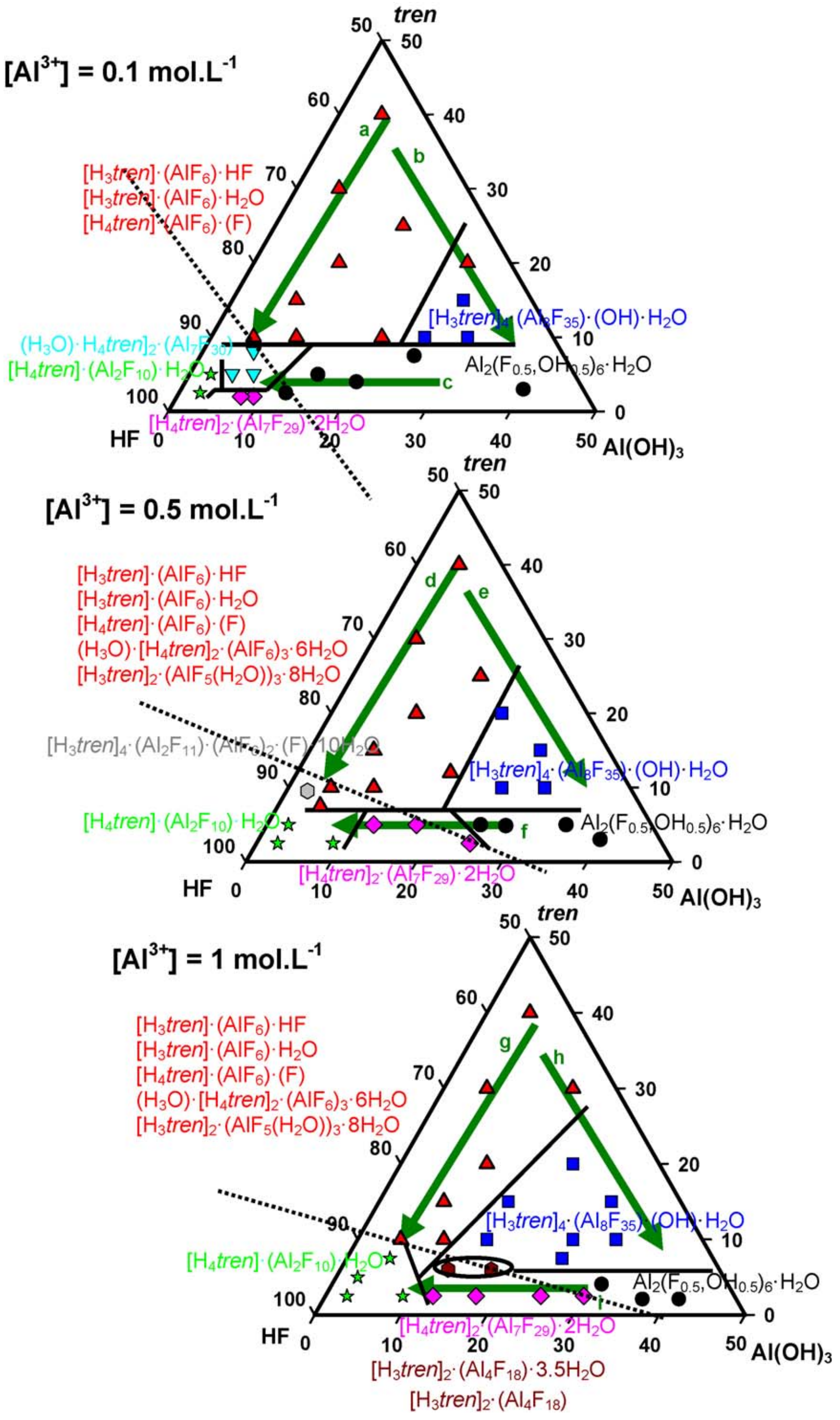

Fig. 1. Composition space representation of the $Al(OH)_3$–*tren*–$HF_{aq.}$–EtOH system for $[Al^{3+}]$ = 0.1, 0.5 and 1.0 mol L^{-1} and T = 190 °C.

The increase of the $[HF]/[Al^{3+}]$ ratio implies the successive crystallisation of $[H_4tren]_2{\cdot}(Al_7F_{29}){\cdot}2H_2O$ and $[H_4tren]{\cdot}(Al_2F_{10}){\cdot}2H_2O$ (Fig. 1, arrows c, f, and i). Similarly, the increase of [HF]/[*tren*] ratio favours the tetraprotonation of amine that occurs in concentrated HF solutions (Fig. 1, arrows a, d, and g). Finally, it must be noted that the evolution of the formulations is also consistent with the variation of the $[Al^{3+}]$/[*tren*] ratio (Fig. 1, arrows b, e, and h).

2.2. Structural diversity

The crystalline solids of the $Al(OH)_3$–*tren*–$HF_{aq.}$–EtOH system exhibit a very impressive structural diversity. Besides the inorganic pyrochlore $Al_2(OH)_3F_3{\cdot}H_2O$, 13 phases are evidenced in the 2D composition space diagram. Two of these phases are built up from original polyanions, $(Al_4F_{18})^{6-}$ in $[H_3tren]_2{\cdot}(Al_4F_{18})$ and $(Al_8F_{35})^{11-}$ in $[H_3tren]_4{\cdot}(Al_8F_{35}){\cdot}(OH){\cdot}H_2O$; one phase, $[H_3tren]_4{\cdot}(AlF_6)_2{\cdot}(Al_2F_{11}){\cdot}(F){\cdot}10H_2O$, presents simultaneously two different types of polyanions and a cluster of one H_3O^+ cation surrounded by six H_2O molecules is found in $(H_3O){\cdot}[H_4tren]_2{\cdot}(AlF_6)_3{\cdot}6H_2O$.

The condensation of the $(AlF_6)^{3-}$ anions to give larger entities can be described from the concerted elimination of one or two fluorine atoms; as a consequence, the AlF_6 octahedral units can be associated by one corner ($[H_4tren]_2{\cdot}(Al_7F_{29}){\cdot}2H_2O$ [3]) or by one edge ($[H_4tren]{\cdot}(Al_2F_{10}){\cdot}H_2O$ [2]).

Table 1
Synthesis conditions of *tren*-based fluoroaluminates.

	Formulation	Inorganic (poly)anion(s)	$[Al^{3+}]$ (mol L^{-1})	Molar ratio $Al(OH)_3$/*tren*/HF/EtOH	Ref
I	$[H_3tren]\cdot(AlF_6)\cdot H_2O$	$(AlF_6)^{3-}$		1/2/7/170	[1]
II	$[H_3tren]\cdot(AlF_6)\cdot HF$			1/2/8/170	[1]
III	$[H_3tren]\cdot(AlF_6)\cdot(F)$			1/2/18/170	[1]
IV	$(H_3O)\cdot[H_4tren]_2\cdot(AlF_6)_3\cdot 6H_2O$			2/30/30/170	New
V	$[H_3tren]_2\cdot(AlF_5(H_2O))_3\cdot 8H_2O$			1/0.5/5/0	New
VI	$[H_3tren]_4\cdot(AlF_6)_2\cdot(Al_2F_{11})\cdot(F)\cdot 10H_2O$	$(AlF_6)^{3-} + (Al_2F_{11})^{5-}$		1/0.04/0.33/340	New
VII	$[H_4tren]\cdot(Al_2F_{10})\cdot H_2O$	$(Al_2F_{10})^{4-}$		3/1/26/170	[2]
VIII	$[H_3tren]_2\cdot(Al_4F_{18})\cdot 3.5H_2O$	$_{c}(Al_4F_{18})^{6-}$		1/0.5/0.5/100	New
IX	$[H_3tren]_2\cdot(Al_4F_{18})$	$_{c+e}(Al_4F_{18})^{6-}$		1/0.46/4.45/20	New
X	$[H_3tren]_4\cdot(Al_8F_{35})\cdot(OH)\cdot H_2O$	$(Al_8F_{35})^{11-}$		1/0.45/1.2/40	New
XI	$(H_3O)\cdot[H_4tren]_2\cdot(Al_7F_{30})$	$(Al_7F_{30})^{9-}$		1/10/4/320[a]	[3]
XII	$[H_4tren]_2\cdot(Al_7F_{29})\cdot 2H_2O$	$(Al_7F_{29})^{8-}$		1/10/2/320[a]	[3]
XIII	$[H_4tren]_{3/2}\cdot(Al_6F_{24})\cdot 2H_2O$	$(Al_6F_{24})^{6-}$		4/2/40/170	[4]

[a] Prepared from Al_2O_3/HF/*tren*/EtOH.

2.3. $(AlF_6)^{3-}$ anions

Five structures, built up from $AlF_6{}^{3-}$ anions, are evidenced. All the AlF_6 units are separated by $[H_3tren]^{3+}$ or $[H_4tren]^{4+}$ or H_3O^+cations and, eventually, water, HF, isolated fluoride or hydroxyl ions. Three of these phases, ($[H_3tren]\cdot(AlF_6)\cdot H_2O$, $[H_3tren]\cdot(AlF_6)\cdot HF$ and $[H_4tren]\cdot(AlF_6)\cdot F$), are isolectronic and were previously described [1].

The crystals of $(H_3O)\cdot[H_4tren]_2\cdot(AlF_6)_3\cdot 6H_2O$ [5] are very small and the number of diffracted intensities with $I > 2\sigma(I)$ is small as compared with the number of refined parameters. In spite of this drawback, the overall characteristics of the structure (geometry of the AlF_6 units and amine cations) are well defined. A very interesting feature concerns the existence of a cluster $H_3O^+(H_2O)_6$ where one $(H_3O)^+$ cation is surrounded by six water molecules located at the vertices of two opposite faces of a distorted

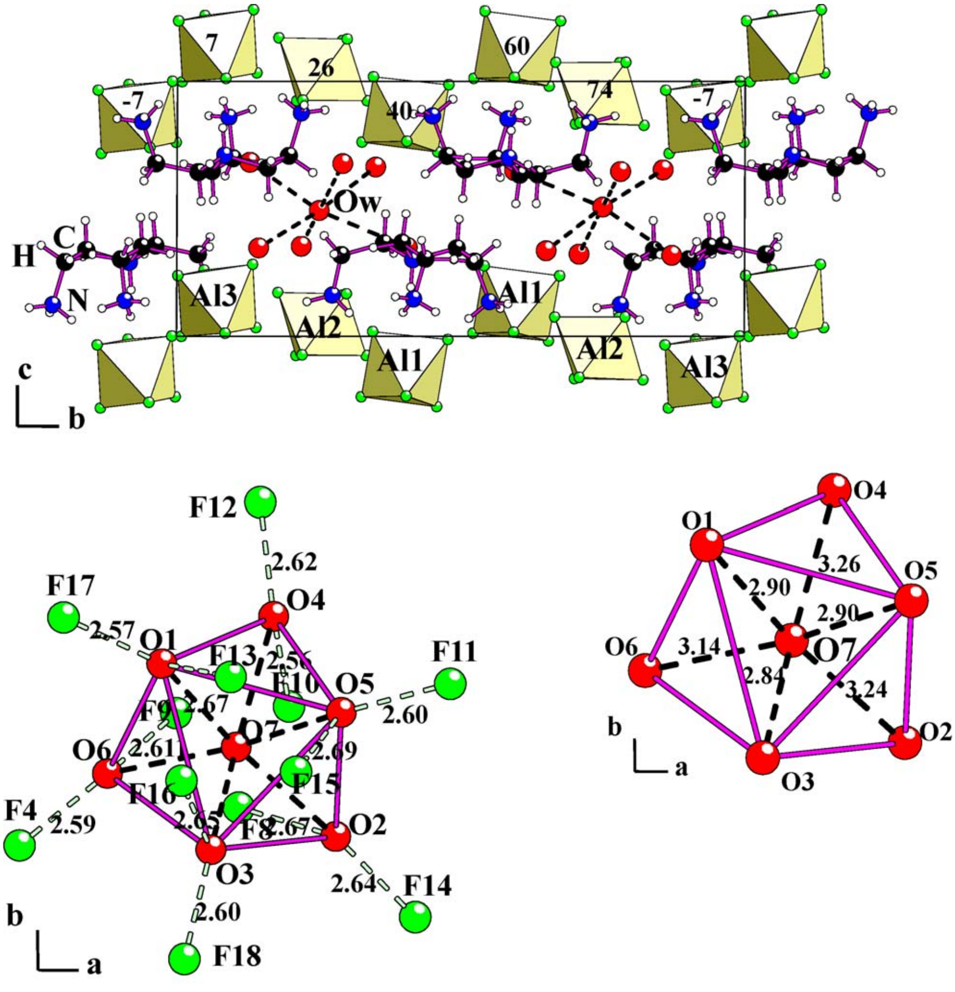

Fig. 2. [1 0 0] projection of the structure of $(H_3O)\cdot[H_4tren]_2\cdot(AlF_6)_3\cdot 6H_2O$ (**IV**). Environment (bottom left) and distances (bottom right) for the cluster $H_3O^+(H_2O)_6$.

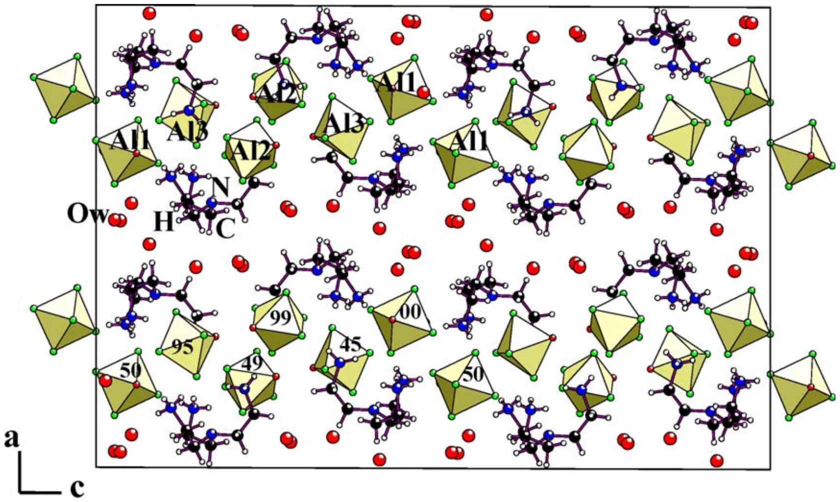

Fig. 3. [0 1 0] projection of the structure of $[H_3tren]_2\cdot(AlF_5(H_2O))_3\cdot8H_2O$ (**V**).

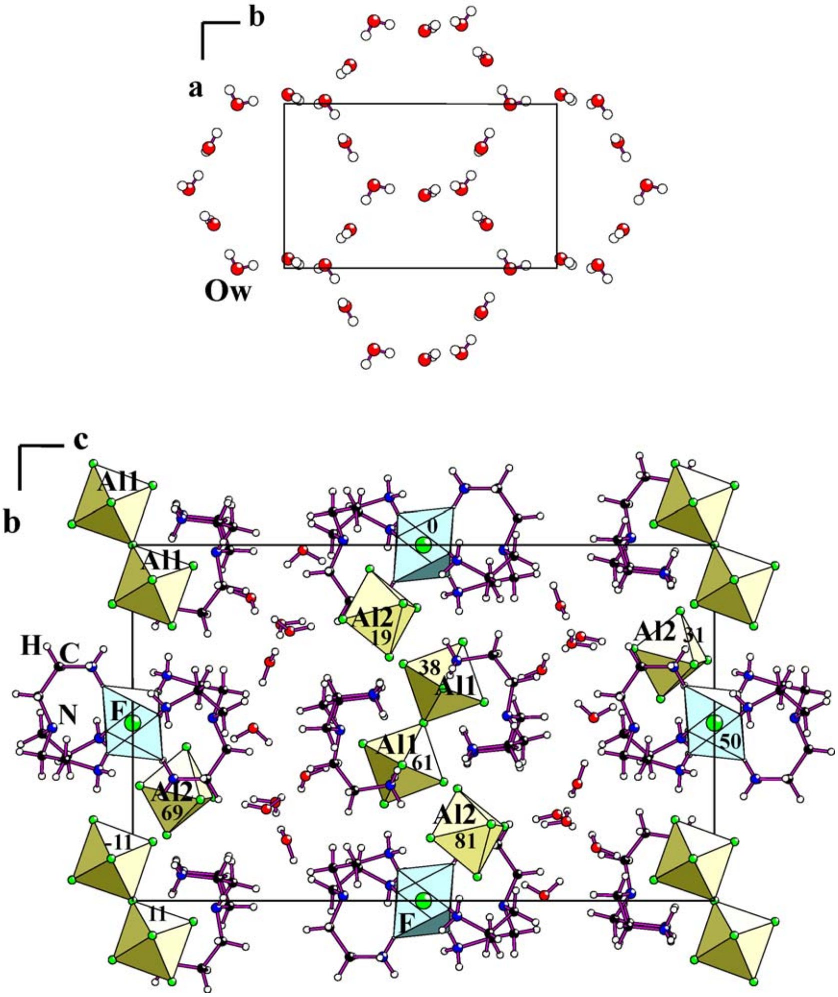

Fig. 4. Water layer at $z \approx 1/4$ (top), "free" fluoride anion environment, AlF_6 and Al_2F_{11} units in $[H_3tren]_4\cdot(AlF_6)_2\cdot(Al_2F_{11})\cdot(F)\cdot10H_2O$ (**VI**) (bottom).

octahedron (Fig. 2). Two sets of distances, around 2.9 Å and 3.2 Å, result from this distortion. The cationic clusters ensure the connection of the infinite layers $[H_4tren]_2\cdot(AlF_6)_3$ (Fig. 2). To our knowledge, such a cluster geometry is still unknown, even in the gas phase [6]; moreover, it is not predicted theoretically [7].

Similarly to the preceding phase, the quality of the structure determination of $[H_3tren]_2\cdot(AlF_5(H_2O))_3\cdot8H_2O$ is poor. However, the characteristics of the structure are also well defined (Fig. 3) and the proposed formulation is in good agreement with the results of TGA experiments.

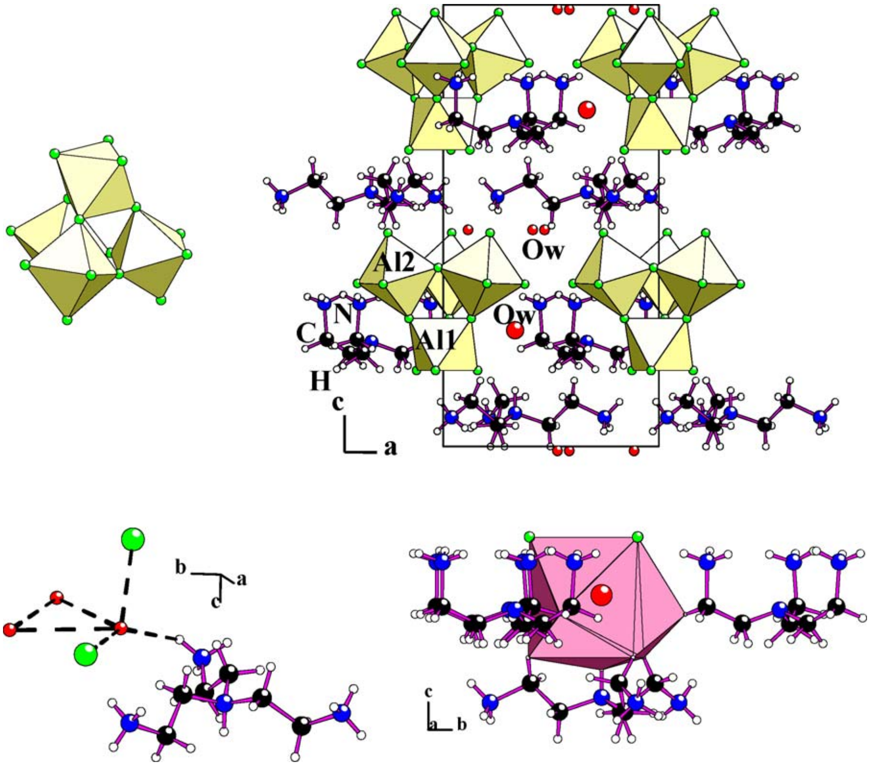

Fig. 5. Al_4F_{18} tetramer (top left) and [0 1 0] projection of the structure of $[H_3$*tren*$]_2\cdot(Al_4F_{18})\cdot3.5H_2O$ (**VIII**) (top right). Environment of water molecules (bottom left and right).

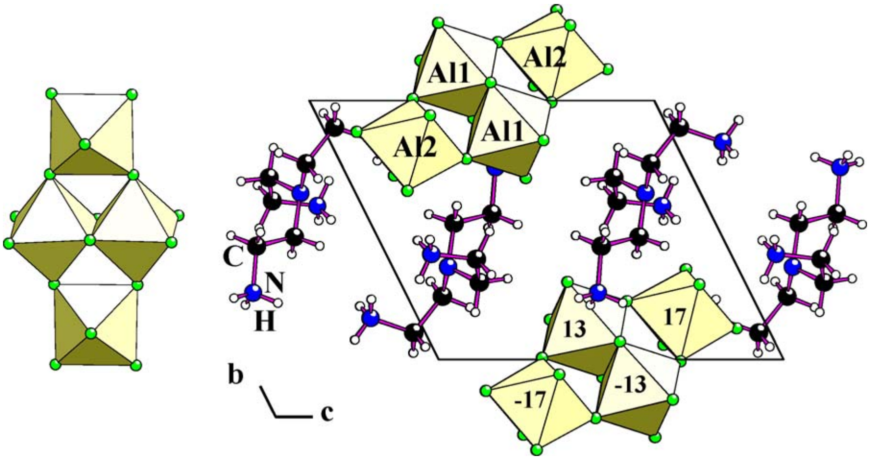

Fig. 6. Al_4F_{18} tetramer (left) and [1 0 0] projection of the structure of $[H_3$*tren*$]_2\cdot(Al_4F_{18})$ (**IX**) (right).

2.4. $(AlF_6)^{3-}$ and $(Al_2F_{11})^{5-}$ polyanions

Both AlF_6 and Al_2F_{11} units are found in $[H_3$*tren*$]_4\cdot(AlF_6)_2\cdot(Al_2F_{11})\cdot(F)\cdot10H_2O$. One "free" fluoride anion is octahedrally coordinated by six hydrogen atoms of NH_3 groups from two amine cations. H_2O molecules, at $z \approx 1/4$ and $z \approx 3/4$, build 12 member hexagonal rings that are inserted between neutral $[H_3$*tren*$]_4\cdot(AlF_6)_2\cdot(Al_2F_{11})\cdot(F)$ layers (Fig. 4).

2.5. $(Al_4F_{18})^{6-}$ polyanions

The highly symmetrical association of four corner sharing AlF_6 octahedra in tetrahedral Al_4F_{18} units was previously reported in $[H_3$*dien*$]_2\cdot(Al_4F_{18})$ [8] and $(H_3O)_2\cdot[H$*gua*$]_{16}\cdot(Al_4F_{18})_3\cdot H_2O$ [9]. It is also found in $[H_3$*tren*$]_2\cdot(Al_4F_{18})\cdot3.5H_2O$ (Fig. 5). The structure is built up from the stacking of $[H_3$*tren*$]\cdot(Al_4F_{18})\cdot3.5H_2O$ and $[H_3$*tren*$]$ layers along c. Water molecules exchange different types of hydrogen bonds. Ow1 molecules are surrounded by six hydrogen atoms of $-NH_3$ groups and by three fluoride ions. Ow2 molecules have two other Ow2 neighbours, two fluoride anions and one hydrogen atom of $-NH_3$ group.

In $[H_3$*tren*$]_2\cdot(Al_4F_{18})$, both corner and edge sharing association of AlF_6 octahedra occurs (Fig. 6). Both connection types were only previously reported in the 2D fluoroaluminate $[C_5NH_6]\cdot(Al_3F_{12})$ [10].

2.6. $(Al_8F_{35})^{11-}$ polyanions

In $[H_3$*tren*$]_4\cdot(Al_8F_{35})\cdot(OH)\cdot H_2O$, two tetrahedral Al_4F_{18} units, linked by one corner, form the largest reported fluoride polyanion

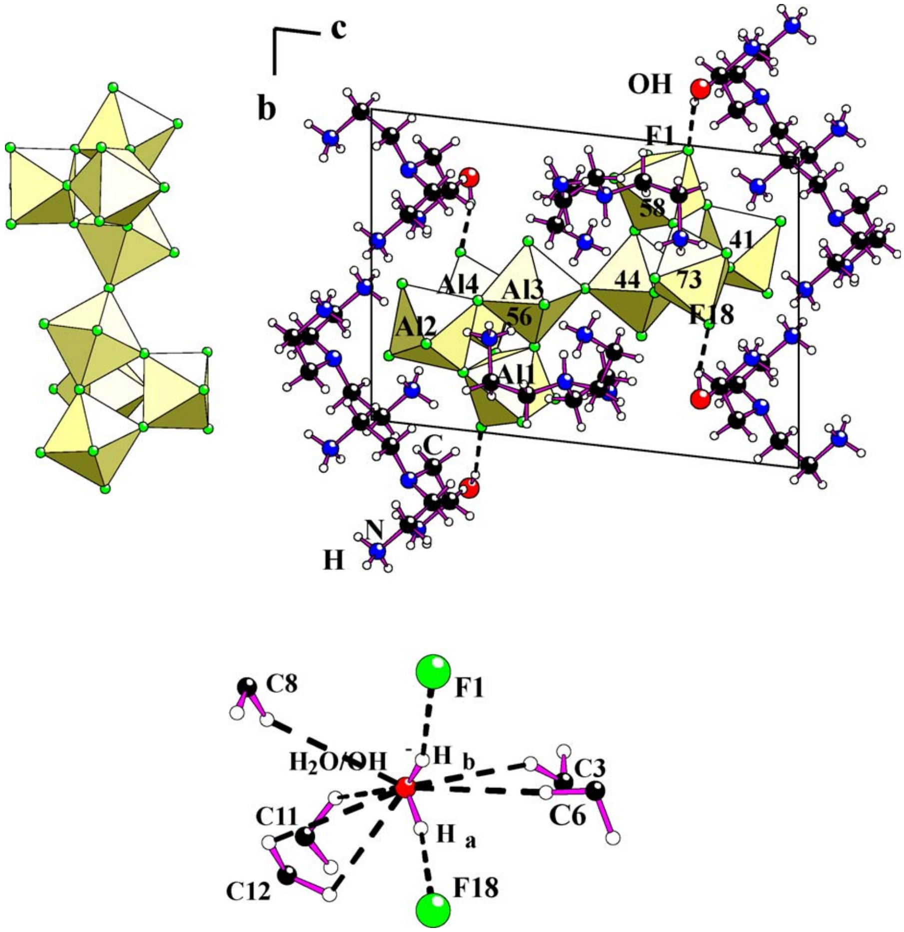

Fig. 7. Al_8F_{35} octamer (top left) and [1 0 0] projection of the structure of $[H_3\textit{tren}]_4\cdot(Al_8F_{35})\cdot(OH)\cdot H_2O$ (**X**) (top right). H_2O/OH^- environment (bottom).

Table 2
Crystallographic data of $(H_3O)\cdot[H_4\textit{tren}]_2\cdot(AlF_6)_3\cdot 6H_2O$ (**IV**), $[H_3\textit{tren}]_2\cdot(AlF_5(H_2O))_3\cdot 8H_2O$ (**V**), $[H_3\textit{tren}]_4\cdot(AlF_6)_2\cdot(Al_2F_{11})\cdot(F)\cdot 10H_2O$ (**VI**), $[H_3\textit{tren}]_2\cdot(Al_4F_{18})\cdot 3.5H_2O$ (**VIII**), $[H_3\textit{tren}]_2\cdot(Al_4F_{18})$ (**IX**) and $[H_3\textit{tren}]_4\cdot(Al_8F_{35})\cdot(OH)\cdot H_2O$ (**X**).

	Compound					
	IV	**V**	**VI**	**VIII**	**IX**	**X**
Formula weight (g mol^{-1})	850.57	862.61	1341.08	811.47	748.42	1512.86
Formula	$Al_3F_{18}O_7N_8C_{12}H_{59}$	$Al_3F_{15}O_{11}N_8C_{12}H_{64}$	$Al_4F_{24}O_{10}N_{16}C_{24}H_{104}$	$Al_4F_{18}O_{3.5}N_8C_{12}H_{49}$	$Al_4F_{18}N_8C_{12}H_{42}$	$Al_8F_{35}O_2N_{16}C_{24}H_{87}$
Crystal system	Triclinic	Monoclinic	Monoclinic	Hexagonal	Triclinic	Triclinic
Space group	*P*-1	*C*2/*c*	*P*2$_1$/*n*	*P*6$_3$	*P*-1	*P*-1
a (Å)	10.742(5)	24.409(1)	8.6539(7)	10.114(4)	7.360(2)	10.027(2)
b (Å)	18.733(8)	8.6059(4)	14.311(2)	10.114(4)	9.866(2)	10.347(2)
c (Å)	8.436(4)	35.672(2)	23.424(7)	17.908(4)	10.996(3)	14.408(3)
α (°)	89.78(6)				112.52(2)	83.05(2)
β (°)	90.86(4)	90.221(1)	90.23(1)		95.15(2)	82.90(2)
γ (°)	90.36(6)				111.13(2)	85.71(1)
V (Å^3), *Z*	1697.3(2), 2	7493.34(6), 8	2900.9(1), 2	1586.4(1), 2	663(1), 1	1470(5), 1
μ (mm^{-1})	0.25	0.23	0.21	0.29	0.32	0.29
$\rho_{calc.}$ (g cm^{-3})	1.665	1.530	1.536	1.699	1.874	1.710
2θ range (°)	2–45	2–60	2–60	2–60	2–60	2–55
Refl. meas/uni/($I > 2\sigma(I)$)	4430/4430/1428	51959/9835/3724	8782/8460/5536	2845/2743/2102	3857/3857/2605	13795/6747/3487
Refined parameters	305	439	393	142	195	399
R_1/wR_2	0.132/0.412	0.149/0.373	0.071/0.221	0.066/0.175	0.049/0.131	0.079/0.221
Goodness of fit	0.977	1.458	1.023	1.034	1.085	1.042
$\Delta\rho_{min}/\Delta\rho_{max}$ (e Å^{-3})	−0.77/0.61	−0.66/3.22	−0.53/1.37	−0.87/0.77	−0.59/0.49	−0.73/1.58

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos 732068 (**IV**), 732067 (**V**), 732069 (**VI**), 732065 (**VIII**), 732064 (**IX**) and 732066 (**X**). Copies of data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

$(Al_8F_{35})^{11-}$ (Fig. 7). A disorder between one hydroxide anion and one water molecule, weakly hydrogen bonded with two fluoride ions and six hydrogen atoms of $–CH_2$ groups, can be noted in this structure.

3. Conclusion

Thirteen phases are now characterised in the ($Al(OH)_3$–*tren*–HF–ethanol) system at 190 °C under microwave heating. The structures of six new phases are determined; a new cluster $H_3O^+(H_2O)_6$ is evidenced together with a very large unknown inorganic polyanion $(Al_8F_{35})^{11-}$. It must be also noted that more than five other phases are identified but their formulations are not yet well defined. To this impressive number of phases in one chemical system, crystalline intermediates, resulting from the thermal decomposition of the preceding phases, must be added.

4. Experimental

All phases were synthesized from a mixture of $Al(OH)_3$ (Merk), tris-(2_aminoetyl)amine (Aldrich), hydrofluoric acid solution (40% HF, Prolabo) and ethanol. The solvothermal reaction was performed at 190 °C in a microwave oven during 1 h and the solid products were washed with ethanol and dried at room temperature. X-ray data were collected on a SIEMENS AED2 four-circle diffractometer (graphite monochromator Mo K_α (λ = 0.71069 Å)) at room temperature using $\omega/2\theta$ scans. The structure solutions were found by direct methods (TREF option) and extended by Fourier maps and subsequent refinements (SHELXS-86 and SHELXL-97 programs [11,12]). All non-hydrogen atoms were refined anisotropically whereas hydrogen atoms of amine were geometrically constrained (HFIX option); O–H distances of water molecules were fixed using DFIX option. Details of the structure determinations are given in Table 2.

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