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Tris(2-ammonioethyl)aminium decafluorodialuminium monohydrate, $(H_4tren)[Al_2F_{10}]\cdot H_2O$

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The title compound, $(C_6H_{22}N_4)[Al_2F_{10}]\cdot H_2O$, was obtained by the reaction of aluminium oxide, tris(2-aminoethyl)amine (tren), HF and ethanol at 463 K for 1 h. It consists of $(Al_2F_{10})^{4-}$ dimers, located on inversion centers, water molecules and tetraprotonated tren cations. A network of hydrogen bonds ensures the three-dimensional cohesion.

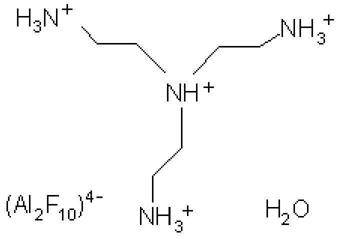
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.123
Data-to-parameter ratio = 20.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Most fluoroaluminates are built up from corner-sharing AlF_6 octahedra. Less frequently, edge-sharing of the octahedra is encountered. Recently, Al_2F_{10} dimers of edge-sharing AlF_6 octahedra were observed in two fluoroaluminates with piperazinium and pyridinium organic cations: $[H_2piperazine]_2\cdot(Al_2F_{10})\cdot 2H_2O$ (Tang *et al.*, 2001) and $[Hpyridine]_4\cdot(Al_2F_{10})\cdot 4H_2O$ (Adamczyk *et al.*, 2000). Earlier, infinite $_\infty(Al_3F_{12})$ chains, which involve edge-sharing and vertex-sharing octahedra, associated with isolated (AlF_4) tetrahedra, were encountered in $[Htrimethylpyridine]_4\cdot(Al_3F_{12})\cdot(AlF_4)$ (Herron *et al.*, 1993).



(I)

A new compound $[H_4tren]\cdot(Al_2F_{10})\cdot H_2O$ (tren is tris(2-aminoethyl)amine), (I), which exhibits Al_2F_{10} dimers, is obtained for a small composition space ($0.2 < tren/Al_2O_3 < 0.8$, $6 < HF/Al_2O_3 < 12$, $Al_2O_3/ethanol = 3/170$) in the Al_2O_3-tren–HF-ethanol phase space. The AlF_6 octahedra are slightly distorted, the longest Al—F distances corresponding to bridging F atoms. The Al_2F_{10} units are built up from two half units (AlF_5), each generated by inversion symmetry. The cohesion between anionic dimers, water molecules and tren cations is ensured by a network of hydrogen bonds (Fig. 1, Table 1). Charge-balance is achieved by the tetraprotonation of tren cations. The $[H_4tren]^{4+}$ cations exhibit a non-planar 'scorpion' shape, with one short [3.29 (3) Å] and two long [3.63 (4) and 3.79 (6) Å] $N_{primary}—N_{tertiary}$ distances. This tren conformation was previously observed in $[H_4tren]_2\cdot(Al_7F_{29})\cdot 2H_2O$ and in $(H_3O)\cdot[H_4tren]_2\cdot(Al_7F_{30})$ (Goreshnik *et al.*, 2002). Owing to the weak interactions between the organic and inorganic parts,

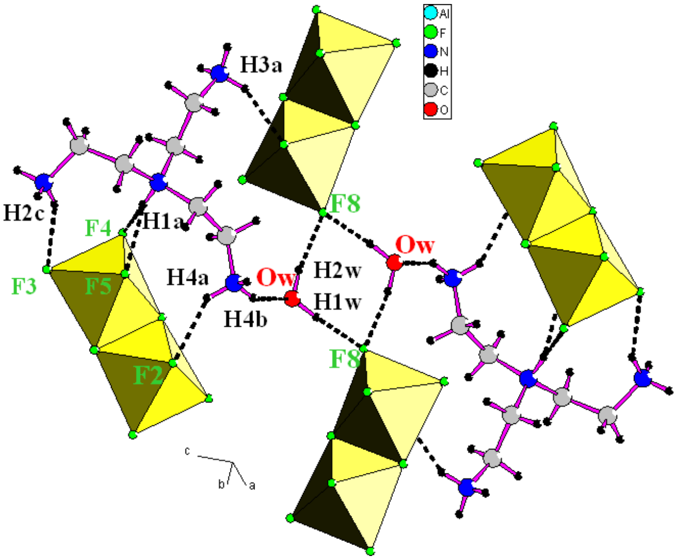


Figure 1
Network of hydrogen bonds between $(Al_2F_{12})^{4-}$ dimers, water molecules and $[H_4tren]^{4+}$ cations in (I).

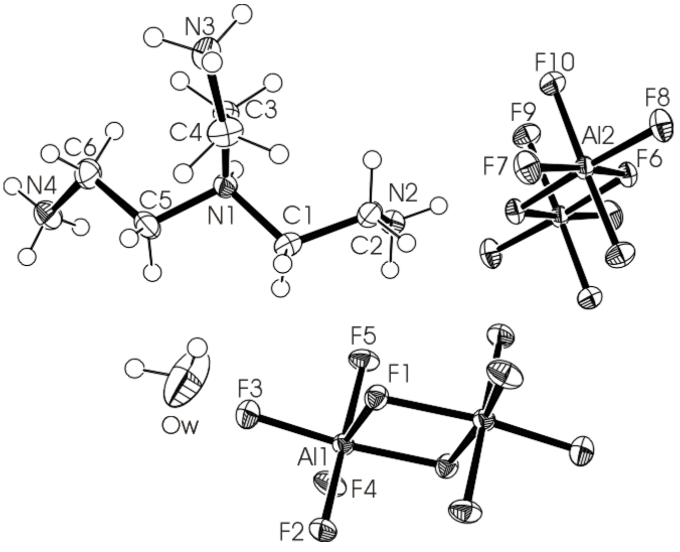


Figure 2
ORTEP (Farrugia, 1997) view of (I). Displacement ellipsoids are drawn at the 50% probability level.

(I) belongs to the Class I hybrids, according to the classification of Sanchez & Ribot (1994).

Experimental

Compound (I) was prepared by microwave synthesis under autogeneous pressure from a starting mixture of Al_2O_3, tris(2-aminoethyl)amine (96%, Aldrich), HF (96%, Prolabo) and ethanol in the molar ratio 3:1:26:170. After stirring, the mixture was introduced into Teflon autoclaves and then placed on the carousel of a CEM microwave oven (MDS 2100). The synthesis, regulated in pressure (Pmax = 23 bar), was performed at 463 K for 1 h. The resulting crystalline products were washed with ethanol and dried in air. Crystals suitable for single-crystal X-ray diffraction were selected from a mixture of microcrystalline α- and γ-$(H_3tren)[AlF_6]\cdot H_2O$ and $(H_3O)_3\cdot(H_3tren)[AlF_6]_3\cdot H_2O$ (unpublished results) using an optical microscope.

Crystal data

$(C_6H_{22}N_4)[Al_2F_{10}]\cdot H_2O$
$M_r = 412.23$
Triclinic, $P\overline{1}$
$a = 7.6996$ (16) Å
$b = 8.838$ (2) Å
$c = 12.197$ (4) Å
$\alpha = 105.87$ (2)°
$\beta = 97.74$ (3)°
$\gamma = 106.317$ (15)°
$V = 745.8$ (4) Å^3
$Z = 2$
$D_x = 1.836$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 32 reflections
$\theta = 28$–32°
$\mu = 0.31$ mm^{-1}
$T = 293$ (2) K
Parallepiped, colorless
0.14 × 0.10 × 0.09 mm

Data collection

Siemens AED-2 diffractometer
$2\theta/\omega$ scans
Absorption correction: Gaussian (*SHELX*76; Sheldrick, 1976)
$T_{\min} = 0.934$, $T_{\max} = 0.967$
4283 measured reflections
4283 independent reflections
3119 reflections with $> 2\sigma(I)$
$\theta_{\max} = 30.0$°
$h = -10 \rightarrow 10$
$k = -12 \rightarrow 11$
$l = 0 \rightarrow 17$
3 standard reflections frequency: 120 min
intensity decay: 15%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.123$
$S = 1.05$
4269 reflections
212 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.5017P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.73$ e Å^{-3}

Table 1
Selected geometrical parameters (Å °).

Al1—F2	1.7538 (15)	Al2—F7	1.7610 (17)
Al1—F4	1.7802 (16)	Al2—F8	1.7742 (15)
Al1—F3	1.7842 (16)	Al2—F10	1.7822 (15)
Al1—F5	1.7989 (15)	Al2—F9	1.7848 (15)
Al1—F1^{i}	1.8821 (15)	Al2—F6^{ii}	1.8955 (15)
Al1—F1	1.8859 (15)	Al2—F6	1.8955 (15)
Al1—F1—Al1^{i}	1102.74 (2)	Al2—F6—Al2^{ii}	103.11 (2)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $x, -y, -z - 1$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···F4^{ii}	0.91	1.89	2.738 (2)	154.3
N1—H1A···F5^{ii}	0.91	2.14	2.796 (2)	128.7
N2—H2A···F5^{i}	0.89	1.81	2.683 (2)	167.3
N2—H2B···F7	0.89	1.79	2.678 (3)	174.8
N2—H2C···F3^{ii}	0.89	2.03	2.814 (3)	145.9
N3—H3A···F10^{iii}	0.89	1.95	2.764 (2)	151.7
N3—H3B···F3^{iv}	0.89	1.88	2.771 (3)	177.2
N3—H3C···F9^{iv}	0.89	1.83	2.650 (2)	152.0
N4—H4A···F2^{v}	0.89	2.10	2.884 (3)	146.4
N4—H4B···OW^{ii}	0.89	1.88	2.694 (4)	150.4
N4—H4C···F10^{vi}	0.89	2.17	2.884 (3)	136.3
N4—H4C···F9^{v}	0.89	2.27	2.869 (3)	124.8
OW—H1W···F8^{vi}	0.895 (3)	1.6924 (15)	2.584 (3)	173.8 (2)
OW—H2W···F8^{iv}	0.927 (3)	1.8713 (16)	2.786 (4)	168.8 (2)

Symmetry codes: (i) $1 - x, -y, -z$; (ii) $x - 1, y, z$; (iii) $-x, 1 - y, -z$; (iv) $1 - x, 1 - y, -z$; (v) $-x, -y, -z$; (vi) $x, y, 1 + z$.

H atoms were placed in calculated positions (N—H = 0.89–0.91, C—H = 0.97 Å) and refined with geometrical constraints; a common isotropic displacement factor of 0.04 Å^2. Water H atoms were located

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in Fourier maps and their positions were adjusted in order to fit with water molecule geometry. The maximum residual electron density peak is located 1.02 Å from O*W*.

Data collection: *Stadi*4 (Stoe, 1998); cell refinement: Stadi4; data reduction: *XRED*32 (Stoe, 1998); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *enCIFer* (Allen *et al.* (2004).

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