

## Organic Cation Salts of the Tetrafluoroaluminate Anion. Yes, It Does Exist, and Yes, It Is Tetrahedral!

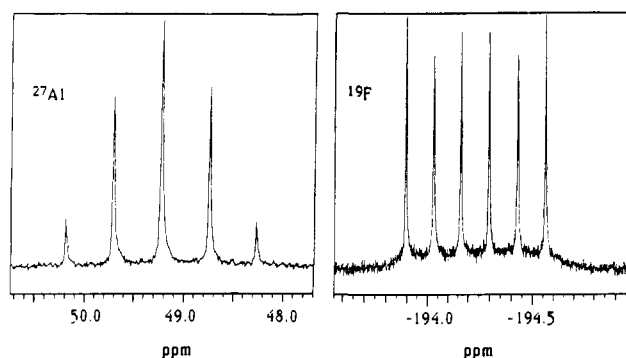
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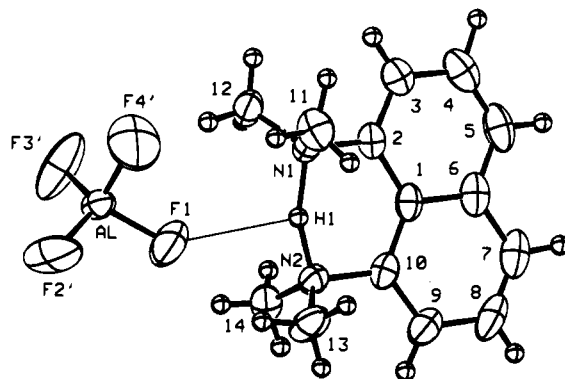
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Haloaluminate chemistry is littered with examples of discrete, tetrahedrally coordinated  $[AlX_4^-]$  species when  $X = Cl, Br, I$ .<sup>1</sup> The equivalent species with  $X = F$  has, however, been controversial, and while there has been indirect evidence for the tetrahedral  $[AlF_4^-]$  anion, citing IR,<sup>2</sup> Raman (in molten salts),<sup>3</sup> and NMR<sup>4</sup> data, structural proof has been lacking. Conversely, the structural data for well-defined  $AlF_3$  and fluoroaluminate species has always revealed octahedral coordination of aluminum having  $AlF_n$  units assembled into a myriad of connectivities—all exclusively based on terminal or corner-shared fluoride.<sup>5</sup> This is true even for those materials with stoichiometries which superficially appear to contain the  $[AlF_4^-]$  anion ( $MAIF_4$ ,  $M = K, Rb, NH_4, Tl^6$ ).

Trimethylaluminum (0.216 g) is dissolved in 20 mL of dry pyridine in a plastic beaker in a nitrogen-filled glovebox. While the solution is stirred, 4 equiv of HF as its  $(HF)_x$ -pyridine adduct (Aldrich) are added slowly. The vigorous exothermic reaction quickly subsides, and the mixture is stirred for 1 h. Dry pyridine (20 mL) is added, and after the solution is allowed to stand undisturbed for several hours, the white precipitate is filtered and dried in vacuum. Powder X-ray diffraction, thermogravimetric, and chemical analyses of the insoluble product reveal a microcrystalline material of stoichiometry [pyridine- $HAIF_4$ ] produced in almost quantitative yield. Metathesis of the pyridinium cation is achieved by slurrying this solid into a solution containing excess 1,8-bis(dimethylamino)naphthalene (Proton Sponge, PS (Aldrich)) dissolved in dry acetonitrile. The slurry quickly becomes homogeneous, and a white solid of mp 260 °C may be recovered by precipitation with diethyl ether. The solid is [PSH][ $AlF_4^-$ ] and is soluble in acetonitrile, methylene chloride, etc. NMR spectra are shown in Figure 1:  $^{19}F$ , -194.2 ppm,  $^1J_{Al-F} = 37.8$  Hz;  $^{27}Al$ , 49.2 ppm,  $^1J_{Al-F} = 37.8$  Hz. Both data suggest a tetrahedral  $[AlF_4^-]$  species in solution. Recrystallization from methylene chloride/toluene provides crystals suitable for X-ray crystallography.<sup>7</sup> The structure is represented in Figure 2 and reveals a simple  $[AlF_4^-]$  anion associated with a [PSH<sup>+</sup>] cation. Although the anion is 2-fold disordered around the Al-F(1) axis (see Figure 2), its tetrahedral nature is confirmed with average Al-F distances of 1.62 Å and F-Al-F = 109°. Interestingly, the closest contact between coordinated fluoride and the chelated proton of the [PSH<sup>+</sup>] cation is 2.77 Å, too long to be considered a hydrogen bond. Thus the  $[AlF_4^-]$  anion exists with only van



**Figure 1.**  $^{27}Al$  (at 78.31 MHz) and  $^{19}F$  (at 282.78 MHz) NMR spectra of [1,8-bis(dimethylamino)naphthaleneH<sup>+</sup>][ $AlF_4^-$ ] (0.002 M in  $CD_3CN$ ) ( $Al(H_2O)_6(NO_3)_3$ , saturated solution in water, and neat  $CFC_{13}$  used as external references). As the concentration of the material in acetonitrile is raised, both  $^{27}Al$  and  $^{19}F$  signals begin to broaden (0.05 M), and eventually all coupling information is lost (0.5 M). This behavior has been interpreted in terms of intermolecular fluoride ion-exchange processes.



**Figure 2.** Molecular structure of the salt of [1,8-bis(dimethylamino)naphthaleneH<sup>+</sup>][ $AlF_4^-$ ]. Selected bond lengths are Al-F(1) = 1.647(2); Al-F(2)<sub>av</sub> = 1.599(6); Al-F(3)<sub>av</sub> = 1.615(5); Al-F(4)<sub>av</sub> = 1.611(5); and F(1)-H(1) = 2.77 Å. The distances to F(2), F(3), and F(4) represent the average of the two positions for each of these atoms which were used to model the disorder about the Al-F(1) axis.<sup>7</sup>

der Waals contacts to either the cations or other anions of the lattice. Vibrational spectra of these crystals show sharp bands at 785 ( $F_2$ , IR)<sup>3</sup> and 635  $cm^{-1}$  ( $A_1$ , Raman)<sup>3</sup> attributable to the  $[AlF_4^-]$  unit, while  $^{19}F$  MAS NMR spectra show a single, sharp line at -187 ppm.

Slurrying the pyridinium salt in neat collidine (collidine = 2,4,6-trimethylpyridine) and heating to 120 °C for 30 min produces, on cooling, crystals of the material [collidine- $HAIF_4$ ]. These crystals are very soluble in acetonitrile and methanol where their NMR properties mimic those of the [PSH<sup>+</sup>] salt above.

(7) Crystal Data:  $C_{14}H_{16}AlF_4N_2$ , from  $CH_2Cl_2$ /toluene, colorless, square plate,  $\sim 0.34 \times 0.10 \times 0.54$  mm, triclinic,  $P1$  (No. 2),  $a = 8.081(1)$ ,  $b = 8.307(1)$ , and  $c = 12.375(1)$  Å,  $\alpha = 82.84(1)^\circ$ ,  $\beta = 76.16(1)^\circ$ , and  $\gamma = 79.13(1)^\circ$ , from the refinement of the Bragg angles of 47 computer-centered reflections,  $\theta = -100$  °C,  $V = 789.4$  Å<sup>3</sup>,  $Z = 2$ ,  $FW = 318.3$ ,  $d_{calcd} = 1.339$  g/cm<sup>3</sup>,  $\mu(Mo) = 1.58$  cm<sup>-1</sup>. Syntex R3 diffractometer, Mo K $\alpha$  radiation, 7858 data collected,  $5.0^\circ \leq 2\theta \leq 55.0^\circ$ , max  $hkl = 10, 10, 31$ , data octants = + + +, + + -, + - +, + - -, - + +, - + -, - - +, - - -, scan method, scan width =  $1.50^\circ \omega$ , scan speed = 3.90–11.70°/min, no absorption correction applied, 1981 unique reflections with  $I \geq 3.0\sigma(I)$ . Structure solved by direct methods (SHELXS), refinement by full-matrix least-squares on  $F$ , scattering factors from *International Tables for X-ray Crystallography, Vol. IV*, including anomalous terms for Al. Three of the fluorine atoms, F(2), F(3), and F(4), were found to be disordered about the Al-F(1) axis. The disordered sites, labeled with a prime and double prime, respectively, were each assigned occupancies of 0.5. These atoms have very large thermal motions (the disorder may well be dynamic) which produces anomalously short Al-F bond lengths. All non-hydrogen atoms refined anisotropic, hydrogen atoms isotropic; 293 parameters, data/parameter ratio = 6.75, final  $R = 0.051$ ,  $R_w = 0.048$ , largest residual density = 0.27 e/Å<sup>3</sup>.

\* Contribution No. 6465.

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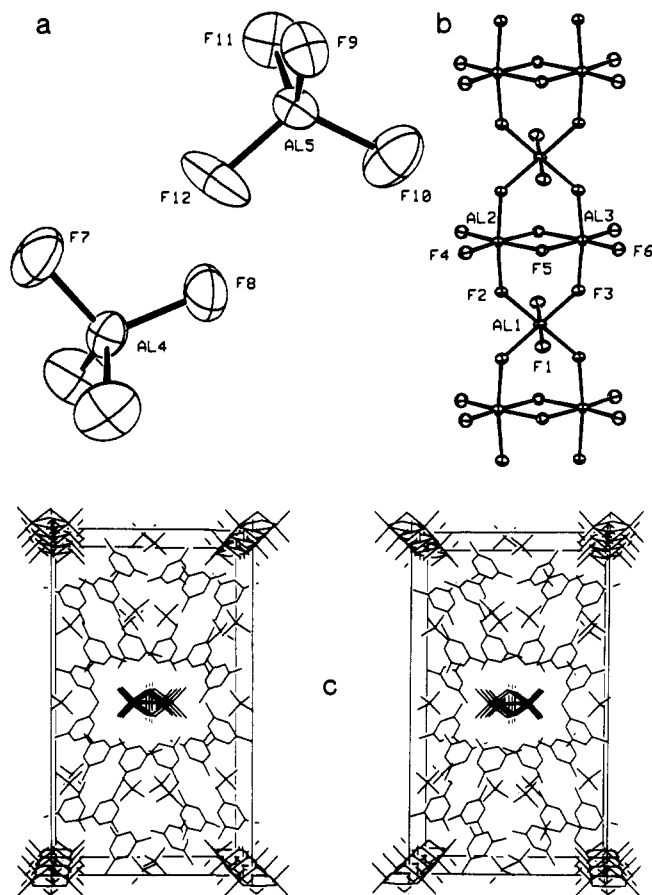
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**Figure 3.** Molecular structure of the salt of [collidineH<sup>+</sup>][AlF<sub>4</sub><sup>-</sup>]. (a) The two crystallographically independent [AlF<sub>4</sub><sup>-</sup>] anions with Al(4) on a 2-fold axis. (b) The [AlF<sub>4</sub><sup>-</sup>]<sub>n</sub> chain with Al(1) on an inversion center and Al(2) and Al(3) on 2-fold axes. (c) The crystal packing viewed, in stereo, along the *c* axis showing the [AlF<sub>4</sub><sup>-</sup>]<sub>n</sub> chains running parallel to the *c* axis, sheathed by collidine, cations and with the [AlF<sub>4</sub><sup>-</sup>] anions between the sheaths. Selected Al–F bond lengths are Al(1)–F(1) = 1.755(1); Al(1)–F(2) = 1.856(2); Al(1)–F(3) = 1.842(2); Al(2)–F(2) = 1.835(2); Al(2)–F(4) = 1.745(2); Al(2)–F(5) = 1.858(2); Al(3)–F(3) = 1.825(2); Al(3)–F(5) = 1.864(2); Al(3)–F(6) = 1.747(2); Al(4)–F(7) = 1.651(3); Al(4)–F(8) = 1.646(2); Al(5)–F(9) = 1.660(2); Al(5)–F(10) = 1.661(3); Al(5)–F(11) = 1.656(3); and Al(5)–F(12) = 1.640(3) Å.

However, crystallographic analysis<sup>8</sup> reveals an unexpectedly complex structure, depicted in Figure 3. The backbone of the structure is a series of infinite [AlF<sub>4</sub><sup>-</sup>]<sub>n</sub> chains which extend along the *c* axis, giving the crystals their needle morphology. The chains consist of AlF<sub>6</sub> octahedra which are corner-shared to two pairs of edge-shared octahedra. This is the first time that edge-shared

(8) Crystal Data: C<sub>8</sub>H<sub>11</sub>AlF<sub>4</sub>N, from hot collidine, colorless, needle, ~0.05 × 0.05 × 0.70 mm, orthorhombic, *Pbcn* (No. 60), *a* = 29.673(6), *b* = 16.644(3), and *c* = 12.439(3) Å, from the refinement of the Bragg angles of 47 computer-centered reflections, *T* = -100 °C, *V* = 6143.3 Å<sup>3</sup>, *Z* = 24, *FW* = 225.17, *d*<sub>calc</sub> = 1.461 g/cm<sup>3</sup>, *μ*(Mo) = 2.10 cm<sup>-1</sup>. Syntex R3 diffractometer, Mo K $\alpha$  radiation, 7782 data collected, 4.1° ≤ 2 $\theta$  ≤ 55.0°, max *hkl* = 38, 21, 16, data octants = - + +,  $\omega$  scan method, scan width = 0.70° $\omega$ , scan speed = 1.00°/min, no absorption correction applied, 3401 unique reflections with *I* ≥ 2.5 $\sigma$ (*I*). Structure solved by direct methods (SHELXS), refinement by full-matrix least-squares on *F*, scattering factors from *International Tables for X-ray Crystallography*, Vol. IV, including anomalous terms for Al. All nonhydrogen atoms refined anisotropic, hydrogen atoms isotropic, 526 parameters, data/parameter ratio = 6.46, final *R* = 0.044, *R*<sub>w</sub> = 0.036, largest residual density = 0.28 e/Å<sup>3</sup>.

AlF<sub>6</sub> octahedral units have been identified in fluoroaluminate materials, and this connectivity is very reminiscent of that in the rhodso cation [Cr<sub>4</sub>(OH)<sub>6</sub>(NH<sub>3</sub>)<sub>12</sub>]<sup>6+</sup>.<sup>9</sup> The three collidine cations form strong hydrogen bonds (F–H = 1.84(3), 1.86(3), and 1.77(4) Å) to the three terminal fluoride ions of the chain and effectively form a sheath around these chains. In between the chains and residing in a hydrophobic region defined by the collidine sheaths are two independent tetrahedral [AlF<sub>4</sub><sup>-</sup>] anions, one on a general position and the other on a crystallographic 2-fold axis. Both well-ordered anions once again confirm the existence of discrete tetrahedral [AlF<sub>4</sub><sup>-</sup>] species with Al–F<sub>av</sub> = 1.65(1) Å and F–Al–F<sub>av</sub> = 109(2)°. Again, the [AlF<sub>4</sub><sup>-</sup>] anions have no contact, other than van der Waals, with other species in the lattice. It is particularly interesting to note that within the same lattice both octahedral AlF<sub>6</sub> units and tetrahedral [AlF<sub>4</sub><sup>-</sup>] ions can coexist, implying no overwhelming thermodynamic driving force toward one or the other of these structure types for fluoroaluminate species. These structures suggest that the octahedral AlF<sub>6</sub> building block dislikes terminal fluorides and therefore forms either fluoride bridges, strong hydrogen bonds to available protonic species (such as the collidine proton), or strong ionic bonds to inorganic ions such as K<sup>+</sup> in KAlF<sub>4</sub>.<sup>6</sup> It is tempting to suggest that in the absence of such interactions the AlF<sub>n</sub> species prefer to adopt the tetrahedral motif, which has little propensity toward further bonding of its terminal fluorides—most likely due to the lower charge and stronger covalent Al–F bonds in the [AlF<sub>4</sub><sup>-</sup>] ion. IR spectra of the collidine crystals again show the 785-cm<sup>-1</sup> band attributed to the tetrahedral [AlF<sub>4</sub><sup>-</sup>] anions but also show several bands at lower frequency for the octahedral AlF<sub>6</sub> units of the chain. The <sup>19</sup>F MAS NMR spectrum has two peaks, one sharp at ca. -188 ppm assigned to the [AlF<sub>4</sub><sup>-</sup>] units and one broad at ca. -155 ppm assigned to the fluorides in the octahedral AlF<sub>6</sub> units of the chains. That the solution-phase NMR spectra show only the tetrahedral [AlF<sub>4</sub><sup>-</sup>] anion indicates that the [AlF<sub>4</sub><sup>-</sup>]<sub>n</sub> chain is easily cleaved into its constituent units in polar organic solvents.

We have demonstrated conclusively the existence of the tetrahedral [AlF<sub>4</sub><sup>-</sup>] anion and shown that it can be solubilized in organic solvents and crystallized as organocation salts. Spectroscopic and structural properties are essentially as predicted, although we note a very low propensity toward formation of hydrogen bonds, especially as compared to terminal fluorides of the more typical AlF<sub>6</sub> octahedral units. In addition, we have revealed a new bonding motif for octahedral AlF<sub>6</sub> units themselves (edge-sharing) in the chain of the collidine salt structure. Numerous other salts of AlF species, displaying a wealth of structural and spectroscopic behaviors, have been prepared, and this data is forthcoming. Finally, the thermochemistry of such salts has proven a rich vein of new fluoroaluminate chemistry, and we will soon report on two new phases of AlF<sub>3</sub> prepared from salts of the type described above.

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**Supplementary Material Available:** Tables of fractional atomic coordinates, thermal parameters, bond distances, and bond angles for all atoms and for both structures (21 pages); tables of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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