Inorg. Chem. **1993**, *32*, 2985–2986

Novel Coordination Geometries in Fluoroaluminate Salts

Norman Herron,* Richard L. Harlow, and David L. Thorn

Central Research and Development Department,† E. I. du Pont de Nemours and Company, Wilmington, Delaware 19880-0328

Received February 10, 1993

Fluorides of aluminum are some of the most important inorganic materials manufactured since they find use both as commodity chemicals[1] (for the aluminum industry) and as catalysts for the new "ozone benign" chlorofluorocarbon alternatives.[2] This latter application is often dependent on the structural form for the Al–F species.[2] An early claim to the production of the tetrahedral $[AlF_4^-]$ anion was for the salt with the organic cation $[N(CH_3)_4^+]$. Bukovec and Siftar[3] concluded that neutralization of an aqueous solution of hydrated aluminum trifluoride in 40% HF with $N(CH_3)_4OH$ gave a material of stoichiometry $N(CH_3)_4AlF_4{\cdot}H_2O$. IR data were used to infer that this material contained octahedral Al–F species but that dehydration at <120 °C gave the very hygroscopic material $N(CH_3)_4AlF_4$, which contained the tetrahedral anion $[AlF_4^-]$ (780 cm^{-1}). Later work provided a material of stoichiometry $(N(CH_3)_4)_2AlF_5$ under very similar conditions.[4] Our own recent work[5] provides direct structural evidence for the existence of discrete tetrahedral $[AlF_4^-]$ ions. As part of that study we have re-examined the $[N(CH_3)_4^+]$ salt prepared using our new synthetic approach and have successfully crystallized both the hydrated and anhydrous materials. Both structures are reported below.

We have previously reported[5] that the insoluble material $[pyridine\text{-}H^+][AlF_4^-]$, prepared using drybox procedures, may be metathesized to the soluble salt of stoichiometry $[collidine\text{-}H^+][AlF_4^-]$ (collidine = 2,4,6-trimethylpyridine). A 0.90-g sample of the latter material is dissolved in 10 mL of very dry methanol in a drybox. With stirring, a second solution of 0.44 g of $N(CH_3)_4Cl$ (dried at 120 °C in high vacuum for 30 min) in 10 mL of dry methanol is added. The clear solution is evaporated to dryness and the white solid extracted into 5 mL of dry acetonitrile, leaving behind a residue of $[collidine\text{-}H^+][Cl^-]$. The acetonitrile is evaporated leaving a white solid, which is a mixture of $[collidine\text{-}H^+][Cl^-]$ and $N(CH_3)_4AlF_4$. TGA analysis of this mixture shows that the $[collidine\text{-}H^+][Cl^-]$ can be sublimed away in flowing nitrogen at >200 °C and that the residual white powder is pure $N(CH_3)_4AlF_4$, which does not begin to decompose until >425 °C. This resulting white powder is very soluble in acetonitrile and methanol. The ^{19}F NMR spectrum in CD_3CN solution (0.002 M) is a sextet of approximately equal intensities ($I(^{27}Al) = {}^5/_2$) ($^1J_{F\text{-}Al} = 37.8$ Hz) centered at −194.9 ppm and is characteristic of isolated $[AlF_4^-]$ tetrahedra in solution.[5] Recrystallization from hot, dry acetone provided a colorless, platelike crystal for X-ray crystallography.[6] Table I details the results of the crystallographic study. As expected, this material contains isolated, tetrahedral, ordered cations $[N(CH_3)_4^+]$ and tetrahedral anions $[AlF_4^-]$, the latter being disordered around the 3-fold crystallographic axes and having Al–F = 1.658(3) Å. These crystals have a single, sharp ^{19}F MAS NMR signal at −190.1 ppm and an IR band at 783 cm^{-1}, both of which are characteristic of the $[AlF_4^-]$ anion in the solid state.[5]

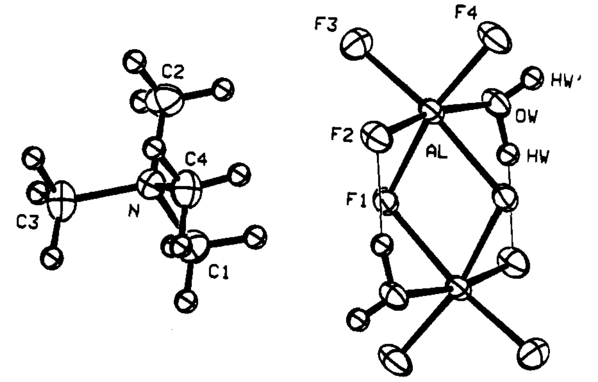

Figure 1. Thermal ellipsoid drawing and atom-labeling scheme for $[N(CH_3)_4^+]_2[Al_2F_8(H_2O)_2^{2-}]$. The dimeric anion sits on a crystallographic center of inversion. Selected bond distances (Å): Al–F(1), 1.869(2); Al–F(1)^a, 1.899(2); Al–F(2), 1.780(2); Al–F(3), 1.729(2); Al–F(4), 1.747(2); Al–O(W), 1.974(2). Selected bond angles (deg): F(1)–Al–F(1)^a, 76.5(1); F(1)–Al–F(2), 89.8(1); F(1)–Al–F(3), 92.9(1); F(1)–Al–F(4), 167.2(1); F(1)^a–Al–F(2), 87.0(1); F(1)^a–Al–F(3), 169.2(1); F(1)^a–Al–F(4), 92.0; F(2)–Al–F(3), 95.2(1); F(2)–Al–F(4), 95.2(1); F(3)–Al–F(4), 98.3; F(1)–Al–O(W), 83.0(1); F(1)^a–Al–O(W), 84.8(1), F(2)–Al–O(W), 170.1(1); F(3)–Al–O(W), 91.9(1); F(4)–Al–O(W), 90.5(1); Al–F(1)–Al^a, 103.5(1). a = $1 - x$, $1 - y$, $1 - z$. There is one crystallographically unique intramolecular hydrogen bond, O(W)–H(W)- -F(2)^a: O(W)–H(W), 0.89(4); H(W)- -F(2)^a, 1.78(4); O(W)- -F(2)^a, 2.633(2) Å; O(W)–H(W)- -F(2)^a, 159(3)°.

Table I. Crystal Structure Information

compd	$[N(CH_3)_4][AlF_4]$	$[N(CH_3)_4]_2[Al_2F_8(H_2O)_2]$
formula	$C_4H_{12}AlF_4N$	$C_8H_{28}Al_2F_8N_2O_2$
fw	177.13	390.28
crystal system	cubic	triclinic
space group	$P\bar{4}3m$	$P\bar{1}$
a, Å	5.985(1)	6.813(1)
b, Å		8.101(1)
c, Å		8.972(1)
α, deg		64.93(1)
β, deg		82.50(1)
γ, deg		73.48(1)
V, $Å^3$	214.4	430.0
T, K	183	213
no. of reflns (tot)	1543	2652
no. of reflns ($I \geq 3.0\sigma(I)$)	71	1249
Z	1	1
D_x, g cm^{-3}	1.372	1.507
μ, cm^{-1}	2.31	2.45
$R(F_o)^a$	0.020	0.041
$R_w(F_o)^a$	0.022	0.034

[a] $R(F_o) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w(F_o) = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$.

When crystals of the $[N(CH_3)_4^+][AlF_4^-]$ salt are exposed to the atmosphere, they quickly deteriorate, and the resulting white powder may be recrystallized from acetone. Alternatively, the original material may be recrystallized from acetone which has not been carefully dried. In both cases, colorless parallelepiped crystals are recovered having identical powder X-ray diffractograms which in turn are quite different from that of the anhydrous starting material. TGA analysis of these crystals reveals a weight loss at 125 °C in flowing nitrogen which corresponds precisely to the loss of 1 equiv of water per formula unit, thus confirming the stoichiometry suggested by Bukovec and Siftar, i.e. $N(CH_3)_4$

---

† Contribution No. 6473.

(1) Cochet-Muchy, B.; Portier, J. In *Inorganic Solid Fluorides, Chemistry and Physics*; Hagenmuller, P., Ed.; Academic Press: Orlando, FL, 1985; p 580.

(2) Christoph, F. J.; Teufer, G. U.S. Patent 3,178,484, 1965. Christoph, F. J.; Teufer, G. G.B. Patent 1,026,105, 1966.

(3) Bukovec, P.; Siftar, J. *Monatsh. Chem.* **1975**, *106*, 483.

(4) Sengupta, A. K.; Sen, K. *Indian J. Chem.* **1979**, *17A*, 107.

(5) Herron, N.; Thorn, D. L.; Harlow, R. L.; Davidson, F. *J. Am. Chem. Soc.* **1993**, *115*, 3028.

0020-1669/93/1332-2985$04.00/0

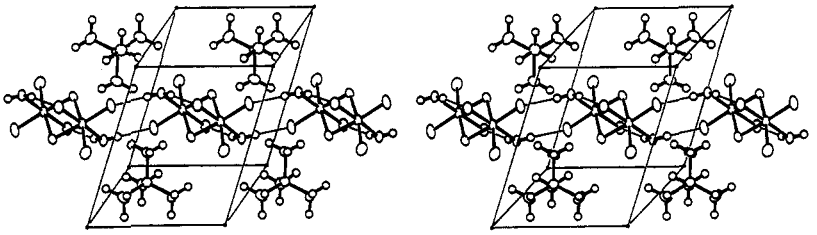

Figure 2. Stereoscopic packing diagram for $[N(CH_3)_4^+]_2[Al_2F_8(H_2O)_2^{2-}]$. The anions are linked by O–H- -F hydrogen bonds into chains that run parallel to the *a* axis: O(W)–H(W)′, 0.71(4); H(W)′- -F(4)^b, 1.87(4); O(W)- -F(4)^b, 2.585(2) Å, O(W)–H(W)′- -F(4)^b, 174(4)°. b = 2 – *x*, 1 – *y*, 1 – *z*. There are numerous C–H- -F contacts between the cation and the anion which might also be described as weak hydrogen bonds; five contacts have H- -F distances which are less than 2.50 Å, ranging from 2.34 to 2.49 Å.

$AlF_4 \cdot H_2O$. X-ray crystallographic analysis[6] provides details of a very unusual structural motif for Al–F species. Crystallographic details are given in Table I while the structure is depicted in Figures 1 and 2.

The structure no longer contains isolated $[AlF_4^-]$ anions but rather consists of $[Al_2F_8(H_2O)_2^{2-}]$ dianions in which each aluminum is octahedrally coordinated to five fluorine ligands and one water molecule. Two of the fluorine ligands serve as bridges between the aluminum atoms, producing the first example of a discrete fluoroaluminate species where the Al–F octahedra are linked by edge-sharing rather than the normal corner-sharing. The dimeric anion sits on a crystallographic center of symmetry and forms a chain with other anions through O–H- -F hydrogen bonds (Figure 2; the packing is similar to that of many dicarboxylic acids). These chains propagate parallel to the *a* axis and give the crystal its needlelike morphology. There is also an intramolecular O–H- -F hydrogen bond between the halves of the dimer. The Al–F distances vary according to whether the fluorine ligands are bridging or terminal and also according to the strength of any hydrogen bonds which they accept (see captions to Figures 2 and 3). One of the terminal fluorine ligands (F(3)) appears to be involved in only very weak hydrogen-bonding with three hydrogen atoms of the tetramethylammonium cation (F(3)–H(1) = 2.42, F(3)–H(2′) = 2.49, F(3)–H(4) = 2.44 Å). The bond distance Al–F(3) = 1.729(2) Å therefore represents a close approximation to a true terminal Al–F distance for an octahedral Al–F unit and, as expected, is one of the shortest such bond lengths recorded. The ^{19}F MAS NMR spectrum of these crystals has a single broad resonance at –159.3 ppm with a shoulder at –146.2 ppm, which are signals characteristic of fluorine coordinated to aluminum in an octahedral environment.[5] CD_3CN solutions (0.002 M) of these crystals, however, have ^{19}F NMR spectra showing the sextet pattern and shift identical to those reported above for the anhydrous material. Clearly, the dimeric units of the solid-state structure do not survive in this solvent and the $[AlF_4^-]$ anion is regenerated by cleavage of the hydrogen-bonding network and loss of the coordinated water molecule from the aluminum coordination sphere.

It is interesting to note that these two structures represent an unusual situation for solid-state coordination compounds. It is usually observed that, as terminal ligands are removed from a metal center, the bonding network reorganizes by forming additional bridges between metals to occupy the vacant coordination sites created by the loss of these terminal ligands. This fusing together of metal centers into a highly bridged network is the basis for many transformations of isolated molecules (or ions) into extended polymeric structures.[9] In the present example, however, we note the reverse phenomenon; i.e., as water ligands are driven out of the aluminum coordination sphere, the dimeric $[Al_2F_8(H_2O)_2^{2-}]$ anion cleaves into monomeric $[AlF_4^-]$ anions.

In conclusion, we have prepared and structurally characterized two salts previously reported by Bukovec and Siftar and shown that the claims to a tetrahedral $[AlF_4^-]$ anion in the anhydrous material were correct. The hydrated salt, on the other hand, contains octahedrally coordinated aluminum and provides the first example of edge-shared octahedra in molecular fluoroaluminate species. An extensive network of intra- and intermolecular hydrogen bonds holds the dimeric $[Al_2F_8(H_2O)_2^{2-}]$ anions together in the solid state, but this dimeric unit is easily cleaved by loss of water either by heat in the solid state or by simple dissolution in polar organic solvents. The controlled, high-temperature decomposition of these, as well as numerous other, organic cation salts leads to AlF_3 materials, including previously unknown phases of AlF_3, that will be reported in the near future.

Acknowledgment. We are grateful for the skilled technical assistance of Mr. J. B. Jensen, Ms. L. Ayers, and Mr. L. Lardear. The MAS NMR spectra were recorded and interpreted with the help of Dr. C. Campbell.

Supplementary Material Available: Tables giving atomic coordinates, anisotropic thermal parameters, and complete interatomic distances and angles for both structures (6 pages). Ordering information is given on any current masthead page. Tables of structure factor amplitudes are available directly from the authors at the given address.

---

(6) The crystallographic investigation of $[N(CH_3)_4][AlF_4]$ was carried out on a Syntex P3 diffractometer with the crystal (0.25 × 0.11 × 0.30 mm) cooled to –90 °C (graphite monochromator, Mo Kα radiation, λ = 0.710 69 Å). The unit cell parameters were refined from the Bragg angles of 40 computer-centered reflections. A total of 1543 data were collected using the ω scan technique: $5.0 < 2\theta < 60.0°$ with scan widths of 2.0° and scan speeds of 4.9–11.7° min^{-1}. Because a possible superlattice could have been hidden by the large mosaicity of the crystal, the data were collected assuming an 11.97-Å cell (2× the determined cell). No superlattice was seen. The intensities of standard reflections were monitored periodically, but only statistical variations were noted over the course of the data collection. An azimuthal scan showed no variation in intensity with ψ; no correction for absorption was made. A total of 71 unique reflections with $I \geq 3.0\sigma(I)$ were used for the structure refinement. Data for the structure of $[N(CH_3)_4]_2[Al_2F_8(H_2O)_2]$ were collected on an Enraf-Nonius CAD-4 diffractometer with the crystal (0.07 × 0.09 × 0.40 mm) cooled to –65 °C (graphite monochromator, Mo Kα radiation, λ = 0.710 69 Å). The crystal system, space group, and approximate unit cell dimensions were determined during a preliminary investigation. The unit cell parameters were subsequently refined from the Bragg angles of 25 computer-centered reflections. A total of 2652 intensity data were collected using the ω scan technique: $5.0 < 2\theta < 60.0°$ with scan widths of 1.3–1.8° and scan speeds of 1.5–3.4° min^{-1}. The intensities of standard reflections were monitored periodically, and a correction was applied for a decrease of 5% during the data collection period. An azimuthal scan showed little variation in intensity; no correction for absorption was made. A total of 1249 unique reflections with $I \geq 3.0\sigma(I)$ were used for the structure refinement. The refinement and analysis of the two structures were carried out using a package of local programs.[7] The atomic scattering factors were taken from the tabulations of Cromer and Waber; anomalous dispersion corrections were by Cromer.[8] In the least-squares refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$ with the weights, *w*, assigned as $[\sigma^2(I) + 0.0009I^2]^{-1/2}$. The structures of the two compounds were solved by direct methods. All of the non-hydrogen atoms were refined with anisotropic thermal parameters; all hydrogens, with isotropic thermal parameters. For $[N(CH_3)_4][AlF_4]$, the fluorine atom was found to be 3-fold disordered around a crystallographic 3-fold axis; when placed on the 3-fold axis, its thermal parameter became very large. Table I details the results of the crystallographic studies.

(7) J. C. Calabrese (**1991**), Central Research and Development, E. I. du Pont de Nemours and Co., P.O. Box 80228, Wilmington DE 19880-0228.

(8) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1.

(9) Farneth, W. E.; Herron, N.; Wang, Y. *Chem. Mater.* **1992**, *4*, 916.