

The DuPont Powder Challenge: The Crystal Structure of $[\text{C}_5\text{NH}_6][\text{Al}_3\text{F}_{10}]$ —A Cautionary Tale

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A compound previously reported as HAlF_4 has been shown to be $[\text{pyridinium}][\text{Al}_3\text{F}_{10}]$. The structure of this phase was solved and refined using a combination of synchrotron X-ray and neutron powder diffraction techniques in association with a number of other analytical techniques. The structure consists of $[\text{Al}_3\text{F}_{10}]_n^-$ sheets containing both corner-sharing (common) and edge-sharing (unusual) AlF_6 octahedra. The sheets are separated by pyridinium cations oriented perpendicular to the sheets. The final crystallographic data are as follows: monoclinic, space group $C2/m$, $a = 8.2706(3)$, $b = 6.1998(3)$, $c = 10.525(1)$ Å, $\beta = 103.38(1)^\circ$, $V = 525.0(1)$ Å³, and $Z = 2$. This compound appears to be another example of a layered “clay-like” aluminum fluoride.

Introduction

The structures of microcrystalline compounds can often be solved directly from their synchrotron powder diffraction patterns. However, the odds decrease as peaks broaden, as unit cell dimensions and the size of the asymmetric unit increase, and as the structural symmetry decreases. Many of the compounds that have a great deal of industrial interest seem to fall into one or more of these categories. Unfortunately, experience has shown that solving structures using techniques derived from single-crystal methods does not always work well with powder data taken on samples with the above “complications”. For the powder technique to be generally useful as a routine method of crystal structure analysis, new techniques for solving structures need to be found.

To promote the search for new structural methodologies, the Corporate Center for Analytical Science at The DuPont Company offered \$1000 to anyone who could solve the crystal structure of a compound first synthesized at DuPont and ultimately published by Herron et al.¹ as HAlF_4 . Made by the thermal decomposition of pyridinium aluminum fluoride, $(\text{PyH})\text{AlF}_4$, its synchrotron diffraction pattern (NSLS, X7a)² consisted of broad peaks with a large amount of anisotropy: typically fwhm's values ranged from 0.05 to 0.20°. This pattern could be indexed on the basis of a C-centered monoclinic cell but not with the usual certainty afforded by

synchrotron patterns of truly crystalline materials. Nonetheless, an attempt was made to solve the structure from the extracted intensities. Standard direct methods and Patterson techniques were applied but both failed to give convincing solutions. In the meantime, it was noted that the b axis of the monoclinic cell was almost exactly the Al··Al “repeat” distance of 6.22 Å found for the $[\text{AlF}_4]_n^-$ infinite chain in the structure of $[\text{collidineH}^+][\text{AlF}_4^-]$.³ Furthermore, the local $2/m$ symmetry of the infinite chain was consistent with the C-centered monoclinic cell if the space group were assumed to be $C2/m$ and if all of the Al atoms had octahedral symmetry as indicated by a solid-state NMR measurement. The C-centering operation, however, puts limits on the manner in which the chain could be inserted into the unit cell. By rotating the chain, it was possible to overlap certain of the fluorine atoms and obtain a chemically reasonable model of $[\text{Al}_3\text{F}_{10}]_n^-$ sheets parallel to the ab plane at a distance of the c axis apart. While the model appeared to fit the X-ray

(2) A powder sample of the compound was compressed into a deep flat plate holder and data were collected in high-resolution mode [Cox, D. E.; Toby, B. H.; Eddy, M. M. *Aust. J. Phys.* **1988**, *41*, 117] at the X7a beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. The beamline was configured with a Si(111) monochromator and Ge(220) analyzer, a scintillation detector, and incident beam-defining slits of 8.0 mm by 1.5 mm. The wavelength, calibrated using a Si powder standard with $a = 5.430\ 825$ Å, was 0.848 78(3) Å. The data were collected in six scans covering a 2θ range from 4 to 40° with a step size of 0.02° and a total count time of 12 s per point. The sample was “rocked” by 0.5° at low angles increasing to 2.0° at the higher angles.

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

(1) Herron, N.; Thorn, D. L.; Harlow, R. L.; Jones, G. A.; Parise, J. B.; Fernandez-Baca, J. A.; Vogt, T. *Chem. Mater.* **1995**, *7*, 75.

pattern to some degree, further difference maps failed to "fill in" the space between the layers, i.e., there were no signs of other Al atoms which might extend above and below the $[\text{Al}_3\text{F}_{10}]_n^-$ layers to keep those layers apart.

At this point, TEM studies were employed to check on the unit cell dimensions. The crystallites of HAlF_4 were found to be platelike (parallel to the *ab* plane) but also very sensitive to the electron beam. Nonetheless, diffraction patterns from several crystallites were obtained and the dimensions of the *a* and *b* axes were confirmed. Intensities from one pattern were extracted and hand phased but the resulting 2-D potential map could not be readily interpreted. However, the platelike habit of the crystals was the cause of some concern: the synchrotron data collected in the flat-plate mode probably suffered from preferred orientation effects. Thus, a second set of synchrotron data (NSLS, X3b1)⁴ was then collected on a capillary sample in the hopes of eliminating any orientation effects. A comparison of the two patterns suggested that the X7a data did indeed suffer from some preferred orientation effects. A fitting of the $[\text{Al}_3\text{F}_{10}]_n^-$ model to the new X3b1 pattern, however, was no better than with the X7a data.

Three further powder data sets were then collected. (1) Even though the compound was known to contain problematic H atoms, a neutron pattern (HFBR-HRNP)⁵ was obtained to check the fit with $[\text{Al}_3\text{F}_{10}]_n^-$ model and to again search for other atoms between the layers. In fact, the fit was relatively poor and various maps failed to extend the structure. (2) Another synchrotron pattern at a very short wavelength, 0.43788(6) Å, but under low-resolution conditions was collected (NSLS, X17B2) to produce a "pair-distribution" pattern. Peaks representing the expected Al-F and F...F interatomic vectors and one of the Al...Al vectors (corresponding to corner-shared AlF_6 octahedra) could be readily assigned. One further peak, although weak, appeared to confirm the presence of an Al...Al vector from edge-shared octahedra. Thus, this analysis appeared to confirm the presence of both edge-shared and corner-shared AlF_6 octahedra as found in the $[\text{Al}_3\text{F}_{10}]_n^-$ layered model. (3) Finally, a synchrotron powder data set was again collected at X7a but using a capillary sample cooled to 20 K in the hopes of "clarifying" the interlayer region. The pattern was, unfortunately, worse in quality than the pattern collected at room temperature.

There was a growing concern at this point that the structure might never be resolved. With the structural solution at an apparent impasse, it was decided to make the two original synchrotron data sets available to the public as the DuPont Powder Challenge.

Experimental Section

All materials were handled in a nitrogen-filled glovebox to protect them from moisture. Thermal analysis was carried out

(4) A powder sample of the compound was sealed in a 1.0-mm glass capillary and data were collected in the high-resolution mode at the X3b1 beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. Other details: $\lambda = 0.69955(1)$ Å; 2θ range from 3.00 to 50.17° with a step size of 0.01°; 10 s per point; 10° rocking angle.

(5) The instrument is described in: Passell, L.; Bar-ziv, S.; Gardner, D. W.; Cox, D. E.; Axe, J. D. *Mater. Sci. Forum* **1991**, *79*, 475. The wavelength used was 1.8857 Å.

using a TA Instruments thermogravimetric analyzer located inside such a drybox. Elemental analysis was performed by MicroAnalysis Inc., Wilmington, DE.

Synthesis of (PyH) Al_3F_{10} . A total of 3.0 g of the precursor material $(\text{PyH})\text{AlF}_4$ ^{1,3} was spread thinly in a quartz boat inside a quartz-lined tube furnace. A flow of 100 mL/min dry nitrogen was established over the sample and the exit gas stream was scrubbed through a pair of slightly acidic (HCl) and then slightly basic (NaOH) water bubblers. All apparatus was located in an efficient fume hood. The furnace was ramped at 10 °C/min to 275 °C and then held at this temperature for 30 min. The resulting white solid was recovered for analysis. Calcd for $\text{C}_5\text{H}_6\text{NF}_{10}\text{Al}_3$: C, 17.11%; H, 1.72%; N, 3.99%; F, 54.12%. Found: C, 16.99%; H, 1.69%; N, 3.91%; F, 54.3%.

Results and Discussion

Once the Challenge was announced and the data posted on the WEB, a number of entries were submitted. Submissions by LeBail⁶ and Neels⁷ contained the same basic $[\text{Al}_3\text{F}_{10}]_n^-$ sheets described above and offered suggestions as to the positioning of $[\text{HFH}]^+$ counterions. These proposed models, however, also failed to fit the neutron data (in particular) and, in addition, left a considerable amount of empty space between the layers. The structure was eventually solved by two authors of this paper (L.S. and S.K.) who also started with $[\text{Al}_3\text{F}_{10}]_n^-$ sheets, but then asked for a sample of the compound for analysis in their own laboratory. They then determined that there was some "organic" still present in the compound. Assuming that the interlayer material was probably "organic" in nature, peaks in a difference map were then interpreted as a six-membered ring with its orientation perpendicular to the $[\text{Al}_3\text{F}_{10}]_n^-$ sheets.

At this point, a reanalysis of the compound was carried out, actively seeking residual organic species in the material. Once again, detailed TGA analysis (Figure 1a) of the precursor material $(\text{PyH})\text{AlF}_4$ revealed a weight loss beginning at room temperature and extending all the way to ~325 °C which seemed consistent with loss of ~1 equiv of pyridine.¹ TGA/MS confirmed that pyridine was being evolved during this process. Continued heating also exhibited a second weight loss at ~325 °C and TGA/MS once again indicated that HF was being evolved but, as with previous analyses, this was also contaminated with some pyridine. A bulk sample of the intermediate material was prepared by carefully controlled heating to 275 °C in dry nitrogen and subjected to XRD, TGA (Figure 1b), and elemental analysis. These combined techniques quickly revealed that the material previously assigned as HAlF_4 and having the diffraction pattern in question, actually corresponded to a stoichiometry of $(\text{pyridineH})_{0.33}\text{AlF}_{3.33}$. Coupled with the diffraction results above, it became clear that the material did, in fact, still contain some pyridine left over from the precursor and had the stoichiometry $(\text{PyH})\text{Al}_3\text{F}_{10}$.

In the meantime, one final data set was collected at the APS on the 5-BMB high-resolution powder diffraction beamline.⁸ Very short wavelength radiation, 0.49583(2) Å, enabled the use of an unusually large 2.0-

(6) Le Bail, A. Laboratoire des Fluorures, CNRS UPRES-A 6010, Faculté des Sciences, Université du Maine, F-72085 Le Mans Cedex 9, France, personal communication.

(7) Neels, A. Institute de Chemie de l'Université de Neuchatel, Avenue de Bellevaux 51, CH-2000, Neuchatel, Switzerland, personal communication.

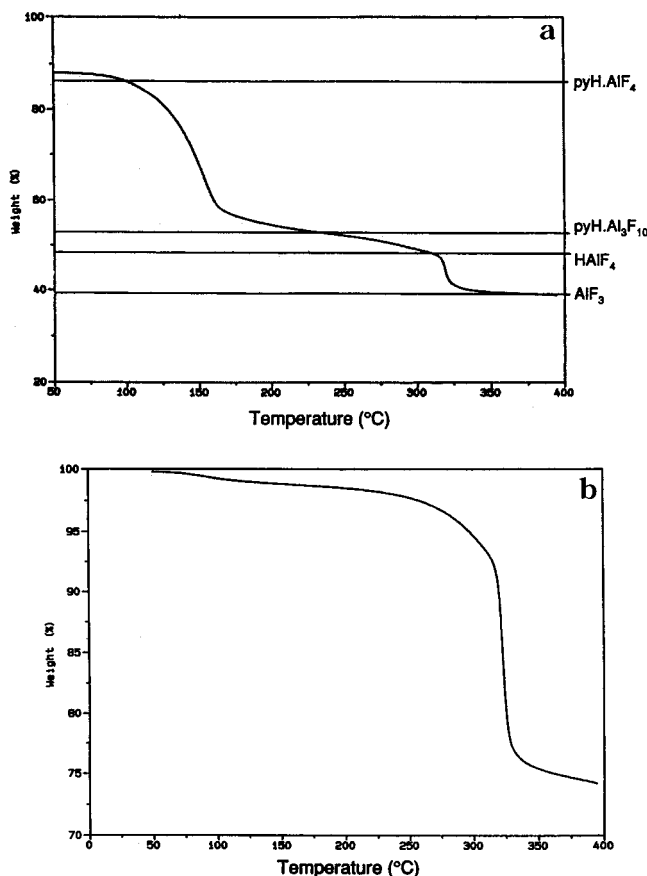


Figure 1. (a) TGA of PyH·AlF₄ and (b) TGA of (PyH)(Al₃F₁₀).

mm capillary that essentially eliminated the preferred orientation without introducing serious absorption effects. This pattern was now used in the final refinement of the structure.

The Rietveld refinement of the structure was carried out with GSAS⁹ and, in the final stages, used only the X-ray data from the APS and the neutron pattern from the HFBR. The refinement converged at the following *R* values: X-ray, wRp = 0.098, Rp = 0.074, *R*(Bragg) = 0.048 for 113 reflections; neutron, wRp = 0.017, Rp = 0.017, *R*(Bragg) = 0.057 for 242 reflections. Variables included in the refinement were the scale factors, shifted Chebyshev background functions, a Lorentzian profile parameter for the X-ray data, three Gaussian profile parameters for the neutron data, anisotropic broadening parameters, and low-angle peak distortion parameters. Atomic coordinates of all atoms were allowed to refine with soft constraints applied to the C–C distances (1.38 with an esd of 0.02) and the C–H distances (1.07 with an esd of 0.02). Without these constraints, the C–C bond lengths, for example, ranged from 1.3 to 1.5 Å. The constraints caused a small rise in the various *R* values but, of course, gave more chemically acceptable bond distances. The fundamental problem is that the positions of the carbon and hydrogen atoms are not well-

Table 1. Atomic Coordinates (Å) and Isotropic Thermal Parameters (Å²) for [Al₁₀F₃][C₅NH₆]^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	100 × <i>U</i> _{iso} ^a
Al(1)	0.0	0.0	0.0	0.5(2)
Al(2)	-0.0707(12)	0.5	0.1100(9)	0.5(2)
F(1)	-0.0683(7)	0.2048(6)	0.0941(8)	0.7(1)
F(2)	0.2080(10)	0.0	0.1101(10)	0.7(1)
F(3)	-0.0073(11)	0.5	0.2956(10)	5.0(4)
F(4)	0.1355(11)	0.5	0.0720(12)	0.7(1)
C(1) ^b	-0.1721(14)	0.0	0.4596(20)	7.3(3)
C(2) ^b	-0.0805(23)	0.0	0.3608(12)	7.3(3)
C(3) ^b	0.0898(22)	0.0	0.4055(17)	7.3(3)
H(1)	-0.299(2)	0.0	0.443(3)	10.3(6)
H(2)	-0.160(2)	0.0	0.270(2)	10.3(6)
H(3)	0.145(3)	0.0	0.322(2)	10.3(6)

^aEstimated standard deviations are in parentheses. ^bThe thermal displacement parameters of all the atoms were initially refined as independent variables. In the final cycles of the refinement, these parameters were constrained for various chemically equivalent atoms: Al, bridging F, C, and H. These constraints had essentially no effect on the *R* values. ^cThe nitrogen atom appears to be disordered around the six-membered ring. It was included in the refinement with an occupancy of 0.167 and its parameters were constrained to match those of the carbon atoms.

Table 2. Selected Interatomic Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses

atoms	mult	distance	atoms	mult	angle
Al(1)–F(1)	4	1.781(6)	F(1)–Al(1)–F(1)	2	89.0(4)
Al(1)–F(2)	2	1.839(9)	F(1)–Al(1)–F(1)	2	91.0(4)
Al(2)–F(1)	2	1.839(4)	F(1)–Al(1)–F(1)	2	180.0
Al(2)–F(2)		1.830(10)	F(1)–Al(1)–F(2)	4	91.2(3)
Al(2)–F(3)		1.902(11)	F(1)–Al(1)–F(2)	4	88.8(3)
Al(2)–F(4)		1.840(8)	F(2)–Al(1)–F(2)		180.0
Al(2)–F(4)		1.867(13)	F(1)–Al(2)–(1)		169.2(8)
C(1)–C(2)		1.42(1)	F(1)–Al(2)–F(2)	2	91.8(4)
C(1)–C(3)		1.43(1)	F(1)–Al(2)–F(3)	2	95.0(4)
C(1)–H(1)		1.03(1)	F(1)–Al(2)–F(4)	2	87.1(3)
C(2)–C(3)		1.38(1)	F(1)–Al(2)–F(4)	2	85.0(4)
C(2)–H(2)		1.03(1)	F(2)–Al(2)–F(3)		92.2(6)
C(3)–H(3)		1.08(1)	F(2)–Al(2)–F(4)		167.8(9)
			F(2)–Al(2)–F(4)		87.2(7)
			F(3)–Al(2)–F(4)		100.0(7)
			F(3)–Al(2)–F(4)		179.4(1)
			F(4)–Al(2)–F(4)		80.6(7)
			Al(1)–F(1)–Al(2)		140.5(5)
			Al(1)–F(2)–Al(2)		142.1(7)
			Al(2)–F(4)–Al(2)		99.4(7)
			C(2)–C(1)–C(3)		121(1)
			C(2)–C(1)–H(1)		125(2)
			C(3)–C(1)–H(1)		114(2)
			C(1)–C(2)–C(3)		115(1)
			C(1)–C(2)–H(2)		110(2)
			C(3)–C(2)–H(2)		134(2)
			C(1)–C(3)–C(2)		124(1)
			C(1)–C(3)–H(3)		128(2)
			C(2)–C(3)–H(3)		108(2)
			C(2)–C(3)–H(3)		111(2)

defined given the high “thermal” displacements associated with the atoms of the pyridinium ring. The problem stems in part from the disorder of the pyridinium ring which is centered on a crystallographic *2/m* site and therefore must be at least 2-fold disordered. It was, however, not possible to distinguish the position(s) of the nitrogen atom within the pyridinium ring. Refinement of the occupancies of the three unique carbon atom sites was uninformative, and various semiordered models led to strange thermal parameters and no reduction in *R* values. Table 1 lists the final atomic coordinates and displacement parameters: some of the thermal parameters were constrained, not because they were unusual, but simply because they were similar in value

(8) The experimental set up is very similar to that described in ref 2 except that a Si(111) analyzing crystal was used and that the sample was placed in a spinning 2.0-mm capillary. Several scans were run and the data were merged: 2θ range from 5.00 to 20° with a step size of 0.005°; 10 s per point.

(9) Larsen, A. C.; Von Dreele, R. B. GSAS, Generalized Structure Analysis System; Los Alamos National Laboratory: Los Alamos, NM, 1986; LAUR 86-748.

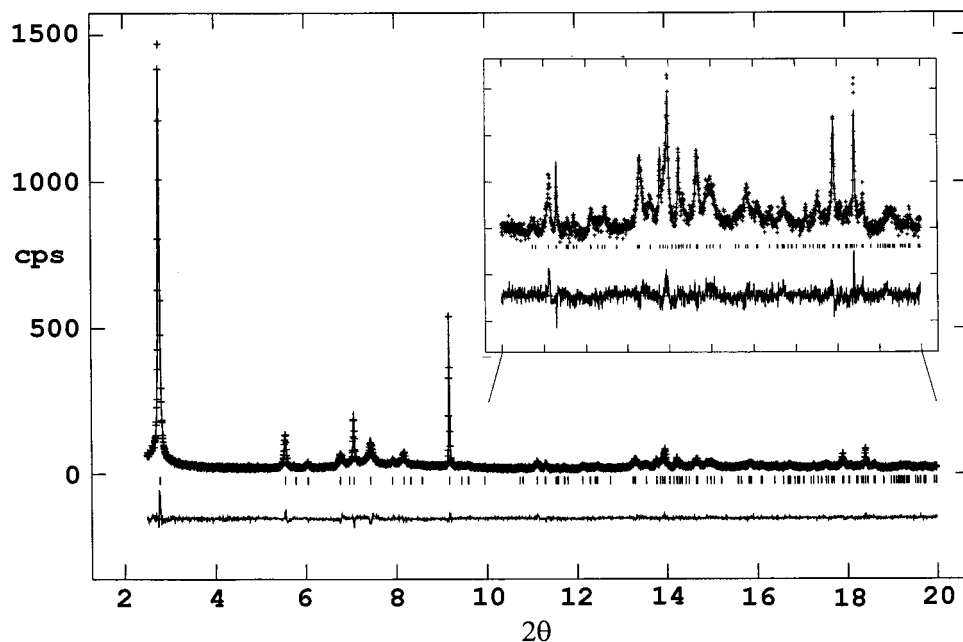


Figure 2. Results of the Rietveld refinement using the APS synchrotron data. Observed (+) and calculated (solid line) intensities are plotted while the difference intensity is plotted below.

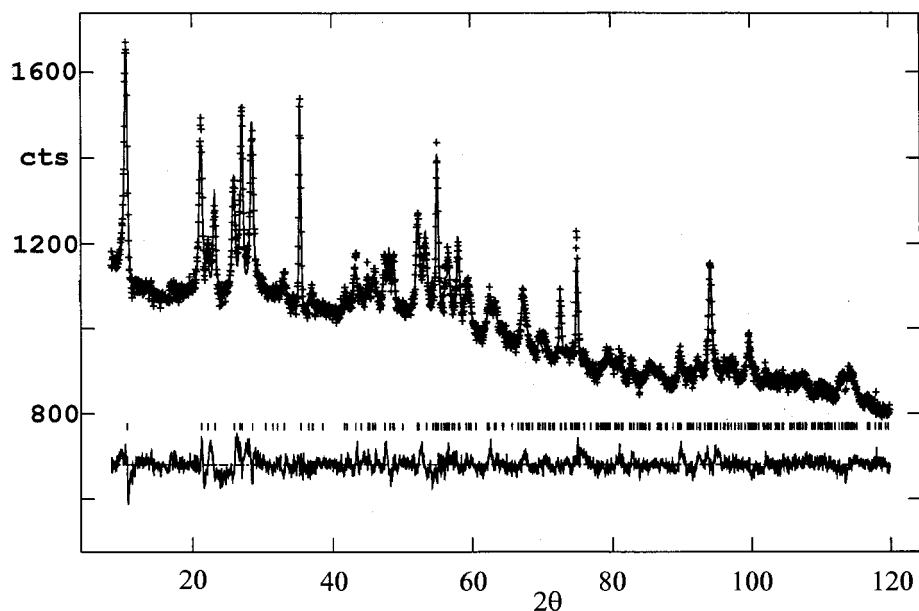


Figure 3. Rietveld refinement of the neutron data.

and constraining them limited the number of variables in the refinement. The final crystallographic data are as follows: monoclinic, space group $C2/m$, $a = 8.2706(3)$, $b = 6.1998(3)$, $c = 10.525(1)$ Å, $\beta = 103.38(1)^\circ$, $V = 525.0(1)$ Å³, and $Z = 2$. Figures 2 and 3 show the fit between the observed and calculated intensities for the X-ray and neutron patterns, respectively.¹⁰

(10) One referee pointed out that the large thermal parameters associated with the pyridinium ion could stem from the fact that the group is tilted off of the crystallographic mirror plane, i.e., either the group is disordered or the space group should, in fact, be $C2$ instead of $C2/m$. Tilting the group, for example, might allow for better hydrogen-bonding contacts between the hydrogen and fluorine atoms. The referee makes a good point, but we believe that the data is not of high enough resolution to distinguish between the tilted and untilted models.

Table 2 contains a listing of the bond distances and angles: atom labels are shown in Figure 4. As can be seen in Figure 5, the structure is composed of $[Al_3F_{10}]_n^-$ sheets containing both edge- and corner-shared octahedrally coordinated Al atoms. The Al(1) resides on a $2/m$ site; Al(2) resides on a mirror plane. Three of the fluorine atoms are bridging and one is terminal, F(3). It is the terminal fluorine that usually serves as an acceptor for hydrogen bonds and, indeed, it does form the closest contact with one of the hydrogen atoms, H(1), of the pyridinium cation, 2.03(3) Å. At first glance, one might guess then that the nitrogen atom is located on the C(1) site. However, the C—H...F angle is not as linear, $\sim 141^\circ$, as one might have expected for a strong N—H...F bond. Contacts between the other two H atoms of the cation to the anionic sheet also exist to confuse

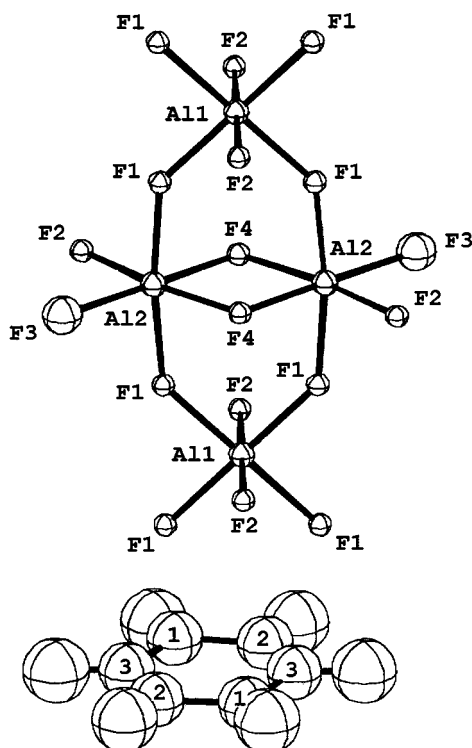


Figure 4. ORTEP drawing showing the basic building blocks of the structure with atom labels. The C(N) atoms are labeled with numbers only: the H atoms have numbers that correspond to the C atoms.

the issue. H(3), for example, forms a single $\text{H}(3)\cdots\text{F}(2)$ which is longer, 2.41 Å, but nearly linear: $\text{C}(3)\text{—H}(3)\cdots\text{F}(2) = 168^\circ$. H(2) is bonded in a trifurcated fashion to three bridging fluorine atoms with distances of 2.36, 2.50, and 2.50 Å. It thus appears that all three hydrogen atoms have hydrogen bonds with the sheets, thus supporting the conclusion that the nitrogen atom is disordered over all three crystallographically independent carbon atom positions.

The existence of the edge-shared octahedral motif in this material is the second example of such connectivity for fused AlF_6 units. Just as in the previously reported³ structure of $[\text{collidineH}^+][\text{AlF}_4^-]$ this relatively new mode of connectivity for fused octahedral Al—F species is the basic building block of the structure. In the present case, the anionic slabs of Al—F material create

a layered “clay-like” structure with charge balancing cations of pyridinium between the layers. The structure appears to be set up for all manner of synthetic chemistry akin to that of the traditional clays including cation exchange, exfoliation/delamination, absorption and pillaring. As such, this material presents another fascinating entry into the potentially interesting class of catalyst materials—the nonoxide clays—and we have not explored this facet of the material to this point.

Finally, it is instructive to consider the previous interpretation of the material’s stoichiometry relative to the actual formula. Most misleading were the TGA and TGA/MS data. The known variable stoichiometry of the precursor compound $(\text{PyH})\text{AlF}_4$ ¹ meant that it was impossible to define an accurate weight change during loss of the pyridine in the initial lower temperature thermal event of Figure 1a. While the weight appears to stabilize above 150 °C this is not strictly true and both the TGA and TGA/MS clearly indicates continued “bleeding” of pyridine from the material up to the onset of the second weight loss event at 325 °C. For the correct stoichiometry, $(\text{PyH})\text{Al}_3\text{F}_{10}$, the expected weight change upon transformation from that compound to the final $\eta\text{-AlF}_3$ phase is 27.8%, whereas the HAlF_4 stoichiometry would predict a weight change of 19.2%. The observed change during the sharpest portion of the weight loss is ~20% (see Figure 1b). We were, therefore, too willingly seduced into the HAlF_4 interpretation of stoichiometry by the combination of TGA data coupled with our desire to interpret the residual pyridine we were seeing in both the TGA/MS and in chemical analysis as traces of unconverted precursor compound $(\text{PyH})\text{AlF}_4$. In retrospect, the chemical behavior of the solid material is now much more reasonable, e.g., we have never observed any indication of solid acid behavior for what we were labeling HAlF_4 .

Conclusions

From the above structural analysis we can conclude: (1) that it is possible to obtain crystal structure information even from poor-quality powder diffraction patterns; (2) that the chemical formula of the compound previously reported as HAlF_4 is actually $[\text{C}_5\text{NH}_6][\text{Al}_3\text{F}_{10}]$ with a layered, “clay-like” structure; and (3) that an incorrect chemical formula is a much bigger impediment to a powder structure analysis than to a single-crystal

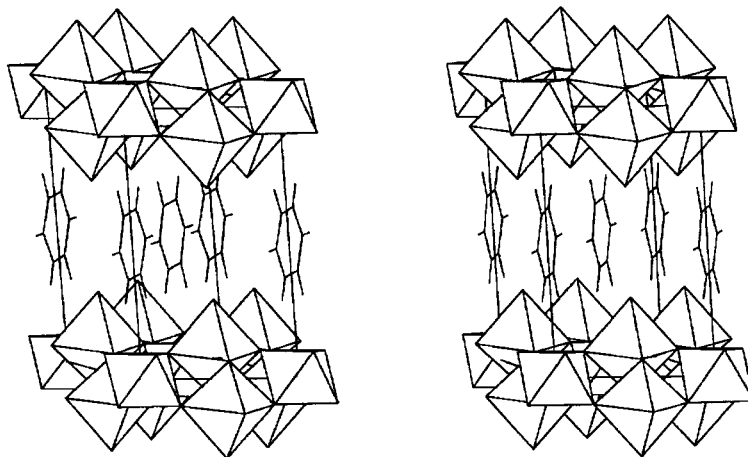


Figure 5. Stereodrawing of the structure of $[\text{C}_5\text{NH}_6][\text{Al}_3\text{F}_{10}]$, viewed nearly parallel to the *a* axis.

structure analysis. In the case of a single-crystal analysis, for example, the presence of a six-membered "organic" ring would have been discovered in the first E-map or in the first difference Fourier map. In the powder case, the failure to solve a structure is more likely to be blamed on the poor quality of the crystal/data, the poor quality of the crystallographic phases, or other experimental problems rather than on the "wrong" formula. This bias persists even in crystallographers with 20 years of experience dealing with chemists with a history of assigning incorrect formulas to their compounds. The moral of this convoluted tale is that, perhaps, we should have more confidence in the powder diffraction technique after all. Amen.

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