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The first crystallographic example of a face-sharing fluoroaluminate anion $\text{Al}_2\text{F}_9^{3-}$

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Abstract

The first example of a face-sharing fluoroaluminate anion, \( \text{Al}_2\text{F}_9^{3-} \), is crystallographically determined in \([\text{C}_{18}\text{MIm}]_3[\text{Al}_2\text{F}_9](\text{CH}_2\text{Cl}_2)_{1.754} \) (\( \text{C}_{18}\text{MIm}^+ = 1\)-methyl-3-octadecylimidazolium cation), and the geometry and bond properties therein are discussed with the aid of quantum chemical calculations.
The structural diversity of aluminium fluoride and fluoroaluminate anions has attracted considerable research interest,\textsuperscript{1–3} partly because of the interest in aluminium fluoride as a Lewis acidic catalyst.\textsuperscript{4–6} A large number of fluoroaluminate anions have been crystallographically determined by introducing metal or organic cations. Although the tetrahedral AlF\textsubscript{4}\textsuperscript{−} anion was determined in three salts with large organic cations,\textsuperscript{7,8} most fluoroaluminate anions consist of an octahedral AlF\textsubscript{6} unit.\textsuperscript{9–14} The trigonal bipyramidal AlF\textsubscript{5}\textsuperscript{2−} anion has not been determined crystallographically, but was spectroscopically observed in a tetramethylammonium salt.\textsuperscript{15} The simplest form of fluoroaluminate anion based on the octahedral AlF\textsubscript{6} unit is AlF\textsubscript{6}\textsuperscript{3−} and larger isolated species.\textsuperscript{16–26} In a few rare cases, edge-sharing bioctahedral motifs were observed in dinuclear,\textsuperscript{8,27,28} chain-like\textsuperscript{7,29,30} and layered\textsuperscript{31,32} structures. One of the cases missing from this series is the face-sharing structure of the bioctahedral Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−} anion. Although such a structure was predicted in molten salts,\textsuperscript{33} no crystallographic work has been reported until now. The small ionic radii of the F and Al atoms, \textit{i.e.} the short Al–F bond, lead to difficulty in forming this type of crowded ion. In this communication, the geometry and bond properties of the first face-sharing fluoroaluminate anion, Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−}, are discussed in comparison with known fluoroaluminate species.

The starting compound, [C\textsubscript{18}MIm][AlF\textsubscript{4}], was prepared by the reaction of [C\textsubscript{18}MIm][AlCl\textsubscript{4}] and a large excess of anhydrous HF followed by elimination of the residual HF and byproduct HCl under vacuum. The Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−} anion was determined in [C\textsubscript{18}MIm]\textsubscript{3}[Al\textsubscript{2}F\textsubscript{9}](CH\textsubscript{2}Cl\textsubscript{2})\textsubscript{n}, which was obtained during an attempt to grow single crystals of [C\textsubscript{18}MIm][AlF\textsubscript{4}] (1-methyl-3-octadecylimidazolium tetrafluoroaluminate) by slow evaporation of the solvent from a CH\textsubscript{2}Cl\textsubscript{2} solution.\textsuperscript{‡} Two CH\textsubscript{2}Cl\textsubscript{2} molecules are found in the asymmetric unit, but their site occupancies are lower than 1 (0.944 and 0.810), resulting in \textit{n} = 1.754. The site occupancies of CH\textsubscript{2}Cl\textsubscript{2} seem to depend on the evacuation time, and the powder X-ray diffraction pattern of the sample after it was thoroughly pumped at room temperature was completely different from the simulated pattern from the single crystal structure of [C\textsubscript{18}MIm]\textsubscript{3}[Al\textsubscript{2}F\textsubscript{9}](CH\textsubscript{2}Cl\textsubscript{2})\textsubscript{1.754}. The reaction that occurred during the crystallisation is
most probably written as:

\[ 3[C_{18}MIm][AlF_4] + nCH_2Cl_2 \]

\[ \rightarrow [C_{18}MIm]_3[Al_2F_9](CH_2Cl_2)_n + AlF_3 \]

The formation of \( Al_2F_9^- \) and loss of \( AlF_3 \) probably result from the large stabilization energy by forming a lattice including \( CH_2Cl_2 \) molecules. Crystalline \( [C_{18}MIm][Al_2F_9](CH_2Cl_2)_n \) with insoluble white powder (probably \( AlF_3 \)) was reproducibly obtained although the quality of the crystals was not always suitable to fully complete single-crystal X-ray diffraction analysis. The \( Al_2F_9^- \) anion consists of two face-sharing \( AlF_6 \) octahedra and has a roughly \( D_{3h} \) symmetry as shown in Fig. 1. The six bridging \( Al-F_b \) bonds (1.874(2)–1.959(3) Å) and the six terminal \( Al-F_t \) bonds (1.723(2)–1.750(2) Å) in \( Al_2F_9^- \) are longer and shorter, respectively, than the \( Al-F \) bond in the octahedral \( AlF_6^- \) (ca. 1.80 Å),\(^{10-14} \) where \( F_b \) and \( F_t \) denote the bridging and terminal \( F \) atoms in \( Al_2F_9^- \), respectively. Accordingly, the \( F_t-Al-F_t \) angles (94.24(12)°–99.81(13)°) are larger than the \( F_b-Al-F_b \) angles (74.47(10)°–77.81(10)°) and the two octahedra in \( Al_2F_9^- \) are slightly distorted from the ideal \( O_h \) symmetry. Bond valence sums of the two \( Al \) atoms in \( Al_2F_9^- \) are 2.91 and 2.95 according to the literature.\(^{34,35} \) These values are consistent with the oxidation state of +3 for \( Al \) as in the cases of the isolated \( AlF_4^- \) (2.98 and 3.02)\(^7 \) and \( AlF_6^- \) (2.96)\(^13 \) anions (see Fig. 1 The structure of \( Al_2F_9^- \) with atom numbering scheme. Selected bond lengths (Å) and angles (°): \( Al-F_t \) range, 1.723(2)–1.750(2); \( Al-F_b \) range, 1.874(2)–1.959(3); \( F_t-Al-F_t \) range, 94.24(12)–99.81(13); \( F_b-Al-F_b \) range, 74.47(10)°–77.81(10), where \( F_t \) and \( F_b \) denote terminal (F1, F2, F3, F7, F8 or F9) and bridging \( F \) atoms (F4, F5 or F6). See Table S2, ESI† for the detailed values.
Fig. 2 Unit cell of [C_{18}MIm]_3[Al_2F_9](CH_2Cl_2)_{1.754} at –100 °C.

Table S4, ESI† for the calculation of bond valence sums).

Such a face-sharing M_2F_9^{3–} structure (M denotes the metal atom) was observed only in three examples with transition metals (Cr_2F_9^{3–}, V_2F_9^{3–} and Fe_2F_9^{3–}) when organic ammonium cations ((CH_3)_4N^+ 36 and (C_2H_5)_4N^+ 37 were introduced. Although their geometries are similar, the M–F_t and M–F_b bond lengths in Al_2F_9^{3–} are significantly shorter than those in the transition metal species (1.987, 2.033 and 2.024 Å for Cr–F_b, V–F_b and Fe–F_b; 1.838, 1.852 and 1.861 Å for Cr–F_t, V–F_t and Fe–F_t, respectively). Consequently, the M···M distance of Al_2F_9^{3–} (2.6866(19) Å) is shorter than those of Cr_2F_9^{3–} (2.773 Å), V_2F_9^{3–} (2.852 Å) and Fe_2F_9^{3–} (2.907 Å).

The packing mode of [C_{18}MIm]_3[Al_2F_9](CH_2Cl_2)_{1.754} is described as the layered structure of domains with high and low polarities (Fig. 2), although this structure is not highly ordered compared to previously known alkylimidazolium salts with long alkyl chains, such as [C_{18}MIm][AF_6] (A = P, As, Sb, Nb, or Ta), 38 [C_{12}MIm][PF_6] 39 and [C_{14}MIm][PF_6]. 40 The highly polar domains, consisting of Al_2F_9^{3–} anions and imidazolium headgroups, are separated by the low polar domains consisting of interdigitated alkyl chains tilted relative to the polar domain. There are three crystallographically independent cations in the unit cell; the alkyl chain of one cation shows
an all-trans conformation (Cation 1, Fig. S1(c), ESI†) and those of the other two cations show bent conformations (Cation 2, bent at C36, Fig. S1(d); Cation 3, bent from C66 to C68, Fig. S1(e), ESI†). The formation of Al₂F₉₃⁻ anion may be attributed to the phase separation caused by the amphiphilic cation, C₁₈MIm⁺, which prevents the anions from coming close to each other to form chain-like structures. The two crystallographically independent CH₂Cl₂ molecules are located near the polar region to fill the space between the alkyl chains.

All the F atoms in the anion are involved in short contacts (below the sum of van der Waals radii, Table S3, ESI†) with H atoms of the imidazolium rings (F2, F3, F4, F5, F7, F8 and F9), alkyl chains (F1, F2, F4, F6, F8 and F9) or CH₂Cl₂ molecules (F3, F8 and F9). Bifurcation of the C–H···F bonds is observed for H atoms which interact with two F atoms (H2 with F4 and F9, H24a with F2 and F4, H32 with F8 and F9, H34 with F3 and F5, H62 with F4 and F7 and H91b with F8 and F9).

**Fig. 3** Calculated geometries of (a) AlF₄⁻, (b) AlF₆³⁻ and (c) Al₂F₉₃⁻ at MP2/aug-cc-pVTZ. The F₁–Al–Fₙ and Fₚ–Al–Fₚ angles in Al₂F₉₃⁻ are 75.1° and 96.2°, respectively.

The calculated geometries of AlF₄⁻, AlF₆³⁻ and Al₂F₉₃⁻ at MP2/aug-cc-pVTZ are shown in Fig. 3 (see Table S5, ESI† for detailed geometrical parameters and vibrational frequencies calculated
at the MP2, B3LYP and PBE1PBE levels combined with cc-pVTZ and aug-cc-pVTZ basis sets). The calculated Al–F bond lengths in these species were slightly overestimated at all levels of theory compared to the experimental data. The F\textsubscript{b}···F\textsubscript{b} distance in Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−} (2.368 Å) is significantly shorter than the F···F distance in AlF\textsubscript{4}− (2.786 Å) and the cis-F···F distance in AlF\textsubscript{6}\textsuperscript{3−} (2.686 Å), which is indicative of the steric crowding at the triply bridged part of Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−}. Natural bond orbital (NBO) charges, valencies and bond orders of the three species are listed in Table 1.\textsuperscript{41,42} In all the cases, the difference between the formal charges (+3 for Al and −1 for F) and NBO charges suggests the polar covalent nature of these Al–F bonds. Although the Al atoms in Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−} and AlF\textsubscript{6}\textsuperscript{3−} have similar positive charges (2.024 for Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−} and 2.049 for AlF\textsubscript{6}\textsuperscript{3−}), the F atoms in Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−} are less negatively charged (−0.808 for F\textsubscript{t} and −0.734 for F\textsubscript{b}) than that in AlF\textsubscript{6}\textsuperscript{3−} (−0.842). The smaller NBO charge of F\textsubscript{t} in Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−} relative to that in AlF\textsubscript{6}\textsuperscript{3−} is caused by the shorter Al–F bond, whereas the NBO charge of F\textsubscript{b} is determined by the balance of two factors: the longer Al–F\textsubscript{b} bond and the sharing of F\textsubscript{b} between the two Al atoms. By forming the Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−} bioctahedral structure, the Al–F bond order decreases from 0.376 to 0.286 for Al–F\textsubscript{b} and increases from 0.376 to 0.415 for Al–F\textsubscript{t}, which indicates that the Al–F\textsubscript{b} and Al–F\textsubscript{t} bonds become more and less polar, respectively. These changes in bond order reflect the changes in bond length. Consequently, the valency (the sum of bond orders) of the Al atom in Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−} (2.104) is smaller than that in AlF\textsubscript{6}\textsuperscript{3−} (2.257). The Al–F bond in the tetrahedral AlF\textsubscript{4}− exhibits the largest bond order of 0.498 among the three species, which results from the short Al–F bond in this sterically less crowded species.

In summary, the first face-sharing fluoroaluminate anion, Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−}, was crystallographically determined in [C\textsubscript{18}MIm]\textsubscript{3}[Al\textsubscript{2}F\textsubscript{9}](CH\textsubscript{2}Cl\textsubscript{2})\textsubscript{1.754}. It consists of two face-sharing AlF\textsubscript{6} octahedra and has a roughly D\textsubscript{3h} symmetry. The two AlF\textsubscript{6} units in Al\textsubscript{2}F\textsubscript{9}\textsuperscript{3−} are distorted from the ideal octahedral geometry and corresponding changes in bond order were observed.
Table 1 Natural bond orbital charges, valencies and bond orders for AlF$_4^-$, AlF$_6^{3-}$ and Al$_2$F$_9^{3-}$ at MP2/aug-cc-pVTZ (see Fig. 3 for the naming of the atoms and Table S5, ESI† for the other results).

<table>
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<th>Charges [Valencies]$^a$</th>
<th>Bond orders$^b$</th>
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<tr>
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<td>AlF$_4^-$ ($T_d$)</td>
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<tr>
<td>Al−F</td>
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<td>0.498</td>
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<tr>
<td>AlF$_6^{3-}$ ($O_h$)</td>
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<tr>
<td>Al</td>
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<td>F</td>
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<tr>
<td>Al−F</td>
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<tr>
<td>Al$_2$F$<em>9^{3-}$ ($D</em>{3h}$)</td>
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<tr>
<td>F$_t$</td>
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<td>F$_b$</td>
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<td>Al−F$_b$</td>
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<td>0.286</td>
</tr>
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</table>

$^a$ Only the Al−F bonds were considered in calculation of valencies and other minor contributions are ignored here. $^b$ Atom-atom overlap-weighted natural atomic orbital bond orders.
Notes and references

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†Electronic Supplementary Information (ESI) available: Additional experimental details, computational and crystallographic data. CCDC 906618. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/.

‡Experimental details are described in ESI†. Crystal data for [C18MIm]3[Al2F9](CH2Cl2)1.754: C67.75H132.51N6F9Al2Cl3.51, M = 1380.67, triclinic, space group P–1 (no. 2), a = 8.8125(6) Å, b = 14.8052(10) Å, c = 30.847(2) Å, α = 96.083(2)°, β = 99.426(2)°, γ = 90.012(2)°, V = 3947.3(5) Å³, Z = 2. T = 173 K, Dc = 1.162 g cm⁻³, F(000) = 1495, R₁ = 0.0702 (810 parameters), wR2 = 0.1752 [I > 2σ(I)], GOF = 1.054 for all 12675 data. CCDC 906618.


