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The discrete ALF fluorooaluminate anion in the structure of [tetraethylammonium][ALF(HO)]

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The discrete $\text{AlF}_5^{2-}$ fluoroaIminate anion in the structure of $[\text{t}r\text{e}t\text{a}a\text{t}h\text{yl}e\text{l}a\text{m}m\text{o}n\text{n}\text{i}u\text{m}][\text{AlF}_5](\text{H}_2\text{O})_2$

Gleb Veryasov[a], Kazuhiko Matsumoto[a], and Rika Hagiwara[a]

Abstract: The first crystallographically defined example of the discrete $\text{AlF}_5^{2-}$ fluoroaIminate anion was elucidated via X-ray analysis of $[\text{Et}_4\text{N}]_2[\text{AlF}_5](\text{H}_2\text{O})_2$ ($\text{Et}_4\text{N}^+$ = tetraethylammonium) single crystals. Intentional preparation of a compound containing the $\text{AlF}_5^{2-}$ anion via the reaction of two equivalents of $[\text{Et}_4\text{N}]_2[\text{AlF}_5]$ with $[\text{Me}_4\text{NF}]$ ($\text{Me}_4\text{N}^+$ = tetramethylammonium) resulted in the formation of $[\text{Et}_4\text{N}][\text{Me}_4\text{N}]_2[\text{AlF}_5]$ with unreacted $[\text{Et}_4\text{N}]_2[\text{AlF}_5]$. Cation exchange between these species in the presence of water furnished $[\text{Et}_4\text{N}_2][\text{AlF}_5](\text{H}_2\text{O})_2$ as a precipitate containing the trigonal biypramidal $\text{AlF}_5^{2-}$ anion. The data from the present study allows supplementing the ligand close packing (LCP) model for the 3rd period of the periodic table. The Raman spectrum of $[\text{Et}_4\text{N}_2][\text{AlF}_5](\text{H}_2\text{O})_2$ was analyzed on the basis of quantum chemical calculations. Agreement with the experimental results presented by Gilbert, and confirmed the existence of $\text{AlF}_5^{2-}$. Recently, Gross and his co-workers prepared $[\text{Me}_4\text{N}_2][\text{AlF}_5]$ ($\text{Me}_4\text{N}^+$ = tetramethylammonium) by the reaction of $[\text{Me}_4\text{NF}]$ and $[\text{Me}_4\text{N}]_2[\text{AlF}_5]$; this compound was characterized by Raman spectroscopy and magic angle spinning (MAS) NMR. However, attempts to prepare single crystals of the compound were unsuccessful.

The present study provides the first crystallographic example of $\text{AlF}_5^{2-}$ in $[\text{Et}_4\text{N}]_2[\text{AlF}_5](\text{H}_2\text{O})_2$ ($\text{Et}_4\text{N}^+$ = tetraethylammonium), which has been the matter for discussion for more than 20 years and important insight into the application of the ligand close packing (LCP) model to the third period elements and compounds thereof, including $\text{SiF}_5^{-}$ and $\text{PF}_5$. The LCP model describes molecular geometries based on ligand−ligand repulsions and can provide a more quantitative prediction than the valence shell electron pair repulsion (VSEPR) model, especially for the second period elements.

Results and Discussion

In our previous work, we discovered the formation of $[\text{C}_{18}\text{H}_{36}\text{Cu}(\text{Im})_2][\text{AlF}_3](\text{CH}_2\text{Cl})_1.754$ ($\text{C}_{18}\text{H}_{36}\text{Cu}^{+} = 1\text{-methyl-3-oxacyclohexadienazolium}$) containing discrete $\text{AlF}_5^{2-}$ units, [10] while attempting to crystalize $[\text{C}_{18}\text{H}_{36}\text{C}(\text{Im})][\text{AlF}_3]$ from $\text{CH}_2\text{Cl}_2$ solution. In the present work, intentional preparation of a compound containing the discrete $\text{AlF}_5^{2-}$ unit was attempted by the reaction of two equivalents of $[\text{Et}_4\text{N}]_2[\text{AlF}_5]$ with a strong fluoride ion donor $[\text{Me}_4\text{N}]_2[\text{F}]$ according to the following route (Eq. (1)).

$$2[\text{Et}_4\text{N}_2][\text{AlF}_5] + [\text{Me}_4\text{NF}] \rightarrow [\text{Me}_4\text{N}]_2[\text{AlF}_3]$$

However, the reaction did not produce $\text{AlF}_5^{3-}$; instead, $[\text{Me}_4\text{N}_2][\text{AlF}_5]$ was obtained as a precipitate and $[\text{Et}_4\text{N}_2][\text{AlF}_5]$ remained in the solution; the compositions of both phases were verified by mass balance and Raman spectroscopy (see discussion and Figure S1, ESI) (Eq. (2)).

$$[\text{Et}_4\text{N}_2][\text{AlF}_5] + [\text{Me}_4\text{NF}] \rightarrow [\text{Me}_4\text{N}]_2[\text{AlF}_5]$$

Although the $[\text{Me}_4\text{N}_2][\text{Et}_4\text{N}][\text{AlF}_5]$ precipitate was largely insoluble in polar solvents (tetrahydrofuran and acetoneitrile), it could be dissolved in dichloromethane. In the presence of water, slow cation exchange between the dissolved $[\text{Me}_4\text{N}_2][\text{Et}_4\text{N}][\text{AlF}_5]$ and $[\text{Et}_4\text{N}][\text{AlF}_5]$ occurred, resulting in crystallization of

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The hydrate, \([\text{EtN}\text{[AlF}_3]\text{[H}_2\text{O}]}\), was reproducibly obtained from different solvents (\(\text{CH}_2\text{Cl}_2\)toluene (5/2), \(\text{CH}_2\text{Cl}_2\), and \(\text{CH}_2\text{Cl}_2\)/THF (10/1)) (see ESI for details). All the crystals collected appeared to be suitable for X-ray diffraction; the highest quality crystals, as determined by X-ray diffraction, were grown from the \(\text{CH}_2\text{Cl}_2\)toluene mixture. Such reproducibility evidently indicates the high stability of the dihydrate, similar to that observed for the \(\text{CH}_2\text{Cl}_2\) system. The most intriguing fact is that crystals did not form in the absence of water, where water is thought to originate from moisture in the air or in the solvent, indicating that water molecules are essential for stabilization of this lattice. It should be noted that direct crystallization of \([\text{EtN}\text{[AlF}_3]\text{[H}_2\text{O}]}\) from dry dichloromethane gave only powder. In addition to \([\text{EtN}\text{[AlF}_3]\text{[H}_2\text{O}]}\), which was obtained as colorless needle-like crystals, a white powder was formed as a by-product after evaporation. Presumably, this precipitate was \([\text{MeN}\text{[AlF}_3]\text{]}\) that may contain water.

Although the thermodynamic data indicate that neither process is spontaneous in the gas phase, the second reaction (Eq. 5) is energetically less favorable than the first reaction (Eq. 4). The lattice energy of \([\text{EtN}\text{[MeN}\text{[AlF}_3]}\) is considered to be large because \([\text{EtN}\text{[MeN}\text{[AlF}_3]}\) is a salt of a doubly charged anion, and consequently the reaction summarized in Eq. (4) can proceed in solution. The reaction presented in Eq. (5) is originally not favorable, and the high solubility of \([\text{EtN}\text{[AlF}_3]}\) prevents the formation of \([\text{MeN}\text{[EtN}\text{[AlF}_3]}\).

The hydrate salt, \([\text{EtN}\text{[AlF}_3]\text{[H}_2\text{O}]}\), crystallizes in the \(P_4/n\) tetragonal space group with \(a = 24.9774(10) \text{ Å} \) and \(c = 7.1969(4) \text{ Å} \) (see X-ray crystallography details, Tables S2 and S3, ESI). Although the crystals obtained were stable in air for a short period (overnight) and did not deliquesce, they may accumulate moisture upon long-term exposure to air, as observed for \([\text{MeN}\text{[AlF}_3]}\). Notably, \([\text{EtN}\text{[AlF}_3]\text{[H}_2\text{O}]}\) had a strong tendency towards twinning. All the crystals checked were twinned with twin fractions ranging from 2 to 50%.

The structure obtained provides the first example of a discrete \(\text{AlF}_5^{2−}\) anion. Previous attempts to crystallize \(\text{AlF}_5^{2−}\) salts were unsuccessful due to difficulties in dissolving these salts; Groß and his co-workers reported that \([\text{MeN}\text{[AlF}_3]}\) has extremely low solubility in polar solvents. \(^{[11]}\) Figure 1 shows the ORTEP diagram of the asymmetric unit of \([\text{EtN}\text{[AlF}_3]\text{[H}_2\text{O}]}\) determined at \(-160^\circ\) C. The \(\text{AlF}_5^{2−}\) anion has an \(\text{AX}_5\)-type trigonal bipyramidal geometry as expected from the VSEPR theory. \(^{[21]}\) The \(\text{Al−F}_\text{eq}\) (where \(\text{F}_\text{eq}\) indicates an equatorial F atom; i.e., F1, F2, and F4 in Figure 1) bonds (1.713(2) − 1.728(2) Å) are shorter than the \(\text{Al−F}_\text{ap}\) (F5 indicates an axial F atom; F3 and F5 in Figure 1) bonds (1.768(2) − 1.771(2) Å). The \(\text{F}_\text{ap}−\text{Al−F}_\text{ap}\) angle is nearly linear (179.84°) and the \(\text{F}_\text{ap}−\text{Al−F}_\text{eq}\) angles (117.0, 127.1, and 115.9°) are close to the ideal angle of 120°. The \(\text{F}_\text{ap}−\text{Al−F}_\text{ap}\) angles generated by the axial and equatorial F atoms are close to right angle dimensions (89.0–91.6°). The bond valence sum \(^{[22]}\) of the Al atom in \(\text{AlF}_5^{2−}\) is 3.00 and is consistent with the formal oxidation state of +3 for Al (see Table S4, ESI) for bond valence sum calculations. The contribution from the \(\text{Al−F}_\text{ap}\) (average bond valence of 0.630 bond) is slightly larger than that of the \(\text{Al−F}_\text{ap}\) (average bond valence of 0.553 bond) as expected for the trigonal bipyramidal molecules.

The confirmation of \(\text{EtN}\) has been discussed in previous studies based on X-ray diffraction and vibrational spectroscopy. \(^{[23]}\) In the \(\text{EtN}\text{[AlF}_3]\text{[H}_2\text{O}]}\) structure, both crystallographically independent \(\text{EtN}\) cations adopt the \(\text{TT}-\text{conformation}\) (trans-trans and trans-trans with \(\text{D}_{\text{sh}}\) symmetry) and the \(\text{TG}-\text{conformation}\) (trans-gauche and gauche with \(\text{S}_\text{g}\) symmetry). \(^{[23]}\) In the \(\text{EtN}\text{[AlF}_3]\text{[H}_2\text{O}]}\) structure, both crystallographically independent \(\text{EtN}\) cations adopt the \(\text{TT}-\text{conformation}\).

The molecular packing of \([\text{EtN}\text{[AlF}_3]\text{[H}_2\text{O}]}\) is shown in Figure 2. The \(\text{AlF}_5^{2−}\) anions and water molecules form one-dimensional columns along the c axis and the \(\text{EtN}\) cations also form a set of one-dimensional columns in the same direction. The distance between two closest axes passing through the Al atoms in the 1D columns is 8.84 Å. The structure is built up by a complicated system of \(\text{D−H−A}\) interactions. The \(\text{D−H−A}\) interactions in \([\text{EtN}\text{[AlF}_3]\text{[H}_2\text{O}]}\) are separated into three classes: \(\text{EtN}−\text{AlF}_5^{2−}, \text{AlF}_5^{2−}−\text{H}_2\text{O}\), and \(\text{EtN}−\text{H}_2\text{O}\).
relevant to Et₄N⁺–AlF₅⁻ and Et₄N⁺–H₂O, respectively. Hence, the 1D columns formed by the AlF₅⁻–H₂O interactions are essential for stabilization of this crystal lattice.

The Raman spectrum of AlF₅⁻ has been a matter of discussion since the first report of the NaF-AlF₅ molten salt. In the present analysis, the Raman spectrum was recorded for a single crystal that was confirmed as [Et₄N][AlF₅]·H₂O₂ by single-crystal X-ray diffraction. The spectra recorded from several different directions suggested that the peak intensities are orientation-dependent. Figure 3 shows the Raman spectrum of the [Et₄N][AlF₅]·H₂O₂ single crystal obtained from random direction. The Raman spectrum of [Et₄N]Cl used for identification of the cation bands is presented in Figure S4, ESI; the relative intensities of the bands are listed in Table S6; the spectrum acquired from another direction is shown in Figure S5, ESI. The following assignments are summarized in Table S8 and the bands from cation are listed in Table S9, ESI and based on the calculation at the MP2/au-gcc-pVTZ level (see discussion, Figure S6 and Table S10, ESI).

The most intense band at 558 cm⁻¹ is assigned to the νₐ(AlF₅) + νₐ(AlF₃) mode. This is the “characteristic” band used by Gilbert and co-workers for identification of AlF₅⁻. The band at 313 cm⁻¹ is tentatively assigned as the σ(AlF₅) mode given that the δ(AlF₅)+ν₁(AlF₃) mode is another possible assignment. The two other bands observed at 588 and 628 cm⁻¹ are the ν₁(AlF₅)+ν₆(AlF₃) and ν₁(AlF₅)+σ(AlF₃) modes, respectively. The three Raman frequencies observed for [Et₄N][AlF₅]·H₂O in good agreement with those observed for [Mg,N][AlF₅] (322, 563, and 644 cm⁻¹).

Presumably, the contribution of Et₄N⁺ and water molecules to the polarizability tensor results in the low intensity of modes Aₚ and E (353 cm⁻¹, 335 cm⁻¹, and 109 cm⁻¹ in the calculated frequencies), which precludes their observation in the recorded spectrum. The peaks listed in Table S8 were evaluated from a single random direction; this may account for the discrepancies between the experimental and calculated intensities. The contribution of H–F interactions would affect the frequencies of some vibrational modes, although this remains unaccounted.

The LCP model describes molecular geometries based on ligand–ligand repulsions and can provide a more quantitative prediction than the VSEPR model, especially for the second period elements. Fluorine ligand provides a variety of examples due to its small size and less compressibility. Coordination numbers of only up to four are possible for non-metal period 2 central atoms such as AX₄, and the X···X distances are nearly constant in these molecules. The non-metals of period 3 are large enough to form six-coordinate molecules such as AX₆, as suggested by the LCP model. However, in the case of the four-coordinate AF₄ and five-coordinate AF₅ Si and P complexes, it is clear that the F atoms are not close packed. This can be explained in terms of the large size of the period 3 central atom and the weakness of the A–F bond which cannot bring the four or five F ligands into contact. The absence of crystallographic evidence of the trigonal bipyramidal AlF5⁻ has hindered discussion of the geometry of fluoroaluminate anions based on the LCP model. The present analysis provides the experimental data for completion of the model. Although the five-coordinate molecules can adopt either trigonal bipyramidal or square pyramidal geometries based on the VSEPR model (and points-on-a-sphere model), the square pyramidal geometry has been observed only in limited cases depending on the compressibility of the ligand. Herein, AlF₅⁻ adopts trigonal bipyramidal geometry, where the axial F atom makes contact with the equatorial F atoms but the equatorial F atoms do not make contact with each other. Consequently, the Fₐ···Fₑq distance is expected to be twice the radius of the F ligand in this molecule. Table 1 lists the A–F bond lengths and F···F distances in AF₄, AF₅, and AF₆ (A = Al, Si, and P) molecules. In all cases, the F···F distance decreases slightly in moving from AF₄ to AF₅ to maintain close packing of the ligand (Fₐ···Fₑq in the case of AF₅) and increases from AF₅ to AF₆, where the F atoms in the AF₆ molecules do not make contact with each other, as mentioned above. The increase in the F···F distance on moving from AlF₅⁻ to AlF₇ is more pronounced compared to the other cases. This may be due to the larger size of the Al atom relative to the Si and P atoms, which prevents the F atoms from approaching the Al atom.
Table 1. Average Al–F bond lengths and F····F distances in AF₅, AF₆, and AF₆ (A = Al, Si, and P) molecules.¹

<table>
<thead>
<tr>
<th>Anion</th>
<th>A–F, Å</th>
<th>F····F distance, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlF₄⁻</td>
<td>1.654</td>
<td>2.78</td>
</tr>
<tr>
<td>AlF₅⁻</td>
<td>1.721 (F₃) and 1.770 (F₂)</td>
<td>2.47</td>
</tr>
<tr>
<td>AlF₆⁺</td>
<td>1.604</td>
<td>2.68</td>
</tr>
<tr>
<td>SiF₄⁻</td>
<td>1.560</td>
<td>2.54</td>
</tr>
<tr>
<td>SiF₅⁻</td>
<td>1.622 (F₂) and 1.660 (F₃)</td>
<td>2.32</td>
</tr>
<tr>
<td>SiF₆³⁻</td>
<td>1.680</td>
<td>2.38</td>
</tr>
<tr>
<td>PF₄⁻</td>
<td>1.460</td>
<td>2.38</td>
</tr>
<tr>
<td>PF₅⁻</td>
<td>1.522 (F₂) and 1.585 (F₃)</td>
<td>2.20</td>
</tr>
<tr>
<td>PF₆²⁻</td>
<td>1.580</td>
<td>2.24</td>
</tr>
</tbody>
</table>

¹ The F····F distance in AF₅ was calculated as an average of the F₄····F₃ distances.

Conclusions

Attempts to prepare an AlF₅³⁻ salt via the 2:1 reaction of [Et₄N][AlF₄] and [Me₄N][AlF₆] resulted in the formation of [Et₄N][Me₄N][AlF₄] and [Et₄N][AlF₆]. This mixture yielded [Et₄N][SiF₆(H₂O)], the presence of water. The structure of [Et₄N][AlF₆(H₂O)] is the first crystallographic example of the isolated AlF₅⁻ anion with D₅h symmetry. The crystallographic data obtained herein was used for completion of the LCP model for discussion of the geometry of 3rd period fluorides (Si, P, and Al). The vibrational spectrum of AlF₅⁻ anion present in [Et₄N][AlF₆(H₂O)]₂ was discussed based on the empirical Raman spectra and quantum chemical calculations.

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Supporting information

Experimental details on the synthesis of [Et₄N][AlF₆(H₂O)], crystallography, ab initio calculations, and Raman spectra measurement. Selected bond lengths for [Et₄N][AlF₆(H₂O)], bond valence calculations, tables and figures for D–H····A interactions, geometric parameters for AlF₄⁻, AlF₅⁻, AlF₆²⁻, and Al₂F₁₀³⁻ anions in stationary points, vibrational band assignments for AlF₅⁻, geometric parameters for Al, Si and P fluorides. CCDC-1401135 (for [Et₄N][AlF₆(H₂O)]₂) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Keywords: fluoroaluminates • crystallography • Raman spectroscopy • ab initio calculations • LCP model

SHORT COMMUNICATION