Vibrational Spectroscopy of Inorganic Coordination Compounds of Fluorine*

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Vibrational spectroscopy has been used many times in successfully elucidating the nature of chemical bonds and structures of molecules. This is fully valid for organic compounds, but in the case of some groups of inorganic compounds, like halide complexes, the results are sometimes necessarily limited by the insufficiently determined problems. This is conveniently illustrated by compounds of fluorine. The following examples are discussed here: correlations between fluorobasicity and chemical bonding with interaction force constants in \( \text{AgF}_4^- \) and \( \text{AuF}_4^- \) ions, the mixing modes in \( \text{XeF}_5^+ \) ion due to symmetry changes, high coordination number and asymmetry in \( \text{UF}_{19}^+ \) ion, different linking of coordination polyhedra and different types of \( \text{N}_2\text{H}_6^{2+} \) ions in the compounds of \( \text{Zr} \) and \( \text{Hf} \), low temperature transformations like reversible hydration/dehydration of \( \text{N}_2\text{H}_6\text{AlF}_5\text{.H}_2\text{O} \), reversible dimer–monomer transitions of \( \text{V}_2\text{O}_2\text{F}_6\text{(OH}_2)^2\text{H}^+ \), decomposition of \( \text{N}_2\text{H}_6\text{TiF}_5\text{.F}_2 \) through proton transfer from \( \text{N}_2\text{H}_6^{2+} \) to \( \text{F}^- \), and failure of simple correlations of spectra with H-bonds strength.

INTRODUCTION

The instrument of vibrational spectroscopy has been developed to the utmost on organic compounds, as many classical works show (see e.g. the books by Bellamy\(^1\) or the chapter by Prof. Hadži in the book edited by Davies\(^2\)). It is used with all its power with inorganic compounds too, but many times with certain limitations. In the case of organic compounds, forming mostly molecular crystals, there are more or less defined molecular shapes and the chemical bonding is relatively clearly presented. In the case of inorganic compounds it is sometimes the same, like with water, \( \text{SO}_4^{2-} \), etc., but many times it is not, as for instance with halogen compounds and complexes. Intricate electronic structures involving many orbitals, especially these containing heavy central atoms, make it difficult to understand the electronic influence on the spectra. Intermolecular forces influence geometries of coordination, and also the agglomeration of coordination polyhedra. The type of agglomerates in crystals, which are either covalent

\* Dedicated to Prof. Dušan Hadži on the occasion of his 70th birthday.
or ionic or both, is sometimes dependent on slight variations in synthesis, which are difficult to control. Assumptions on the structure or shape may be often uncertain or outright wrong.

As illustrations, we shall survey some appropriate examples in the coordination chemistry of fluorine, studied in this laboratory, showing the influence of electronic effects and the influence of packing forces on the geometries, unusual coordinations, low temperature processes, like dehydration or decomposition, and the riddle of H-bonding in the compounds of hydrazine (Figure 1).

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Figure 1. Overview of the examined examples. The dashed area includes hydrazinium or ammonium complexes with hydrogen bonding.

1. ELECTRONIC EFFECTS IN POTASSIUM TETRAFLUORARGENTATE(III), $\text{KAg}_4\text{F}_4$

The normal coordinate analysis of $\text{AgF}_4^-$ ion (square planar, $D_{4h}$) shows the interaction force constant for the stretching of $trans$ bonds to be smaller than that for $cis$ bonds$^3$ (Table I). Interactions are caused by kinematic couplings and electronic changes during vibration and the kinematic coupling should be larger for $trans$ bonds, as easily demonstrated by calculation. This is fulfilled in a series of isostructural ions (Table I). Larger $cis$ bonds interaction implies a greater influence of electronic effects and, therefore, an altered electronic structure. The explanation, in terms of changes in molecular orbital structure during vibrations, analogously to the treatment$^6$ of $\text{CO}_2$, is likely to be a very difficult and ambiguous task, as indicated by MO diagrams of a 5-atom inorganic species (see e.g. Royer$^7$). In 1963, the analysis of $\text{XeF}_4$ and $\text{ICl}_4$ presented a similar problem. It has been concluded that the $cis$ interaction constant should be larger than the $trans$ one if the bonds have a smaller ionic character and
the ligands smaller negative charge. If applied to our case, we shall have a larger covalent character and smaller negative charge on F in AgF$_4^-$ than in AuF$_4^-$ (Table I). This is in accordance with the relative fluoro-basicity of these compounds and with their fluorinating abilities. The concept is consistent with the expected trends in charge distributions in other square planar halogen complexes of gold and palladium (Table I).

2. FLUOROMETALLATES OF XeF$_5^+$

Ionic fluorometallate complexes of XeF$_5$ may be classified into two groups according to the Raman spectra. The spectra of XeF$_5^+$ in the first group, containing monomeric anions, have been carefully assigned. They are of the same type even in the case of dimerization of the XeF$_5^+$ ion. This is not surprising, because crystal structures, where known, reveal the XeF$_5^+$ ions of C$_{4v}$ symmetry and similar dimensions. The other group, a series of five compounds synthesized in our laboratory, shows a very different kind of spectra with shifted bands and changed intensities. However, the spectra show two overlapping bands of comparable intensity with the frequencies having nearly the same arithmetic mean (Table II). In the spectra of the first group these two bands appear as a strong band and as a shoulder (or a very weak band) (Figure 2) and are assigned to stretching vibrations of different symmetry in the base of the XeF$_5^+$ pyramid (C$_{4v}$, v$_2$, A$_1$, in-phase stretching, stronger band, and v$_4$, B$_1$, our of phase stretching, weaker band; their frequencies are sometimes interchanged, but never the intensities – compare). In the second group of compounds,

### TABLE I

Interaction stretching GVFF constants$^a$ for some square planar halogenometallates (D$_{4h}$) in 10$^2$ N m$^{-1}$

<table>
<thead>
<tr>
<th></th>
<th>$\Gamma_{rr}$</th>
<th>$\Gamma_{rr}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>KAgF$_4$</td>
<td>0.14</td>
<td>0.09</td>
<td>3</td>
</tr>
<tr>
<td>KAuF$_4$</td>
<td>0.09</td>
<td>0.19</td>
<td>4</td>
</tr>
<tr>
<td>AuCl$_4^-$</td>
<td>0.09</td>
<td>0.17</td>
<td>5</td>
</tr>
<tr>
<td>AuBr$_4$</td>
<td>0.09</td>
<td>0.13</td>
<td>5</td>
</tr>
<tr>
<td>BaPdF$_4$</td>
<td>0.09</td>
<td>0.31</td>
<td>4</td>
</tr>
<tr>
<td>PdCl$_4^{2-}$</td>
<td>0.09</td>
<td>0.17</td>
<td>5</td>
</tr>
<tr>
<td>PdBr$_4^{2-}$</td>
<td>0.07</td>
<td>0.15</td>
<td>5</td>
</tr>
</tbody>
</table>

$^a$\(\Gamma_{rr}\) – interaction force constant for stretching of cis bonds;  
$\Gamma_{rr}$ – interaction force constant for stretching of trans bonds.

### TABLE II

Frequencies (cm$^{-1}$) of two in-base stretching vibrations of XeF$_5^+$ ion in complexes with polymeric anions, and their arithmetic mean

<table>
<thead>
<tr>
<th></th>
<th>$\nu_2$</th>
<th>$\nu_4$</th>
<th>$\Delta$</th>
<th>arithmetic mean</th>
<th>References</th>
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<tr>
<td>XeF$_5^+$·ZrF$_5$</td>
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<td>584</td>
<td>15</td>
<td>591.5</td>
<td>17</td>
</tr>
<tr>
<td>XeF$_5^+$·HfF$_5$</td>
<td>507</td>
<td>581</td>
<td>16</td>
<td>589</td>
<td>17</td>
</tr>
<tr>
<td>XeF$_5^+$·FeF$_4$</td>
<td>507</td>
<td>580</td>
<td>17</td>
<td>588.5</td>
<td>16</td>
</tr>
<tr>
<td>XeF$_5^+$·Al$_2$F$_7$</td>
<td>501</td>
<td>585</td>
<td>6</td>
<td>588</td>
<td>15</td>
</tr>
<tr>
<td>XeF$_5^+$·GaF$_4$</td>
<td>508</td>
<td>580</td>
<td>18</td>
<td>589</td>
<td>15</td>
</tr>
</tbody>
</table>
there is obviously an interaction between the two vibrations with the bands sharing intensity. Symmetry analysis shows them as the only neighbouring bands obtaining the same representation upon deformation of XeF$_5^+$ (Figure 3), which may be achieved by changing the axial bond angles. Other bands, obtaining the same representation, are rather separated. PED demonstrates the two vibrations as pure in the undistorted ion and as completely mixed in the slightly deformed one (Table III). A scrutiny of the compounds shows that in all of them the anionic part should form polymeric chains or plates$^{15,17}$ and that XeF$_5^+$ placed in-between has to be distorted due to molecular forces.

3. AMMONIUM DECAFLUOROURANATE(IV), (NH$_4$)$_4$UF$_{10}$

A number of fluorouranates of different valence and composition are known. It has been observed that their stability decreases with higher stoichiometric ratios of cation/fluorouranate anion and with higher uranium valences. The upper left part of
TABLE III

PED for stretching vibrations of XeF$_5^+$ ion

| Undistorted XeF$_5^+$, C$_{4v}$, $\beta_1 = \beta_2 = 80.4^0$ |
|-----------------|------|------|------|------|------|------|------|
| $\nu_1$, A$_1$  | 90.4 | 6.0  | 3.6  | 95.1 | 2.3  | 1.1  | 100.0 |
| $\nu_7$, E      |      |      |      |      |      |      |       |
| $\nu_2$, A$_1$  | 6.4  | 93.6 |      |      |      |      |       |
| $\nu_4$, B$_1$  |      |      |      |      |      |      | 100.0 |

| Deformed XeF$_5^+$, C$_{2v}$($\alpha_v$), $\beta_1 = 90.0^0$, $\beta_2 = 80.4^0$ |
|-----------------|------|------|------|------|------|------|------|
| $\nu_1$, A$_1$  | 93.4 | 1.5  | 3.5  | 3.5  | 95.3 | 2.2  | 1.1  |
| $\nu_7$, B$_1$  |      |      |      |      |      |      |       |
| $\nu_2$, A$_1$  | 3.2  | 48.4 | 48.4 |      |      |      |       |
| $\nu_4$, A$_1$  |      | 50.0 | 50.0 |      |      |      |       |

*Wilson GF-matrix method; Simplified General Valence Force Field; symmetry coordinates according to Begun$^{21}$; $\beta_1$ and $\beta_2$, cis axial angles in XeF$_5^+$; geometry and frequencies in cm$^{-1}$ ($\nu_1$, 673; $\nu_2$ 625; $\nu_3$ 355; $\nu_4$ 610; $\nu_5$ 251; $\nu_6$ 300; $\nu_7$ 652; $\nu_8$ 410; $\nu_9$ 218; see also Figure 3) of undistorted XeF$_5^+$ according to Christe$^{11}$; program for normal coordinate analysis of Schachtschneider$^{22}$ were applied.*

![Diagram](image)

Figure 3. Correlation diagram for XeF$_5^+$ ion (C$_{4v}$) and its possible distorted configurations. Numbering of modes according to Christe.$^{11}$ Bands numbered 1,2,4 and 7 are stretching vibrations and bands numbered 3,5,6,8 and 9 are deformation vibrations.

Table IV had been vacant until a new method of low temperature oxidation with XeF$_2$ was applied (acting with XeF$_2$ on (NH$_4$)$_3$UF$_6$ at 55 °C$^{23}$). The compound is interesting also because its stoichiometry suggests a high coordination number yet unknown in mononuclear uranium(VI) complexes (see the discussion on the unlikelyness of coordination number 9 in isolated anions of actinide fluorides).$^{24}$ Synthesis of monocrystals suitable for X-ray structure determination was unsuccessful and vibrational spectra
TABLE IV

<table>
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<th></th>
<th>4:1</th>
<th>3:1</th>
<th>2:1</th>
<th>1:1</th>
<th>1:2</th>
<th>1:3</th>
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<tbody>
<tr>
<td>VI</td>
<td>(NH₄)₄UF₁₀&lt;sup&gt;δ&lt;/sup&gt;</td>
<td>(NH₄)₂UF₈&lt;sup&gt;β&lt;/sup&gt;</td>
<td>NH₄UF₇&lt;sup&gt;ε&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>(NH₄)₃UF₈&lt;sup&gt;δ&lt;/sup&gt;</td>
<td>(NH₄)₂UF₇&lt;sup&gt;δ&lt;/sup&gt;</td>
<td>NH₄UF₆&lt;sup&gt;ε&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>(NH₄)₄UF₈&lt;sup&gt;β&lt;/sup&gt;</td>
<td>(NH₄)₂UF₆&lt;sup&gt;β&lt;/sup&gt;</td>
<td>NH₄UF₅&lt;sup&gt;ε&lt;/sup&gt;</td>
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</tbody>
</table>


Figure 4. Infrared and Raman spectra of the UF₁₀<sup>4-</sup> ion in (NH₄)₄UF₁₀.
were used to prove the composition. The spectra of the anionic part are simple (Figure 4). Correlation of the UF breathing mode (the strongest band in Raman) with the other U(VI) compounds of fluorine clearly shows that the coordination number should be larger than 8. Infrared spectrum displayed a moderate hydrogen bond with the absorption almost three times wider than in various ammonium halides. This suggested polarization effects known to be present in other fluorouranates. Thus, a deformed UF$_{10}^{1-}$ ion has been proposed with one of the F atoms having a significant ionic character.

4. HYDRAZINUM (1+) AND 2(+) FLUOROZIRCONATES

Stoichiometries of the fluorozirconate series suggest the presence of octahedral structures in some of the compounds (Table V). But the frequency of the strong Raman band of the totally symmetric stretching mode of the anion unambiguously indicates

**Table V**

Known hydrazinium and ammonium fluorozirconates(IV) classified according to the ratio of cation charge per zirconium atom

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Cation</th>
<th>Anion</th>
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<td>1:1</td>
<td>N$_2$H$_5$$^+$</td>
<td>N$_2$H$_5$ZrF$_6$ $^b$</td>
</tr>
<tr>
<td></td>
<td>N$_2$H$_5$$^*$</td>
<td>(N$_2$H$_5$)$_2$ZrF$_6$ $^c$</td>
</tr>
<tr>
<td></td>
<td>NH$_4$$^+$</td>
<td>NH$_4$ZrF$_6$ $^d$</td>
</tr>
</tbody>
</table>


![Raman bands](image)

Figure 5. Examples of Raman active N–N stretching bands of hydrazinium (1+) and 2(+) ions, which are environment sensitive.
coordinations larger than 6 in all cases.\textsuperscript{25} This is in accordance with X-ray structures, where known. Polyhedra with 8 F ligands are connected in different ways to chains or dimers \((\text{N}_2\text{H}_6\text{ZrF}_{12})\) \textsuperscript{26} \((\text{N}_2\text{H}_6\text{Zr}_2\text{F}_{13}\cdot\text{F}_2)\) \textsuperscript{27} \((\text{NH}_4)_2\text{ZrF}_6\).\textsuperscript{28} Two types of hydrazinium ions appear in some structures, which is shown by the split band of N-N stretching vibration which is environment sensitive\textsuperscript{29,30} (Figure 5). This is confirmed by the X-ray data displaying one type bonded with weaker bonds to coordinated F and the other forming chains with stronger bonds to free F-ions (e.g. \((\text{N}_2\text{H}_6)_2\text{Zr}_2\text{F}_{13}\cdot\text{F}_2)\).\textsuperscript{27} Hafnium gives a parallel series of compounds.

5. LOW TEMPERATURE TRANSFORMATIONS

5.1. Hydrazinium(1+) Fluoroaluminates(III), \((\text{N}_2\text{H}_6)_2\text{AlF}_5\cdot\text{H}_2\text{O}\)

An interesting and puzzling example of low temperature transformations is the aluminium compound \((\text{N}_2\text{H}_6)_2\text{Al}_4\cdot\text{H}_2\text{O}\) which loses water at 118 °C, forming \((\text{N}_2\text{H}_6)_2\text{AlF}_5\) and receiving it back reversibly from the air at room temperature in the course of a few weeks. The infrared spectra are changed accordingly. Librational bands of coordinated water disappear and appear again, and the \text{AlF}_5\ part of the spectra changes significantly. In the case of hydrate it is very similar to the spectra\textsuperscript{32,33} of \((\text{NH}_4)_2\text{AlF}_5\cdot\text{H}_2\text{O}\), whose structure\textsuperscript{34} is known, and in the case of anhydrous derivative the splitting of the strong Al–F stretching absorption suggests condensation of fluoroaluminate octahedra (see also ref. 32). Consequently, zeolitic character has been excluded and two coordination polyhedra proposed, \[\text{AlF}_5\cdot\text{H}_2\text{O}\]\textsuperscript{2–} and \[\text{AlF}_4\text{F}_2\]\textsuperscript{2–} (Figure 6). There is not enough evidence for discerning cis or trans bonding in chains of \[\text{AlF}_4\text{F}_2\]\textsuperscript{2–} octahedra. No suggestions on the mechanism of interconversion are yet possible.

5.2. Tetramethylammonium Di-\(\mu\)-fluoro-bis[aquadifluorooxo vanadate(IV)], \[\{(\text{CH}_3)_4\text{N}\}_2\cdot\text{VO}_2\cdot\text{H}_2\text{O}\] (Figure 6). The second example is the hydrate of a vanadium compound, \((\text{CH}_3)_4\text{N}\cdot\text{VO}_2\cdot\text{H}_2\text{O}\)\textsubscript{2}, whose structure is known.\textsuperscript{35} The anion is a dimer with the center of inversion clearly displayed by vibrational spectra.\textsuperscript{35} The center of inversion is lost upon reversible dehydration. Bands of coordinated water disappear and the spectrum is reversibly changed to what may be expected of an \text{VOF}_3\textsuperscript{–} ion.

![Figure 6](image)

\((\text{N}_2\text{H}_6)_2\text{AlF}_5\cdot\text{H}_2\text{O}\) \((\text{N}_2\text{H}_6)_2\text{AlF}_5\)
5.3. Hydrazinium(2+) Hexafluorotitanate(III) Fluoride, \((N_2H_6)_2TiF_6.2F\)

The crystals of the unstable titanium compound, \((N_2H_6)_2TiF_6.2F\), contain \(TiF_6^{2-}\)octahedra sandwiched between sheets of \(N_2H_6^{2+}\) and \(F^-\) ions. The sheets are interconnected by hydrogen bonds, one of which is unusually short (2.658(5) Å). A very strong N-H···F stretching absorption in the infrared is reminiscent of (i) type hydrogen bond spectra of the oxygen compounds of Prof. Hadzi. Under the heat of the laser beam in the Raman instrument the compound decomposes and the spectrum monotonously transforms to the spectrum of \((N_2H_6)_2TiF_6\). Changes in the intensity of the stretching N–N bands, which are environment sensitive, indicate the disappearance of the initial \(N_2H_6^{2+}\) ion, appearance of two new types of \(N_2H_6^{2+}\) ions, whose quantity rises to a certain maximum and then vanishes altogether, and a steady increase of \(N_2H_6^+\) ion. In the end, the new compound is formed. The bands are sharp and do not shift. Obviously, there is a proton transfer from the \(N_2H_6^{2+}\) ion to \(F^-\), HF escapes, \(N_2H_5^+\) ion is formed. The process proceeds gradually and the environment of the still present \(N_2H_6^{2+}\) ions is modified, which results in two changed \(N_2H_6^{2+}\) bands which appear, go to the maximum and then disappear.

6. HYDROGEN BONDING IN FLUOROMETALLATES OF HYDRAZINUM

Hydrogen bonds have an important place among the intermolecular forces in hydrazinium complexes. Useful conclusions may be drawn from their manifestations in vibrational spectra, as in the case of \((NH_4)_4UF_{10}\). But many times the relations in the solid state are too intricate to enable a clear picture. For instance, the hydrogen bond strength may be judged by several parameters, like the distance between donor and acceptor atoms and the shift and half-width of the infrared absorption (see e.g.

![Diagram](image)

Figure 7. An attempt to arrange several hydrazinium(2+) fluorometallates according to some parameters for evaluating hydrogen bond strength. Centers and half widths at half heights in cm\(^{-1}\) of N–H stretching absorptions in infrared are estimated from: \(N_2H_6F_2\) (2550, 500, \(N_2H_6)_3ZrF_13F\) (2850, 900), \(N_2H_6TiF_6\) (2750, 700) and \((N_2H_6)_2TiF_6.2F\) (2600, 21000) and N–F distances in Å from: \(N_2H_6F_2\) (2.62), \((N_2H_6)_3ZrF_13F\) (2.437), \(N_2H_6TiF_6\) (2.568), \(N_2H_6TiF_6\) (2.612).
ref. 39). Stronger bonds with free F ions and weaker with coordinated ones may be expected. Correlation of these parameters for some hydrazinium(2+) fluorometallates, listed in order of the expected H-bond strength, gives a confused picture (Figure 7). The correlations are obviously too crude, because hydrazinium(2+) ion may act in 6 donor hydrogen bonds, and hydrazinium(1+) ion in 5 donor and one acceptor bond to two acceptors, free and coordinated F ions. The bonds may have different multiplicities and different geometries.\textsuperscript{43} The conditions are even more complex than in the case of NH\textsubscript{4}\textsuperscript{+} complexes, for which some thorough correlations with crystal structures have been made (e.g. refs. 44, 45 and the literature cited within).

REFERENCES

19. Professor B. Žemva, private communication.

**SAŽETAK**

**Vibracijska spektroskopija anorganskih koordinacijskih spojeva fluora**

*S. Milićev*

Vibracijska spektroskopija mnogo se puta uspješno koristila za tumačenje prirode kemijske veze i strukture molekula. To u potpunosti vrijedi za organske spojeve, ali u slučaju nekih skupina anorganskih spojeva, kao što su kompleksi halogenida, rezultati su katkada nužno ograničeni needefiniranošću problema. To se može zgodno prikazati na spojevima fluora. Na primjer: korelacije između bazičnosti fluora i kemijske Vete s interakcijskom sile u ionima AgF₄⁻ i AuF₄⁻, miješanje vibracija u ionu XeF₅⁺ uslijed simetrijskih promjena, visoki koordinacijski broj i nesimetrija u ionu UF₁₀⁺, različito vezanje koordinacijskih poliedara i raznih tipova iona N₂H₅⁺ u spojevima cirkonija i hafnija, niskotemperaturne transformacije kao što su reverzibilna hidratacija/dehidratacija N₂H₅AlF₆ × H₂O, reverzibilni prijelazi dimer-monomer u V₂O₅F₅(OH)₂⁺, raspad (N₂H₅)₂TiF₆ × F₂ putem prijenosa protona s N₂H₅⁺ na F⁻, te izostanak jednostavnih korelacija spektrala s jakošću vodikovih veza.