CROATICA CHEMICA ACTA CCACAA **65** (1) 125–135 (1992)

ISSN 0011-1643
UDC 543.42
CCA–2047

Original Scientific Paper

Vibrational Spectroscopy of Inorganic Coordination Compounds of Fluorine*

S. Milićev

Institute J. Stefan, Ljubljana, Slovenia

Received July 17, 1991

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 AgF_4^- and AuF_4^- ions, the mixing modes in XeF_5^+ ion due to symmetry changes, high coordination number and asymmetry in UF_{10}^+ ion, different linking of coordination polyhedra and different types of $N_2H_6^{2+}$ ions in the compounds of Zr and Hf, low temperature transformations like reversible hydration/dehydration of $N_2H_6AlF_5.H_2O$, reversible dimer–monomer transitions of $(V_2O_2F_6(OH_2)_2^{2-}$, decomposition of $(N_2H_6)_2TiF_6.F_2$ through proton transfer from $N_2H_6^{2+}$ to 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, 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 outrightly 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).

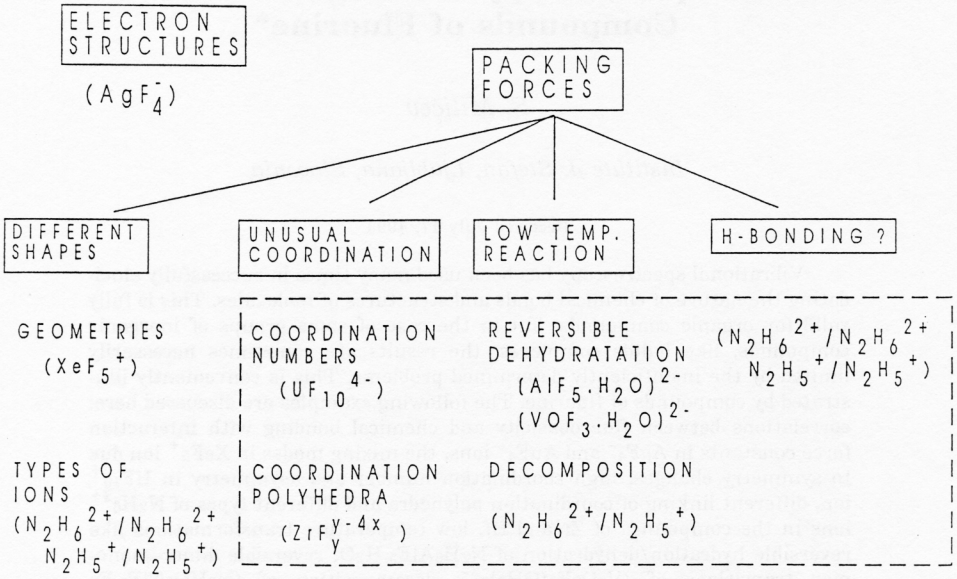


Figure 1. Overview of the examined examples. The dashed area includes hydrazinium or ammonium complexes with hydrogen bonding.

1. ELECTRONIC EFFECTS IN POTASSIUM TETRAFLUROARGENTATE(III), KAg,F_4

The normal coordinate analysis of 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 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 XeF_4 and 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

TABLE I

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

	f_{rr}	f'_{rr}	References
$KAgF_4$	0.14	0.09	3
$KAuF_4$	0.09	0.19	4
$AuCl_4^-$	0.09	0.17	5
$AuBr_4$	0.09	0.13	5
$BaPdF_4$	0.09	0.31	4
$PdCl_4^{2-}$	0.09	0.17	5
$PdBr_4^{2-}$	0.07	0.15	5

[a] f_{rr} – interaction force constant for stretching of *cis* bonds; f'_{rr} – interaction force constant for stretching of *trans* bonds.

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.[6] 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_6 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.[10,11,12] This is not surprising, because crystal structures, where known, reveal the XeF_5^+ ions of C_{4v} symmetry and similar dimensions.[13,14] The other group, a series of five compounds synthesized in our laboratory, shows a very different kind of spectra[15,16,17] 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}, ν_2, A_1, in-phase stretching, stronger band, and ν_4, B_1, our of phase stretching, weaker band; their frequencies are sometimes interchanged, but never the intensities – compare[11,18]). In the second group of compounds,

TABLE II

Frequencies (cm^{-1}) of two in-base stretching vibrations of XeF_5^+ ion in complexes with polymeric anions, and their arithmetic mean

	ν_2	ν_4	Δ	arithmetic mean	References
$XeF_5^+ \cdot ZrF_5^-$	599	584	15	591.5	17
$XeF_5^+ \cdot HfF_5^-$	597	581	16	589	17
$XeF_5^+ \cdot FeF_4^-$	597	580	17	588.5	16
$XeF_5^+ \cdot Al_2F_7^-$	591	585	6	588	15
$XeF_5^+ \cdot GaF_4^-$	598	580	18	589	15

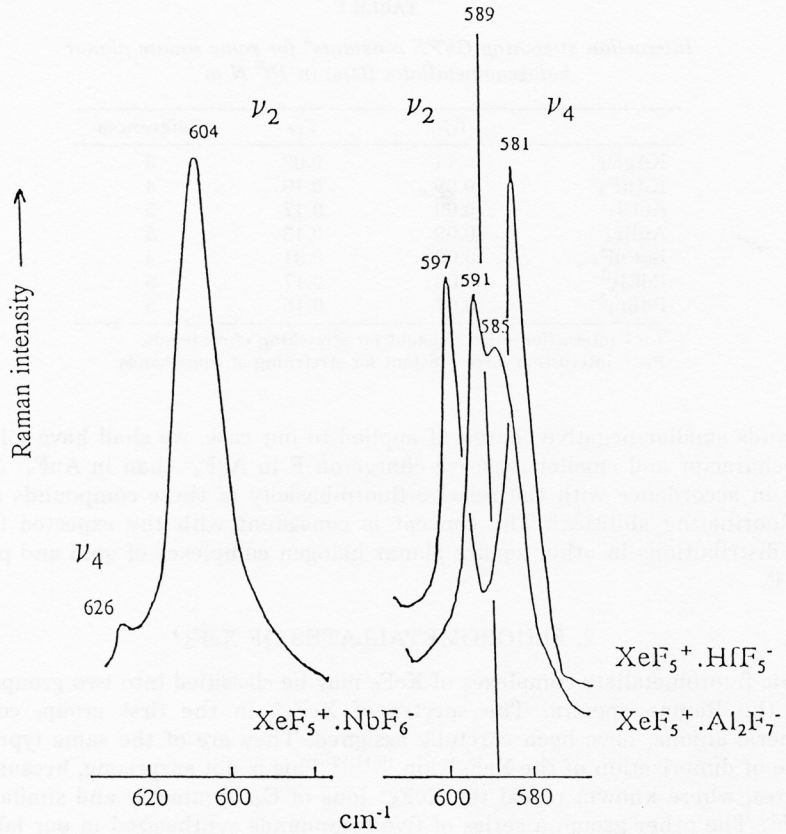


Figure 2. Region of the stretching Xe-F vibrations in the base of the pyramid of XeF_5^+; ν_2 – in phase vibration, ν_4 – out of phase vibration. Compound with a monomeric anion: XeF_5^+ NbF_6^- (spectrum[19], structure[20]); polymeric anions: $XeF_5^+HfF_5^-$ [17] and $XeF_5^+Al_2F_7^-$.[15]

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), $(NH_4)_4UF_{10}$

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[a]

Undistorted XeF_5^+, C_{4v}, $\beta_1 = \beta_2 = 80.4°$

	S_1	S_2	S_3	S_4	S_7	S_8	S_9
ν_1, A_1	90.4	6.0	3.6				
ν_7, E					95.1	2.3	1.1
ν_2, A_1	6.4	93.6					
ν_4, B_1				100.0			

Deformed XeF_5^+, $C_{2v}(\sigma_v)$, $\beta_1 = 90.0°$, $\beta_2 = 80.4°$

	S_1	S_2	S_3	S_4	S_7	S_8	S_9
ν_1, A_1	93.4	1.5	3.5	1.5			
ν_7, B_1					95.3	2.2	1.1
ν_2, A_1	3.2	48.4		48.4			
ν_4, A_1		50.0		50.0			

[a] Wilson GF-matrix method; Simplified General Valence Force Field; symmetry coordinates according to Begun[21]; β_1 and β_2, *cis* axial angles in XeF_5^+; geometry and frequencies in cm^{-1} (ν_1, 679; ν_2 625; ν_3 355; ν_4 610; ν_5 261; ν_6 300; ν_7 652; ν_8 410; ν_9 218; see also Figure 3) of undistorted XeF_5^- according to Christe[11]; program for normal coordinate analysis of Schachtschneider[22] were applied.

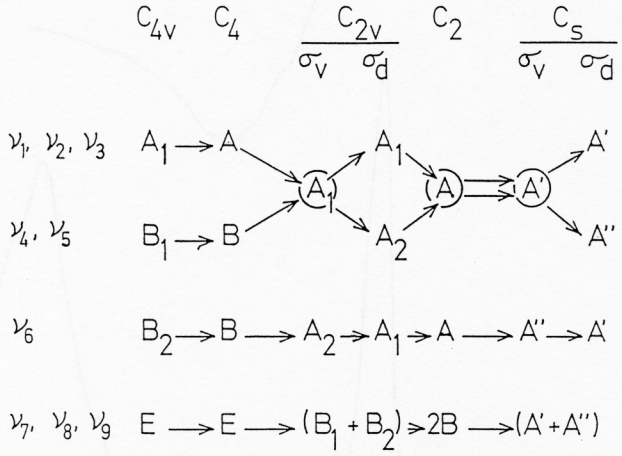


Figure 3. Correlation diagram for XeF_5^+ ion (C_{4v}) and its possible distorted configurations. Numbering of modes according to Christe.[11] Bands numbered 1,2,4 and 7 are stretching vibrations and bands numbered 3,5,6,8 and 9 are deformation vibrations.

Table IV had been vacant until a new method of low temperature oxidation with XeF_2 was applied (acting with XeF_2 on $(NH_4)_4UF_8$ 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 unlikeliness 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

Known ammonium fluorouranates arranged according to the stoichiometric ratio NH_4^+/U and the valence of uranium

	4 : 1	3 : 1	2 : 1	1 : 1	1 : 2	1 : 3
VI	$(NH_4)_4UF_{10}$[a]		$(NH_4)_2UF_8$[b]	NH_4UF_7[c]		
V		$(NH_4)_3UF_8$[d]	$(NH_4)_2UF_7$[d]	NH_4UF_6[e]		
IV	$(NH_4)_4UF_8$[f]		$(NH_4)_2UF_6$[f]	NH_4UF_5[f]	$(NH_4)_7U_6F_{31}$[f]	$NH_4U_3F_{13}$[f]

Syntheses: [a]B. Družina, S. Milićev, and J. Slivnik, *J. Chem. Soc., Chem. Common.* (1984) 364. [b]R. Bougon, P. Charpin, J. P. Desmoulin, and J. G. Malm, *Inorg. Chem.* **19** (1976) 2532. [c]B. Volavšek, *Croat. Chem. Acta* **33** (1961) 181. [d]R. A. Penneman, G. D. Sturgeon, and L. B. Asprey, *Inorg. Chem.* **3** (1964) 126. [e]R. A. Penneman, L. B. Asprey, and G. D. Strugeon, *J. Amer. Chem. Soc.* **84** (1962) 4608. [f]R. Benz, R. M. Douglas, F. M. Kruse, and R. A. Penneman, *Inorg. Chem.* **2** (1963) 799.

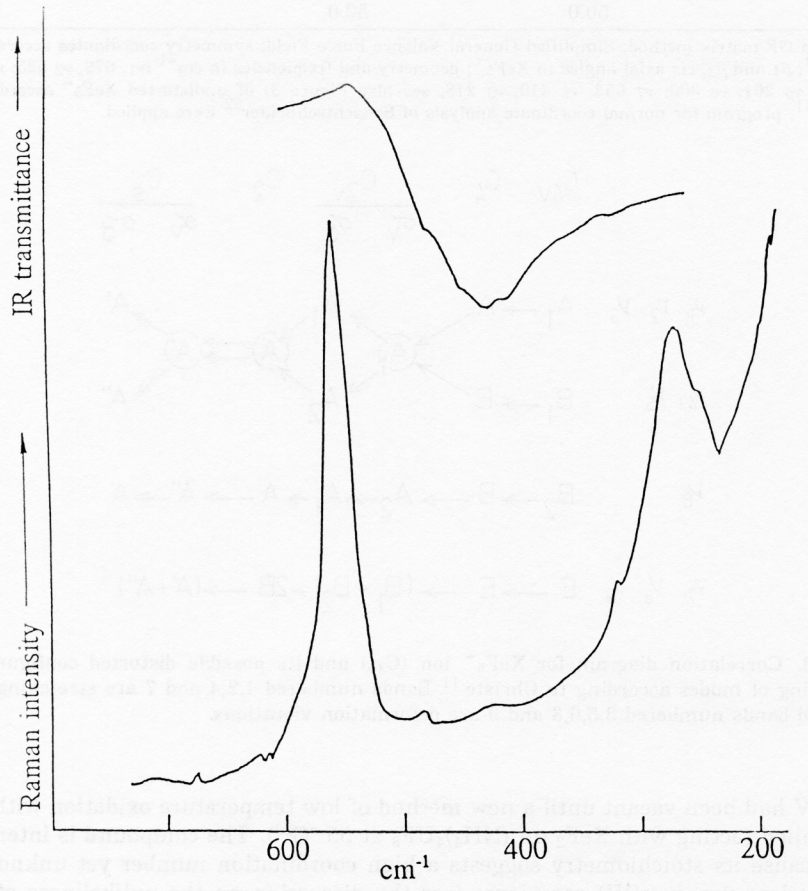


Figure 4. Infrared and Raman spectra of the UF_{10}^{4-} ion in $(NH_4)_4UF_{10}$.

were used to prove the composition.[23] 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}^{4-} ion has been proposed with one of the F atoms having a significant ionic character.

4. HYDRAZINIUM (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

	1 : 1	2 : 1	3 : 1
$N_2H_6^{2+}$		$N_2H_6ZrF_6$[a]	$(N_2H_6)_3Zr_2F_{14}$[a]
$N_2H_5^+$	$N_2H_5ZrF_5$[b]	$(N_2H_5)_2ZrF_6$[c]	$(N_2H_5)_3ZrF_7$[d]
NH_4^+	NH_4ZrF_5[e]	$(N_2H_4)_2ZrF_6$[e]	$(NH_4)_3ZrF_7$[e]

Synthesis: [a]J. Slivnik, A. Šmalc, B. Sedej, and M. Vilhar, *Vestn. Slov. Kem. Drus.* **11** (1964) 53; J. Slivnik, B. Jerkovič, and B. Sedej, *Monatsh. Chem.* **97** (1966) 820. [b]D. Gantar and A. Rahten, *J. Fluorine Chem.* **34** (1986) 63. [c]D. Gantar, A. Rahten, and B. Volavšek, *J. Fluorine Chem.* **41** (1988) 335. [d]A. Rahten, S. Milićev, *Thermochim. Acta* **171** (1990) 185. [e]P. W. Smith, R. Stoessiger, and A. G. Turnbull, *J. Chem. Soc. A (1968) 3013.*

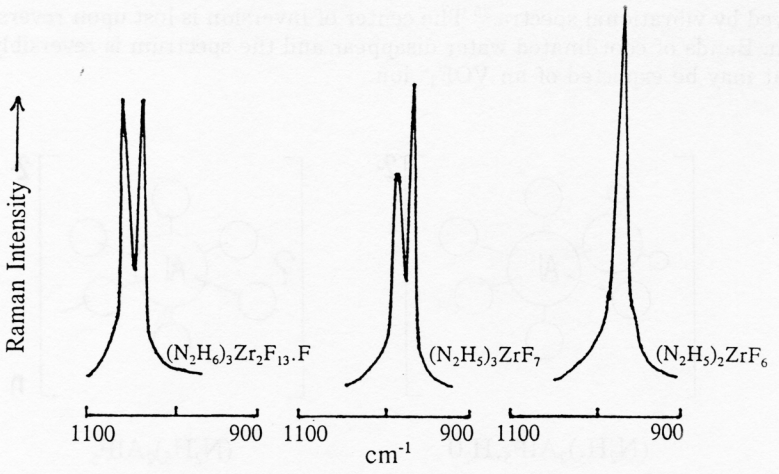


Figure 5. Examples of Raman active N–N stretching bands of hydrazinium (1+) and 2(+) ions, which are environment sensitive.

coordinations larger than 6 in all cases.[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 ($N_2H_6ZrF_6$,[26] ($(N_2H_6Zr_2F_{13}.F$,[27] $(NH_4)_2ZrF_6$).[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[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.* $(N_2H_6)_3Zr_2F_{13}.F$).[27] Hafnium gives a parallel series of compounds.

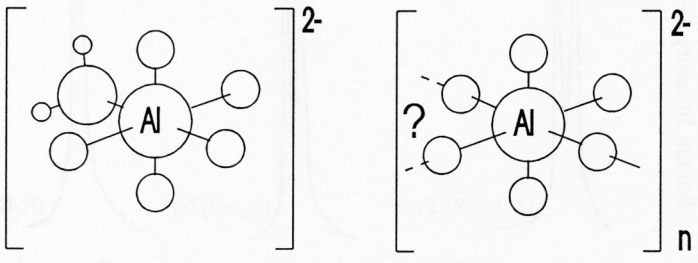
5. LOW TEMPERATURE TRANSFORMATIONS

5.1. Hydrazinium(1+) Fluoroaluminates(III), $(N_2H_5)_2AlF_5 \cdot H_2O$

An interesting and puzzling example of low temperature transformations is the aluminium compound $(N_2H_5)_2Al_5 \cdot H_2O$ which loses water at 118 °C, forming $(N_2H_5)_2AlF_5$ 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 AlF_5 part of the spectra changes significantly. In the case of hydrate it is very similar to the spectra[32,33] of $(NH_4)_2AlF_5 \cdot H_2O$, whose structure[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, $[AlF_5 \cdot H_2O]^{2-}$ and $[AlF_4F_{2/2}]^{2-}$ (Figure 6). There is not enough evidence for discerning *cis* or *trans* bonding in chains of $[AlF_4F_{2/2}]^{2-}$ octahedra. No suggestions on the mechanism of interconversion are yet possible.

5.2. Tetramethylammonium Di-μ-fluoro-bis[aquadifluorooxovanadate(IV)], $[(CH_3)_4N]_2.[V_2O_2F_6(H_2O)_2]$

The second example is the hydrate of a vanadium compound, $(CH_3)_4N.[VOF_3.H_2O]_2$, whose structure is known.[35] The anion is a dimer with the center of inversion clearly displayed by vibrational spectra.[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 VOF_3^- ion.



$(N_2H_5)_2AlF_5.H_2O$ $(N_2H_5)_2AlF_5$

Figure 6. Coordination polyhedra in monomeric $(N_2H_5)_2AlF_5.H_2O$ and presumably in polymeric $(N_2H_5)_2AlF_5$. There is no evidence for *cis* or *trans* bonding in chains of $(N_2H_5)_2AlF_5$.

5.3. Hydrazinium(2+) Hexafluorotitanate(III) Fluoride, $(N_2H_6)_2TiF_6.2F$

The crystals of the unstable titanium compound, $(N_2H_6)_2TiF_6.2F$,[36] contain TiF_6^{2-} octahedra sandwiched between sheets of $N_2H_6^{2+}$ and F^- ions.[37] 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[30] is reminiscent of (*i*) type hydrogen bond spectra of the oxygen compounds of Prof. Hadži.[38] Under the heat of the laser beam in the Raman instrument the compound decomposes and the spectrum monotonously transforms to the spectrum of $(N_2H_5)_2TiF_6$. Changes in the intensity of the stretching N–N bands, which are environment sensitive,[29,30] 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 $N_2H_5^+$ 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 HYDRAZINIUM

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.*

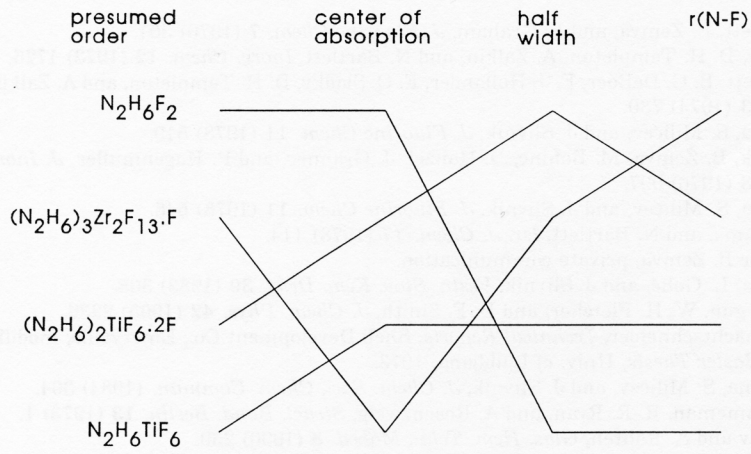


Figure 7. An attempt to arrange several hydrazinium(2+) fluorometallates according to some parameters for evaluating hydrogen bond strength. Centers and half widths at half heights in cm^{-1} of N–H stretching absorptions in infrared are estimated from: $N_2H_6F_2$ (~2550, ~500),[40] $(N_2H_6)_3Zr_2F_{13}F$ (~2850, ~900),[27] $N_2H_6TiF_6$ (~2750, ~700) and $(N_2H_6)_2TiF_6.2F$ (~2600, 21000),[30] and N–F distances in Å from: $N_2H_6F_2$ (2.62),[41] $(N_2H_6)_3Zr_2F_{13}.F$ (2.437),[27] $(N_2H_6)TiF_6.2F$ (2.568),[37] $N_2H_6TiF_6$ (2.612).[42]

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.[43] The conditions are even more complex than in the case of NH_4^+ complexes, for which some thorough correlations with crystal structures have been made (*e.g.* refs. 44, 45 and the literature cited within).

REFERENCES

1. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules,* Chapman and Hall, London, 3rd edition, 1975; *Advances in Infrared Group Frequencies,* Methuen & Co., 1968.
2. D. Hadži, *Characteristic Features in the Spectra of Organic Molecules* in: M. Davies (Ed.), *Infra-red Spectroscopy and Molecular Structure,* Elsevier, Amsterdam, 1963, pp. 226-269.
3. K. Lutar, S. Milićev, B. Žemva, B. G. Müller, B. Bachmann, and R. Hoppe, *Eur. J. Solid Inorg. Chem.* **28** (1991) 1335.
4. B. G. Müller, *Habilitation Thesis*, Univ. of Giessen, 1981.
5. P. L. Goggin and J. Mink, *J. Chem. Soc. Dalton Trans.* (1974) 1479.
6. H. W. Thompson and J. W. Linnett, *J. Chem. Soc.* (1937) 1384.
7. D. J. Royer, *Bonding Theory*, McGraw-Hill, New York, 1968.
8. D. F. Smith, *Information on Bonding in Xenon Compounds from Infrared Spectra,* in: H. H. Hyman (Ed.), *Noble-Gas Compounds,* Univ. of Chicago Press, Chicago, 1963, p. 295.
9. K. Lutar, A. Jesih, I. Leban, B. Žemva, and N. Bartlett, *Inorg. Chem.* **28** (1989) 3467.
10. K. Leary, A. Zalkin, and N. Bartlett, *Inorg. Chem.* **13** (1974) 775.
11. K. O. Christe, E. C. Curtis, and R. D. Wilson, *J. Inorg. Nucl. Chem.* Supplement 1976, in: J. J. Katz and I. Sheft (Ed.), *H. H. Hyman Memorial Volume*, Pergamon Press, Oxford, 1976, p. 159.
12. N. Bartlett, B. Žemva, and L. Graham, *J. Fluorine Chem.* **7** (1976) 301.
13. K. Leary, D. H. Templeton, A. Zalkin, and N. Bartlett, *Inorg. Chem.* **12** (1973) 1726.
14. N. Bartlett, B. G. DeBoer, F. J. Hollander, F. O. Sladky, D. H. Templeton, and A. Zalkin, *Inorg. Chem.* **13** (1974) 780.
15. B. Žemva, S. Milićev, and J. Slivnik, *J. Fluorine Chem.* **11** (1978) 519.
16. J. Slivnik, B. Žemva, M. Bohinc, D. Hanžel, J. Grannec, and P. Hagenmuller, *J. Inorg. Nucl. Chem.* **38** (1976) 997.
17. B. Žemva, S. Milićev, and J. Slivnik, *J. Fluorine Chem.* **11** (1978) 545.
18. C. J. Adams, and N. Bartlett, *Isr. J. Chem.* **17** (1978) 114.
19. Professor B. Žemva, private communication.
20. B. Žemva, L. Golič, and J. Slivnik, *Vestn. Slov. Kem. Druš.* **30** (1983) 365.
21. G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.* **42** (1965) 2236.
22. J. H. Schachtschneider, *Technical Reports*, Shell Development Co., Emeryville; modified by B. Barlič, *Master Thesis,* Univ. of Ljubljana, 1973.
23. B. Družina, S. Milićev, and J. Slivnik, *J. Chem. Soc., Chem. Commun.* (1984) 364.
24. R. A. Penneman, R. R. Ryan, and A. Rosenzweig, *Struct. Bond. Berlin,* **13** (1973) 1.
25. S. Milićev and A. Rahten, *Glas. Hem. Tehn. Maked.* **8** (1990) 259.
26. B. Kojić-Prodić, S. Šćavničar, and B. Matković, *Acta Crystallogr.* **B27** (1971) 638.
27. A. Rahten, I. Leban, S. Milićev, and B. Žemva, *J. Crystallogr. Spectrosc. Research* **20** (1990) 9.
28. A. Zalkin, D. Eimerl, and S. P. Velsko, *Acta Crystallogr.* **C44** (1988) 2050.
29. S. Milićev and J. Maček, *Spectrochim. Acta* **41A** (1985) 651.
30. S. Milićev and J. Maček, *J. Chem. Soc., Dalton Trans.* (1984) 297.
31. S. Milićev and A. Rahten, *Eur.J. Solid State Inorg. Chem.*, **28** (1991) 557.
32. U. Bentrup, R. Stodolski, and L. Kolditz, *Z. Chem.* **26** (1986) 187.
33. U. Bentrup and L. Kolditz, *J. Thermal. Anal.* **33** (1988) 827.

34. O. Knop, T. S. Cameron, S. P. Deraniyagala, D. Adhikesavalu, and M. Falk, *Canad. J. Chem.* **63** (1985) 516.
35. P. Bukovec, S. Milićev, A. Demšar, and L. Golič, *J. Chem. Soc., Dalton Trans.* (1982) 1802.
36. J. Slivnik, J. Maček, B. Orel, and B. Sedej, *Monatsh. Chem.* **104** (1973) 624.
37. L. Golič, V. Kaučič, and B. Kojić-Prodić, *Acta Crystallogr.* **B36** (1980) 659.
38. D. Hadži, *Chimia* **26** (1972) 7.
39. M. D. Joesten and L. J. Schaad, *Hydrogen Bonding*, Marcell Dekker, New York, 1974.
40. R. G. Snyder and J. C. Decius, *Spectrochim. Acta* **13** (1959) 280.
41. M. L. Kronberg and D. Harker, *J. Chem. Phys.* **10** (1942) 309.
42. B. Kojič-Prodić, B. Matković, and S. Šćavničar, *Acta Crystallogr.* **B27** (1971) 635.
43. R. Liminga, *Arkiv Kemi* **28** (1968) 483.
44. G. J. Kearley and I. A. Oxton, *Recent Advances in the Vibrational Spectroscopy of the Ammonium Ion in Crystals* in: R. J. H. Clark and R. E. Hester (Ed.), *Advances in Infrared and Raman Spectroscopy* Vol. 10., John Wiley & Sons, Chichester, 1983, p. 111.
45. O. Knop, W. J. Westerhaus, M. F. Falk, and W. Massa, *Can. J. Chem.* **63** (1985) 3328.

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 nedefiniranošću problema. To se može zgodno prikazati na spojevima fluora. Na primjer: korelacije između bazičnosti fluora i kemijske Vete s interakcijskom konstantom sile u ionima AgF_4^- i AuF_4^-, miješanje vibracija u ionu XeF_5^+ uslijed simetrijskih promjena, visoki koordinacijski broj i nesimetrija u ionu UF_{10}^+, različito vezanje koordinacijskih poliedara i raznih tipova iona $N_2H_6^{2+}$ u spojevima cirkonija i hafnija, niskotemperaturne transformacije kao što su reverzibilna hidratacija/dehidratacija $N_2H_6AlF_5 \times H_2O$, reverzibilni prijelazi dimer-monomer u $V_2O_2F_6(OH_2)_2^{2-}$, raspad $(N_2H_6)_2TiF_6 \times F_2$ putem prijenosa protona s $N_2H_6^{2+}$ na F^-, te izostanak jednostavnih korelacija spektara s jakošću vodikovih veza.