Vibrational Spectra of Hydrazinium(1+) and Hydrazinium(2+) Hexafluorotitanates(IV) and the Decomposition of Hydrazinium(2+) Hexafluorotitanate(IV) Difluoride followed by Raman Spectroscopy

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The Raman spectra of $[N_2H_5]_2[TiF_6]$, $[N_2H_6][TiF_6]$, and $[N_2H_6]_2[TiF_6]F_2$ are reported and analysed together with the already known infrared spectra, for which a corrected assignment is given. Raman spectra of the $[TiF_6]^{2-}$ ion show a previously unobserved ν_2 (455 cm^{-1}) and a symmetry inactive ν_6 mode (*ca.* 210—220 cm^{-1}) in O_h, appearing under the influence of the site group. An inactive torsional vibration of $[N_2H_6]^{2+}$ was observed at 509 cm^{-1} in the Raman spectrum of $[N_2H_6]_2[TiF_6]F_2$. An i.r. type (i) strong hydrogen-bond spectrum was displayed by this compound. $[N_2H_6]_2[TiF_6]F_2$ is unstable and its decomposition to $[N_2H_5]_2[TiF_6]$ under the heat of a laser beam was followed by means of Raman spectra. Changes in the spectra suggest that the decomposition occurs *via* a proton transfer from $[N_2H_6]^{2+}$ to a F^- ion, producing $[N_2H_5]^+$ and liberating a molecule of HF.

Since 1964 a larger number of hydrazinium fluorometalates, including all the metals of the first transition series, with the exception of nickel, have been prepared and characterized at the Jožef Stefan Institute.[1] Three anhydrous titanium complexes [2] have also been isolated, $[N_2H_5]_2[TiF_6]$, $[N_2H_6][TiF_6]$, and $[N_2H_6]_2[TiF_6]F_2$. The last is thermally unstable, decomposition starting without melting at 80 °C with evolution of HF. The resulting product has the same formula and i.r. spectrum and similar further thermal behaviour to the newly prepared [2] $[N_2H_5]_2[TiF_6]$. This suggested the formula of $[N_2H_5]_2[TiF_6]\cdot 2HF$ for the complex before decomposition. A crystal structure [3] determination, however, showed the structure to be $[N_2H_6]_2[TiF_6]F_2$ which led to speculation about the apparently obvious decomposition path for this complex *via* a proton transfer from $[N_2H_6]^{2+}$ to a F^- ion. Herein we examine the previously unobserved Raman spectra of these complexes and try to find proof for the suggested decomposition mechanism by following the decomposition of $[N_2H_6]_2[TiF_6]F_2$ to $[N_2H_5]_2[TiF_6]$ caused by the heat of a laser beam using Raman spectroscopy.

Experimental

All compounds were kindly supplied to us by the late Professor J. Slivnik.

Infrared spectra were recorded on a Perkin-Elmer 521 grating spectrophotometer. For exciting Raman spectra an Ar^+ ion laser, Coherent Radiation model CR-3 (4 579, 4 880, and 5 145 Å), and a Kr^+ ion laser, Coherent Radiation model CR-500 K (5 682 and 6 471 Å), were used. The spectra were recorded in reflection geometry (180°) on an instrument constructed by ourselves, using a Spex-1401 double monochromator, at the Department for Fluorine Chemistry, Jožef Stefan Institute, Ljubljana. The samples were placed in capillary tubes, and in the case of $[N_2H_6]_2[TiF_6]F_2$, also in a rotating sapphire cell.

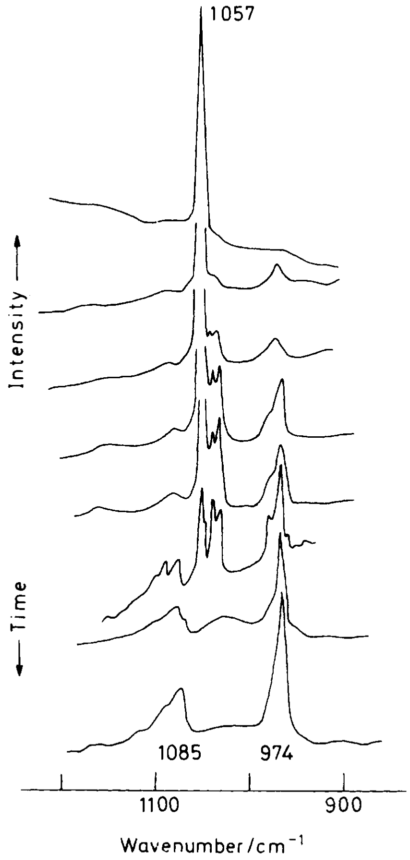

Figure 1. Changes in the Raman spectrum of $[N_2H_6]_2[TiF_6]F_2$ caused by heat generated by a laser beam. The bottom spectrum is also identical with the Raman spectrum of $[N_2H_5]_2[TiF_6]$

Results and Discussion

Spectra of $[TiF_6]^{2-}$ *Ions.*—The part of the spectra arising from the Ti–F vibrations is of similar shape in all three complexes (Table) and is assigned according to the literature.[4] The totally symmetric Ti–F stretching band (ν_1, A_{1g} in O_h, Raman active) is slightly split only in $[N_2H_5]_2[TiF_6]$. In both $[N_2H_6][TiF_6]$ and $[N_2H_6]_2[TiF_6]F_2$ only the degenerate bands are split, which is probably caused, in view of the four formula units in the primitive cell [3] of the latter complex, by site symmetry effects.

A Raman active mode, ν_2 (E_g in O_h), which is generally very weak in octahedral fluorometalates, has not yet been directly

Table. Infrared and Raman spectra [a] of the complexes below 1 800 cm^{-1}

$[N_2H_6][TiF_6]$		$[N_2H_6]_2[TiF_6]F_2$		$[N_2H_5]_2[TiF_6]$		
I.r.	Raman	I.r.	Raman	I.r.	Raman	Assignment [b]
				1 640 (sh)	1 640 (5)	$(NH_2)_d$
	1 640 (6)		1 647 (2)			$(NH_3^+)_d$
			1 619 (2)	1 596s	1 602 (2)	
1 560m	1 552 (3)	1 580s,br	1 575 (2)	1 550m	1 585 (2)	
		1 530vw		1 520s	1 530 (3)	
1 500ms						
		1 490w [c]		1 490m		$(NH_2)_r$
		1 480w [c]		1 480w		
		1 420vw [c]		1 420w	1 410 (1)	
			1 378 (2)			$(NH_3^+)_r$
			1 352 (2)			
1 285w		1 290vw	1 302 (4)			
			1 256 (4)	1 235mw		
		1 155w				
1 112vs		1 115w		1 120s		
				1 105w	1 105 (sh)	
1 060w		1 085mw		1 090s	1 083 (16)	
					1 035 (2)	
	1 040 (53)	1 050vw	1 057 (44)	990 (sh)	982 (sh)	$(NN)_s$
		970w [c]		975s	972 (38)	
		950w [c]				
965w						$\nu_2 + \nu_3$
	630 (100)		609 (100)		612 (sh)	ν_1
					608 (100)	
600 (sh)		580 (sh)		611s		ν_3
550vs,br		545vs		555vs,br		
525 (sh)						
	509 (2)					$(N_2H_6^{2+})_t$
	455 (2)					ν_2
315m		300m		293m		ν_4
				280m		
	298 (sh)		300 (39)		283 (95)	ν_5
	290 (38)		295 (sh)		275 (sh)	
	215 (5)		212 (7)		219 (7)	ν_6
			152 (8)		168 (4)	Lattice vibrations
	120 (3)				121 (10)	
	85 (3)		102 (18)		109 (8)	
	56 (20)					

[a] Intensities are given in parentheses. [b] d = Deformation, r = rocking, s = stretching, and t = torsion. Intensities: s = strong, m = medium, w = weak, br = broad, sh = shoulder, and v = very. [c] Bands due to decomposition of $[N_2H_6]_2[TiF_6]F_2$ (see text).

Figure 2. Hydrogen-bond i.r. spectra of (*a*) $[N_2H_5]_2[TiF_6]$, (*b*) $[N_2H_6][TiF_6]$, and (*c*) $[N_2H_6]_2[TiF_6]F_2$. Bands marked with an asterisk are due to decomposition products (see text)

observed in the spectra of the $[TiF_6]^{2-}$ ion.[4b] Of the two weak bands in $[N_2H_6][TiF_6]$ at 509 and 455 cm^{-1}, appearing in the likely region of this vibration, we assigned that at 455 cm^{-1} to ν_2. This is in accord with the observed combination band in the i.r. spectrum at 965 cm^{-1} $(\nu_2 + \nu_3)$.[4b]

The ν_6 mode, inactive in O_h symmetry (F_{2u}), is expected at *ca.* 200—210 cm^{-1} (calculated from ν_5) or lower if the angle interactions are not neglected.[5] It appears weakly in the Raman spectra of the three complexes at *ca.* 210—220 cm^{-1}. This is consistent with activity predicted by site symmetry in $[N_2H_6]_2[TiF_6]F_2$ [F_{2u} inactive in O_h and $2A + B$, active in Raman and i.r. in C_2 (C_2') site symmetry,[3] space group no. 56, D_{2h}^{10}] but not with the structure assumed for $[N_2H_6][TiF_6]$.[6] However, there is disagreement between the data (D_{3d}) and their interpretation (C_{3i}) concerning the distortion of the $[TiF_6]^{2-}$ octahedron in this structure.

Spectra of Hydrazinium Ions.—The assignments are given according to the literature [7] (Table). Partial decomposition of unstable $[N_2H_6]_2[TiF_6]F_2$ occurred during the preparation of i.r. mulls and some i.r. bands can be attributed to traces of decomposition products. These bands are mostly identical to the bands of $[N_2H_5]_2[TiF_6]$, which is the expected main decomposition product. The stretching vibration of the N–N bond in $[N_2H_6]^{2+}$, which is i.r. inactive and the strongest band in the Raman, appears as a very weak, sharp band in the i.r. spectrum of $[N_2H_6]_2[TiF_6]F_2$, indicating some slight influence of the site group (C_1 site symmetry,[3] A species, i.r. and Raman active). A weak Raman band at 509 cm^{-1}, mentioned in the discussion of ν_2 of the $[TiF_6]^{2-}$ ion, lies within the region reasonably expected for the inactive torsional vibration ν_4[7b,8] (C_1 site symmetry, A species, i.r. and Raman active).

Raman Spectra and the Decomposition of $[N_2H_6]_2[TiF_6]F_2$.—The complex $[N_2H_6]_2[TiF_6]F_2$ does not decompose in a rotating cell or if cooled in liquid nitrogen. However it will decompose with a laser beam focused on the sample in a capillary, irrespective of the laser wavelength. We surmise this decomposition to be caused primarily by the heat generated by the laser beam. The spectrum transforms with time into the spectrum of $[N_2H_5]_2[TiF_6]$. Significant changes happen only in the region of the N–N stretching vibration (Figure 1). The bands change their intensities, but are always well defined and sharp and do not shift. It may be concluded that well defined ions are continuously present. Obviously, $[TiF_6]^{2-}$ ions persist throughout and the $[N_2H_6]^{2+}$ ions transform consecutively into $[N_2H_5]^+$. A type (i) spectrum, thought to arise from strong hydrogen bonds,[9] with its A (2 650 cm^{-1}), B (2 400 cm^{-1}), and C (2 020 cm^{-1}) bands, is observed for $[N_2H_6]_2[TiF_6]F_2$ but not for the other two complexes (Figure 2). Hence, we consider the spectrum to arise from a strong hydrogen bond between $[N_2H_6]^{2+}$ and F^- and in view of the well defined ions throughout, suggest that the decomposition occurs by proton transfer between them, producing $[N_2H_5]^+$ and liberating HF [equation (1)]. The crystal

$$[N_2H_6]_2[TiF_6]F_2 \longrightarrow [N_2H_5]_2[TiF_6] + 2HF \qquad (1)$$

structure[3] of $[N_2H_6]_2[TiF_6]F_2$ consists of $[TiF_6]^{2-}$ layers sandwiched between composite layers in which each F^- ion is surrounded by four $[N_2H_6]^{2+}$ ions and *vice versa*. Escaping HF molecules should change the environment of neighbouring $[N_2H_6]^{2+}$ ions, and we see additional proof for the proposed mechanism in two transient bands of N–N stretching vibration (1 044 and 1 036 cm^{-1}) which gradually replace the declining band at 1 057 cm^{-1}, rise to a maximum and then disappear.

Acknowledgements

We are grateful to the late Professor J. Slivnik for initiating this work and for his constant interest and encouragement. The financial support of the Research Community of Slovenia is gratefully acknowledged.

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Received 28*th March* 1983; *Paper* 3/498