

SHORT COMMUNICATION

On the Synthesis of Ammonium Hexafluorovanadate (V)

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A series of hexafluorovanadates (V) of the type MVF_6 with the metal being Li, Na, K, Rb, Cs, Ag, Tl have been isolated and their structures determined [1,2,3,4]. Now we describe the isolation and some properties of ammonium hexafluorovanadate (V).

Ammonium hexafluorovanadate (V) was prepared by the reaction between hydrazinium (1+) fluorovanadate (III) and excess xenon difluoride in a nickel reaction vessel at room temperature. Hydrazinium (1+) fluorovanadate (III) was prepared as described elsewhere [5], and xenon difluoride was prepared by photosynthesis using a near U.V. lamp [6]. In a typical experiment, 3-6 mmoles of hydrazinium (1+) fluorovanadate (III) were weighed in the reaction vessel and thoroughly dried in a dynamic vacuum. An excess amount of xenon difluoride was sublimed onto the hydrazinium (1+) fluorovanadate (III) and allowed to react for a few days at room temperature.

The reaction proceeds in two different directions; that is, towards the formation of an adduct with xenon difluoride ($XeF_2 \cdot VF_5$) [7], or towards the formation of ammonium hexafluorovanadate (V). Low temperature and a nearly stoichiometric amount of xenon difluoride increase the yield of ammonium hexafluorovanadate (V). However, the final product is always contaminated to some extent by the other one, but this does not represent any problem because $XeF_2 \cdot VF_5$ has a vapour pressure of about 5 mm Hg at room temperature [7] while NH_4VF_6 is not volatile.

After the reaction between hydrazinium(1+) fluorovanadate(III) and excess xenon difluoride was complete, the volatiles were separately pumped off at -196°C (nitrogen), at -100°C (xenon), at -40°C (hydrogen fluoride) and at 20°C (excess xenon difluoride and $\text{XeF}_2 \cdot \text{VF}_5$) as shown by mass spectrometry and I.R. spectroscopy. The non volatile residue was found to be NH_4VF_6 by chemical analysis. Calcd. for NH_4VF_6 : NH_4 , 9.84%; V, 27.84%; F, 62.32%. Found: NH_4 , 9.2%; V, 27.2%; F, 61.3%. Ammonium hexafluorovanadate(V) is a white solid which is extremely sensitive to traces of moisture with which it reacts immediately, to form most probably oxofluorovanadates.

I.R. spectra were recorded using Perkin-Elmer 521 and Zeiss UR-20 spectrometers. Ammonium hexafluorovanadate(V) was finely powdered and dusted onto silver chloride plates sandwiched in a leak tight brass holder. Raman spectra were recorded using a Spex 1401 spectrometer. As exciting radiation the 5145 \AA line of a Coherent Radiation Ar^+ laser and the 6471 \AA line of a Coherent Radiation Kr^+ laser were used. A dry box which was dry enough to manipulate titanium tetrafluoride was not dry enough in the case of NH_4VF_6 , and slight decomposition of the compound took place. The bands which could be attributed to the resulting oxofluorovanadate ($\nu_{\text{V=O}} = 1030 \text{ cm}^{-1}$ and $\nu_{\text{V-F}} = 596 \text{ cm}^{-1}$) [8,9] were eliminated from the spectrum of NH_4VF_6 . The intensity of these two bands increased significantly when the I.R. cell was allowed to leak.

Vibrational spectrum of ammonium hexafluorovanadate(V) is presented in Table 1. Octahedral coordination of the VF_6^- anion is assumed and the spectrum accordingly assigned. The exclusion rule is strictly observed with ν_1 (a_{1g} , R active) and ν_2 (e_g , R active) sharp and symmetrical in shape and ν_3 (f_{1u} , I.R. active) and ν_5 (f_{2g} , R active) split.

The splittings may arise either from a deformed octahedron or because of the solid state effects. The only subgroups of the O_h group that allow such a pattern of intensities are D_{3d} or S_6 [10]. It is unlikely that the octahedron is deformed in such a way, and therefore a rather regular octahedron with the site symmetry responsible for the observed splitting of the degenerate ν_3 and ν_5 modes is proposed. These site symmetries appear only in cubic or hexagonal space groups [11] which is in accordance with the crystal symmetries usual with other fluorovanadates(V) [3,4]. ν_4 (I.R. active) was not observed, hence it

should be found below 320 cm^{-1} . The limit of the instrument is at 320 cm^{-1} with the identical AgCl windows placed in the reference beam. In O_h symmetry the inactive ν_6 mode should gain infrared activity with any of the proposed site symmetries. It should be expected below 240 cm^{-1} (calculated from ν_5 on the basis of MUBFF [12]) if the angle interaction constants are not neglected. Consequently, the weak and broad absorption in the infrared ranges $420\text{--}560\text{ cm}^{-1}$ and $1080\text{--}1350\text{ cm}^{-1}$ are assigned as combination and overtone bands, while absorptions in the infrared range $880\text{--}970\text{ cm}^{-1}$ are assigned as combination bands.

TABLE 1
Vibrational spectrum* of NH_4VF_6

I.R.	R		
3220 vs, br		ν_3] NH_4^+
	3198 (0.3)	ν_1	
3065 s, br		$\nu_2 + \nu_4$	
2830 s, br		$2\nu_4$	
1425 s		ν_4	
1350] 1080]		combination and overtone bands] VF_6^-
970] 880]		combination bands	
	660 (10)	ν_1, a_{1g}	
730 sh] 660 vs]		ν_3, f_{1u}	
	527 (1.2)	ν_2, e_g	
560] 420]		combination and overtone bands	
	339 (1.4)] 310 (0.5)]	ν_5, f_{2g}	

* Observed frequencies in cm^{-1} .

The evidence for hydrogen bonding is not conclusive. The ammonium ν_3 band is only slightly shifted to lower frequencies and ν_4 correspondingly to higher. But $2\nu_4$ and $\nu_2 + \nu_4$ appear with considerable intensity [13,14]. The evidence for rather regular VF_6^- octahedra also supports the suggestion of very weak, if any, hydrogen bonding.

The magnetic susceptibility was measured in a screw capped Kel-F container using Faraday method on a modified Newport Instrument magnetic balance. The sample was diamagnetic thus confirming that vanadium is in the 5+ valence state.

The systems $(\text{N}_2\text{H}_5)_3\text{CrF}_6 \cdot \text{XeF}_2$ and $(\text{N}_2\text{H}_5)_2\text{MnF}_4 \cdot \text{XeF}_2$, analogous with the vanadium case, were also studied. The obtained products were not homogeneous materials but were mixtures of the corresponding ammonium fluorometalate, metal fluoride and xenon fluorometalate (only in the case of manganese). The yield of ammonium fluorometalate is the largest at room temperature and with stoichiometric amount of xenon difluoride. The isolated compounds are the most probably NH_4MnF_5 and NH_4CrF_4 .

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