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SHORT COMMUNICATION

The Adduct $VF_5.SbF_5$

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Whereas NbF_5 and TaF_5 form solid adducts with SbF_5, which contain cis-bridged chains of octahedra, but strongly distorted for the transition metal, so that the coordination number is 4(+2) (distorted tetrahedron), [1,2], VF_5 was predicted to behave similarly [3], but by dissolving SbF_5 in an excess of VF_5 no reaction was observed and the starting materials were recovered unchanged by fractional distillation [4].

We succeeded in obtaining a solid white adduct $VF_5.SbF_5$ by two ways:

1) Small amounts were formed by fluorinating a 1 : 2 mixture of V and Sb with 85 atm F_2 at 25o°C in a Ni autoclave (reaction time 5o hours)
2) By condensing a slight excess (25 mmole) SbF_5 on 16 mmole VF_5 at -196°C; on heating the liquifying SbF_5 (Fp. +7°C) reacted with the still solid VF_5, which was dissolved. After some time the mixture solidified to a paste-like material, which on pumping off the excess of SbF_5 gave a dry white powder.

Elemental analysis showed the product to be the 1 : 1 adduct $VF_5.SbF_5$: V: 14% (found 13%), Sb: 33.6% (found 33.1%), F: 52.4% (found 56%).

The material was further characterized by its vibrational spectra. The Raman spectrum of the crystal powder was recorded on a Cary 82 instrument at -196°C, the infrared spectrum of the dry powder or of a halocarbon mull between AgCl windows at various temperatures on a Perkin-Elmer Model 325. The spectra obtained are depicted in Fig. 1.

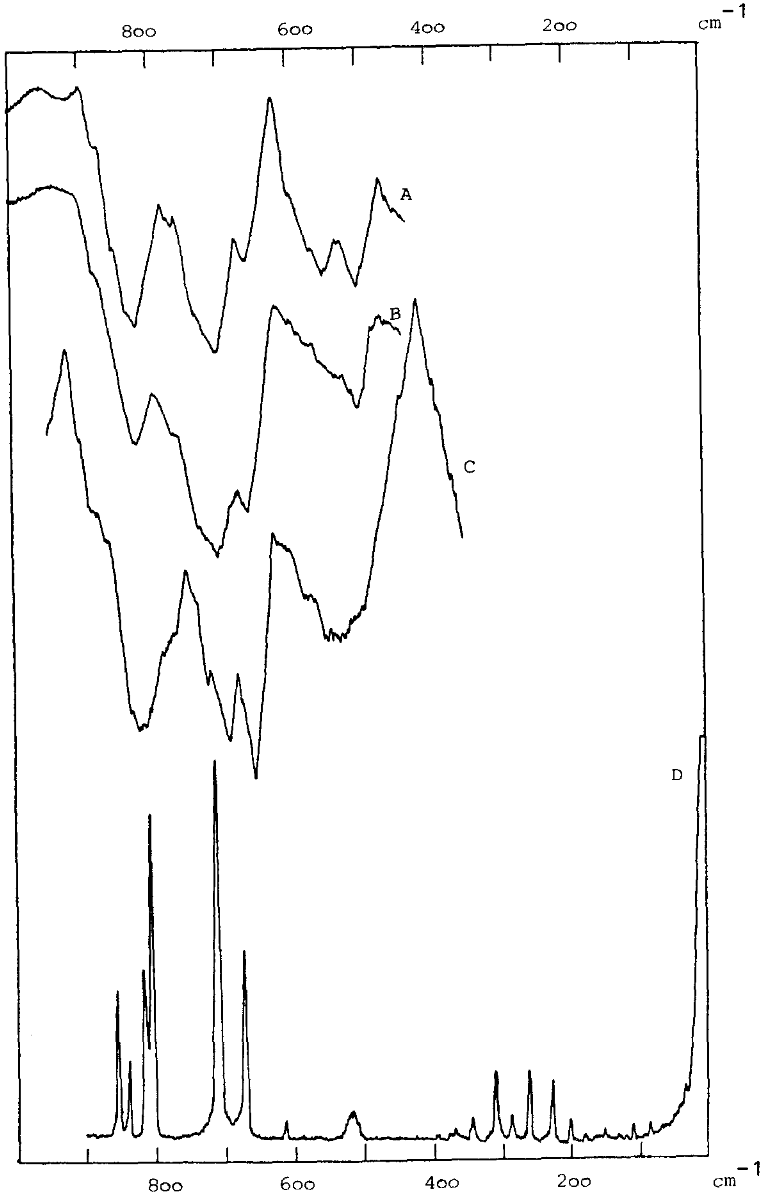

Fig.1. The vibrational spectra of VF_5SbF_5. Trace A-C: infrared spectra (A: dry powder at -196°C; B: dry powder at + 25°C; C: halocarbon mull at + 25°C); Trace D: Raman spectrum of dry powder at - 196°C.

TABLE 1

Vibrational spectra of $MF_5.nSbF_5$ adducts

$TaF_5.1.13\ SbF_5$ solid	$NbF_5.2.13\ SbF_5$ liquid	$VF_5.SbF_5$ solid		$CrF_5.2SbF_5$ [5] liquid		Assignment
RA [2]	RA [2]	RA	IR	RA	IR	
764 vs	770 s	852 m		835 m	830 s	ν_{MF}
		839 w				
743 wm	746 m	814 m	812 vs(b)	780 s	780 m	
		805 s				
713 m	711 s	712 s	715 w(sh)	710 s		ν_{SbF}
695 s	699 s		691 s		695 s	
668 s	678 m	673 m	670 m(sh)	665 m	665 s	
	667 s					
		621 vw		605 m		ν_{M-F-Sb}
532 w		517 vw	504 m		525 s(b)	
		342 vw				δ_{VF}
305 w		309 w				δ_{MF} and δ_{SbF}
279 sh		281 vw(b)			280 w	
272 s	273 w	261 w				
236 m	241 m	228 w				
197 w		198 vw				
182 w						
	153 w					
124 wm		107 vw				

Table 1 gives the frequency values, compared with those of $NbF_5.2SbF_5$ [2], $TaF_5.SbF_5$ [2] and $CrF_5.2\ SbF_5$ [5]. There is a close resemblence: the two highest frequencies (in the Raman spectrum of $VF_5.SbF_5$ split into two components each, for a MF_4 part of symmetry C_{2v} or lower, 4 frequencies are to be expected from the selection rules) belong to the MF stretching vibrations, those at ca. 71o, 695 and 67o cm^{-1} are SbF stretchings, the bands between 5oo and 54o cm^{-1} and probably 621 cm^{-1} for VF_5SbF_5 (6o5 cm^{-1} for $CrF_5.2SbF_5$) are due to vibrations within the M-F-Sb bridges and frequencies below 35o cm^{-1} belong to deformational modes, of which 342 cm^{-1} (only observed for $VF_5.SbF_5$) may be identified as a δ_{VF}.
The increase of the ν_{VF}, compared with VF_5 (gas: 6o8/719/784/81o cm^{-1} [6], solid: 676/687/751/788/833 cm^{-1} [7]) and VOF_3 (gas: 721/8o6 cm^{-1} [8], solid: 741 cm^{-1} [9]) indicates a considerable amount of positive charge on the V atom. Thus, one may formulate the compound as $VF_4^+\ SbF_6^-$ but with additional F-bridges from the anions to the cations, very much like (or even identical) to the structure found for $NbF_5.SbF_5$ [1].
Although $VF_5.SbF_5$ is strongly reactive against organic compounds, there is not such an oxidative power as it was observed for $CrF_5.2SbF_5$ [5].

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