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ON THE EXISTENCE OF A $\text{CrF}_4\text{O}\cdot\text{SbF}_5$ ADDUCT

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SUMMARY

CrF_4O is capable of forming a stable adduct with SbF_5 . Based on its low-temperature Raman spectrum, this adduct has a predominantly covalent, fluorine bridged structure, similar to that of $\text{MoF}_4\text{O}\cdot\text{SbF}_5$.

INTRODUCTION

In a recent paper the amphoteric nature of CrF_4O has been investigated. It was shown that CrF_4O is a very strong Lewis acid, but only a rather weak Lewis base and does not form a stable adduct with AsF_5 at temperatures as low as -78°C [1]. In view of the fact that the closely related MoF_4O , WF_4O and ReF_4O molecules can form stable 1:1 adducts with SbF_5 [2], it was interesting to study the interaction between CrF_4O and SbF_5 .

EXPERIMENTAL

Materials. Literature methods were used for the synthesis of CrF_4O [1] and the drying of the HF solvent [3]. SbF_5 (Ozark Mahoning) was distilled prior to its use.

Apparatus. Volatile materials were manipulated in stainless-steel vacuum lines equipped with Teflon-FEP U-traps, 316 stainless steel bellows-seal or Teflon-PFA (Fluoroware, Inc.) valves, and a Heise Bourdon tube-type pressure gauge [4]. The vacuum lines and other hardware employed were passivated with ClF_3 and HF. Nonvolatile or low volatility materials were handled in the dry nitrogen atmosphere of a glove-box. Raman spectra were recorded on a Spex Model 1403 spectrophotometer using the 647.1-nm exciting line of a Kr ion laser. The sample was contained in a sealed 1 mm o.d. quartz capillary, and the spectra were recorded at -140°C using a previously described device [5].

Reaction of CrF_4O with SbF_5 . A passivated 0.5" o.d. Teflon-FEP U-tube, closed by two valves, was loaded in the dry-box with SbF_5 (0.89 mmol). The U-tube was connected to the vacuum line and HF (1.08g) and CrF_4O (0.31 mmol) were condensed in at -196°C . The contents of the tube were warmed to room temperature resulting in a light red solution. All material volatile at room temperature was pumped off and passed through a -78° and a -196°C trap. Nothing was trapped at -78°C , but the -196°C trap contained the HF solvent. The residue was a dark red-brown liquid which upon heating to 55°C for 15 hr in a dynamic vacuum condensed on the colder parts of the tube. The volatile material trapped at -78°C was white and consisted of SbF_5 . The condensate (143 mg) consisted of dark red droplets and crystals. The appearance of some liquid material can be accounted for by the fact that, based on the material balance, the condensate still contained 31 mg (0.14 mmol) of SbF_5 in excess over that required for the 1:1 adduct $\text{CrF}_4\text{O}\cdot\text{SbF}_5$. The crystals were characterized by low-temperature Raman spectroscopy but were not suitable for a crystal structure determination because of twinning or disorder.

RESULTS AND DISCUSSION

CrF_4O , when combined with an excess of SbF_5 in anhydrous HF solution, forms after removal of the solvent a dark brown-red liquid adduct. In a dynamic vacuum at 55°C , most of the excess SbF_5 can be pumped off. As the $\text{CrF}_4\text{O}\cdot\text{SbF}_5$ mol ratio approaches 1:1, dark red crystals are obtained which are stable at 55°C . Attempts to determine their structure by single crystal x-ray diffraction techniques failed because of twinning or disorder. However, their low-temperature Raman spectrum (see Fig.1) indicates that their structure closely resembles those of the mainly covalent $\text{MoF}_4\text{O}\cdot\text{SbF}_5$ and $\text{WF}_4\text{O}\cdot\text{SbF}_5$ adducts [2], (see Table 1). The minor differences

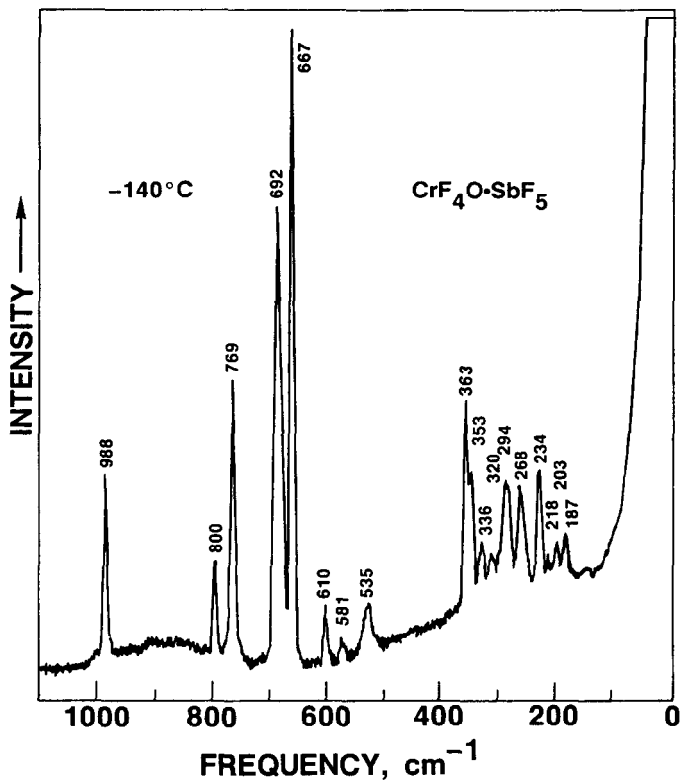


Fig. 1. The Raman Spectrum of $\text{CrF}_4\text{O}\cdot\text{SbF}_5$ at -140° .

TABLE 1.
Raman Spectrum of $\text{CrF}_4\text{O}\cdot\text{SbF}_5$ Compared to Those of $\text{MoF}_4\text{O}\cdot\text{SbF}_5$,
 $\text{WF}_4\text{O}\cdot\text{SbF}_5$ and Their Parent Molecules. Observed frequencies (cm^{-1}) and relative intensities

$\text{WF}_4\text{O}\cdot\text{SbF}_5$ [2]	$\text{MoF}_4\text{O}\cdot\text{SbF}_5$ [2]	$\text{CrF}_4\text{O}\cdot\text{SbF}_5$	WF_4O [2]	MoF_4O [2]	CrF_4O [1]	SbF_5 [2]
1061 vs	1047 s	988 (3)	1058 vs	1042 s	999 m	
758 mw	766 mw	{ 800 (1.5) 769 (4.4)	744 m	740 m	789 mw	
710 s	704 m	692 (7.1)	728 w	721 mw	{ 718 sh 704 m	718 s
670 s	675 s	667 (10)	687 vw	688 s	{ 692 m 666 mw 650 vs	670 vs
556 vw	621 w	610 (0.9)	669 vw, sh			
	578 w	581 (0.3)	663 mw			
		535 (0.9)	563 m	571 w		
			532 vw	529 w	528 w	
			523 w	506 vw	517 vwv	
			388 w		377 w	
			367 vw		350 mw	
334 w	338 w	336 (0.7)	330 mw	333 m		349 vw
		320 (0.3)	318 m, sh			
312 w	314 w	294 (1.5)	314 s	309 ms	293 w	
279 w		268 (1.5)	265 w	275 w	273 w	268 m
242 vw	233 w	234 (1.6)	242 mw	222 mw		231 mw
		218 (0.2)	215 mw			
		203 (0.4)	151 mw			
133 vw		187 (0.6)	135 w		188 vw	189 mw

in the observed spectra can be attributed to (1) the low temperature at which the $\text{CrF}_4\text{O}\cdot\text{SbF}_5$ spectrum was recorded which may cause some additional splittings, (ii) the mass and force constant differences between Cr, Mo, and W, and (iii) the increasing ionicity of the metal-F bonds from Cr to W which causes the relative Raman intensity of the metal oxygen vibrations to increase with respect to those of the metal-fluorine vibrations. Thus, the above results show that CrF_4O is also capable of forming a stable adduct with SbF_5 and that the resulting adduct has a mainly covalent, fluorine bridged structure similar to that of $\text{MoF}_4\text{O}\cdot\text{SbF}_5$ [2].

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