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PREPARATION, CHARACTERIZATION AND ACCEPTOR PROPERTIES OF TRIS(FLUOROSULPHATO)VANADIUM(III)

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SUMMARY

Tris(fluorosulphato)vanadium(III) has been synthesised by interacting vanadium(III) chloride and fluorosulphuric acid. Its complexes with pyridine, ethylenediamine and triphenylphosphine oxide have also been isolated. In all these complexes, the infrared spectra suggest the lower symmetry of fluorosulphate groups and the magnetic moment values are in close proximity for a d^2 system. The reflectance spectra reveal the hexacoordination around vanadium(III). Thermal analysis corresponds to four steps decomposition for tris(fluorosulphato)vanadium(III).

INTRODUCTION

There have been a number of reports recently on the preparation and characterization of metal fluorosulphates, including binary metal mono- (1,2), bis-(3-7), tris- (3,8,9) and tetrakis-(9,10) fluorosulphates, chloro- and organotin fluorosulphates (10-13) oxyfluorosulphates (14-16) and their complexes with methyl cyanide (17) and pyridine (18). In most instances, infrared spectra have been recorded and evidence regarding structure and bonding has been deduced from the number and energies of observed anion vibrations. Fluorosulphates of oxovanadium(IV) and (V) are also known (19,20). We are now reporting the preparation and the characterization of a hitherto unknown compound, tris(fluorosulphato)vanadium(III), $V(SO_3F)_3$ and its coordination complexes with a few nitrogen and oxygen donors.

RESULTS AND DISCUSSION

The direct reaction between vanadium(III)chloride and fluorosulphuric acid does not yield a pure product. However, in the presence of potassium chloride, a pure product has been obtained. It appears that $V(SO_3F)_3$ formed provides a sort of protective layer around vanadium(III)chloride and stops further reaction. Potassium chloride forms potassium fluorosulphate with fluorosulphuric acid which probably prevents the formation of such a protective coating. Similar observations have been reported in the preparation of iron(III)fluorosulphate (3). Like other metal fluorosulphates, tris(fluorosulphato)vanadium(III) is also insoluble in usual organic solvents.

Infrared Spectra

The salient features of the infrared spectra of tris(fluorosulphato)vanadium(III) and its complexes with various ligands are given in Table I. An isolated fluorosulphate anion has C_{3v} symmetry. When it acts as a mono- or bidentate group, the symmetry is lowered to C_s and the degeneracy of the doubly degenerate E modes, i.e., ν_4, ν_5, and ν_6, is lifted. These vibrations in $V(SO_3F)_3$ show splitting (Table I), indicating a lower symmetry and the covalent character of the fluorosulphate groups. A decision, whether a mono- or a bidentate fluorosulphate

TABLE I

Infrared spectra of tris(fluorosulphato)vanadium(III) and its adducts with ligands.

$V(SO_3F)_3$	$V(SO_3F)_3.2py$	$V(SO_3F)_3.en$	$V(SO_3F)_3.2ph_3PO$	Assignments
1380 1230	1375 1265	1370 1290	1375 1265	$\nu_4(E)$
1090	1170	1180	1150	$\nu_1(A_1)$
865	855	880	785	$\nu_2(A_1)$
630 579	675 590	680 555	695 530	$\nu_5(E)$
555	550	550	550	$\nu_3(A_1)$
425 310	- -	425 360	420 385	$\nu_6(E)$
-	480	475	-	ν V-N
	1605 624 425	-	-	pyridine ring vibrations
-	-	3435	-	ν N-H
-	-	1620	-	N-H bend
-	-	1225	-	ν C-N
-	-	-	1110	ν P=O
-	-	-	1460	ν P-C

group is present, can be made on the basis of the position of the three sulphur-oxygen stretching modes. When the fluorosulphate groups act as bidentate ligands, the two higher νS-O are found around 1355-1380 and 1130-1180, while the third νS-O is observed at 1080 cm^{-1} (8). The appearance of these bands at 1380, 1230 and 1090 cm^{-1} indicates the bidentate nature of the fluorosulphate groups in tris(fluorosulphato)vanadium(III), where vanadium acquires a hexacoordination.

In case of bis(pyridine)tris(fluorosulphato)vanadium(III), ethylenediaminetris(fluorosulphato)vanadium(III) and bis(triphenylphosphine oxide)tris(fluorosulphato)vanadium(III), the symmetry of the fluorosulphate groups is lower than C_{3v}, as their spectra show splitting of the doubly degenerate E modes. The positions of the various sulphur-oxygen stretching modes in the above complexes (Table I) suggest that the fluorosulphate groups are in different environments; one is a bidentate, while the other two are monodentate groups, thereby retaining the hexacoordination of vanadium(III) in these complexes.

In liquid pyridine, an out-of-plane ring deformation occurs at 403, while the in-plane ring deformations occur at 601 and 1578 cm^{-1} respectively. The upward shift of these vibrations are usually diagnostic of pyridine coordination to metals (21). As expected, these three bands show significant shift to higher frequencies, indicating the coordination of pyridine to vanadium. In ethylenediamine the prominent absorption bands occur at 3505 (ν N-H), 1655 (N-H bend) and 1225 cm^{-1} (ν C-N). In $V(SO_3F)_3$.en these bands occur respectively at 3435, 1620 and 1225 cm^{-1}. The considerable lowering of the ν N-H shows coordination of ethylenediamine to vanadium. The ν V-N can be of particular interest because the position of these bands can provide valuable information about the nature of coordination. The ν V-N in the adducts of $VOCl_2$, $VO(SO_3X)_2$, where X=F or Cl and $VO(O_2CR)_2$, where R = CH_3-, CH_2Cl-, $CHCl_2$- or CCl_3, with nitrogen donors, have been observed in the range 410-486 cm^{-1} depending on the environments of vanadium-nitrogen bonds (19,22). In the complexes, $V(SO_3F)_3.2py$ and $V(SO_3F)_3.en$, the presence of the bands at 480 and 475 cm^{-1} respectively may be assigned to ν V-N.

In pure triphenylphosphine oxide, the ν P=O and νP-C are at 1190 and 1440 cm^{-1} respectively (23,24). In bis(triphenylphosphine oxide)tris(fluorosulphato)vanadium(III), the ν P=O shifts to lower region at 1110 cm^{-1}, which indicates that triphenylphosphine oxide has coordinated to vanadium through oxygen atom.

Magnetic Properties : Magnetic moment values at room temperature: $V(SO_3F)_3$; 2.80, $V(SO_3F)_3.2py$; 2.73, $V(SO_3F)_3.en$; 2.80 and $V(SO_3F)_3.2(C_6H_5)_3PO$; 2.82 BM, lie in the range close to spin only values for a d^2 system. These values also suggest the absence of antiferromagnetic interaction in these complexes in the solid state.

Electronic Spectra : For the six coordinated vanadium(III) complexes two main adsorption bands are generally observed in the range 15-18 kK ($^3T_{2g} \longleftarrow {}^3T_{1g}$) and 24-26 kK ($^3T_{1g}(P) \longleftarrow {}^3T_{1g}$). The third spin allowed transition ($^3A_{2g} \longleftarrow {}^3T_{1g}$) is mostly not observed (25). These two significant transitions occur at 16.0 and 25.0 kK in $V(SO_3F)_3$, at 16.2 and 25.3 kK in $V(SO_3F)_3.2py$, at 16.3 and 25.3 kK in $V(SO_3F)_3.en$ and at 15.8 and 24.8 kK in $V(SO_3F)_3.2(C_6H_5)_3PO$ respectively. These observations support the hexacoordination of vanadium in these complexes.

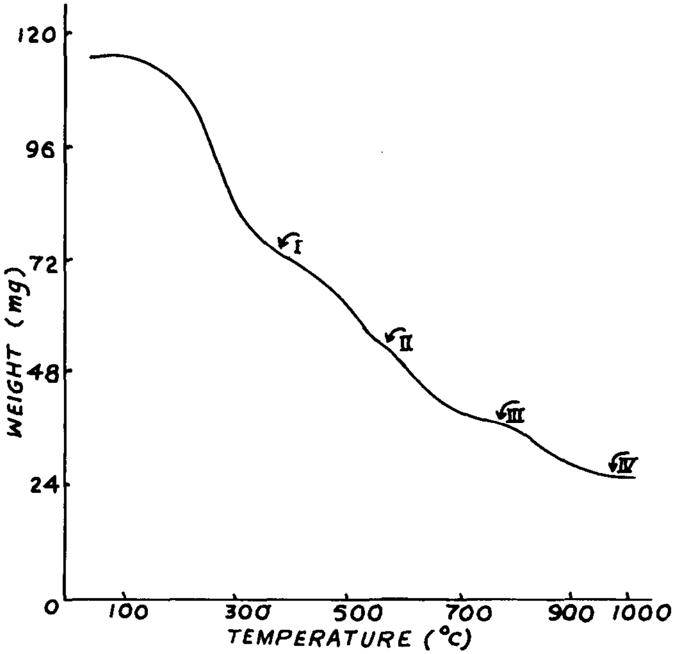

Figure 1: Thermal Decomposition of $V(SO_3F)_3$, DTG minima (not shown here) have been projected on TG curve to get various inflexion points.

<u>Thermal Analysis</u> : The TG and the DTG curves recorded in the presence of air show (figure 1) the thermal decomposition of tris(fluorosulphato)vanadium(III) as a process consisting of the following steps. The TG curve indicates that before actual decomposition sets in, there is a small gain in weight, which may be due to uptake of some moisture by the compound. The decomposition of $V(SO_3F)_3$ starts at 140°. The weight loss upto 380° corresponds to the formation of $V_2(SO_4)_3.SO_3$. The gaseous products of decomposition may be oxyfluorides of sulphur, e.g., SO_2F_2 and SO_4F. The evolution of sulphuryl fluoride has been confirmed by the IR spectrum of the gaseous products obtained

on heating $V(SO_3F)_3$ in an evacuated tube upto 380° in a separate experiment. Its IR spectrum had the peaks which could be attributed to the presence of sulphuryl fluoride. Above 380°, SO_3 is lost; the loss of SO_3 is complete at 540°, leaving behind $V_2(SO_4)_3$. Between 540-730°, $V_2(SO_4)_3$ decomposes. The loss in weight may be attributed to the following mode of decomposition :

$$2V_2(SO_4)_3 \longrightarrow V_2O_4 + 2VOSO_4 + 2SO_2 + 2SO_3$$

Finally, the end product obtained corresponds to vanadium(V) oxide, V_2O_5.

EXPERIMENTAL

Materials : Vanadium(III) chloride was prepared by refluxing vanadium(V) oxide with sulphur monochloride (26). Fluorosulphuric acid was prepared and purified as described earlier (19). Pyridine and ethylenediamine were purified by distilling these over potassium hydroxide. Triphenylphosphine oxide (E. Merck) was used as such. Solvents were purified and distilled before use.

Preparation of $V(SO_3F)_3$: Excess of fluorosulphuric acid was added to the equimolar mixture of vanadium(III)chloride and potassium chloride. The reaction mixture was refluxed till there was no more evolution of HCl gas. The solid product isolated was filtered in an atmosphere of dry nitrogen, washed with fluorosulphuric acid, followed by sulphuryl chloride and finally dried under high vacuum. The product was tested for the absence of potassium and chloride ions.

TABLE II

Analytical data of tris(fluorosulphato)vanadium(III) and its adducts with nitrogen and oxygen donors

COMPOUND	Found %						Required %					
	V	S	F	C	H	N	V	S	F	C	H	N
$V(SO_3F)_3$	14.18	26.93	17.12	-	-	-	14.65	27.59	16.38	-	-	-
$V(SO_3F)_3.2py$	9.20	18.80	12.10	24.12	2.14	6.01	10.08	18.97	11.27	23.71	1.97	5.53
$V(SO_3F)_3.en$	12.65	22.98	12.90	6.10	1.74	6.64	12.50	23.52	13.97	5.88	1.96	6.86
$V(SO_3F)_3.2ph_3PO$	6.12	11.12	7.12	48.36	3.91	-	5.64	10.62	6.30	47.78	3.32	-

Preparation of Complexes : The complexes of tris(fluorosulphato) vanadium(III) with pyridine or ethylenediamine were prepared by adding pyridine or ethylenediamine dropwise (1:3 molar ratio) to the suspension of $V(SO_3F)_3$ in dichloromethane, while stirring. The contents were stirred for another two hours, filtered, washed with dichloromethane and finally dried in vacuo. In case of triphenylphosphine oxide, benzene was used as the reaction medium, while the rest of the procedure is the same. The analytical data are given in Table II.

Physical Measurements : The infrared spectra of the compounds were recorded as Nujol and hexachlorobutadiene mulls in silver chloride and polythene plates, using Perkin Elmer 621 spectrophotometer. Magnetic measurements were carried out at room temperature on a Gouy's balance calibrated with $Hg[Co(NCS)_4]$ Reflectance spectra were recorded at Indian Institute of Technology, Delhi. Thermal analysis was carried out by means of an MOM Budapest Derivatograph (type: Paulik, Paulik and Erdey) at a heating rate of 5°/minute and covering a temperature range between 20-1000°C.

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