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STUDIES ON OXOPENTAFLUOROVANADATES(IV)

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SUMMARY

A large number of new salts of the ion $[VOF_5]^{3-}$ have been obtained by crystallising a solution of vanadyl sulphate containing the respective cations as their fluorides. The cations are Rb^+, $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$ and protonated bases, viz., guanidine, 1,2-diamino benzene, ethylene diamine and hydrazine. The molecular conductances of the rubidium salt indicate the presence of uni-trivalent electrolyte. The magnetic moments of the salts are almost equal to the spin-only value. The i.r. spectra of the salts give strong absorption bands between 910 to 965 cm^{-1} showing the presence of terminal V=O group. The $[VOF_5]^{3-}$ ion breaks up completely on passing a salt solution through a column of cation exchange resin.

INTRODUCTION

In course of our work on the oxofluorovanadates(IV) [1,2], it was observed that only ammonium, potassium and mixed alkali metal salts of $[VOF_5]^{3-}$ are reported in the old literature [3]. Physico-chemical properties of the salts have attracted attention in recent years [4-7]. The detailed methods of preparation of the salts are lacking. The low solubility of many fluorides and vanadates of inorganic ions often makes the crystallisation of fluorovanadates difficult from aqueous solution. The availability of many organic base fluorides soluble in water or in aqueous hydrofluoric acid leads to the possibility of preparing a large number of oxofluorovanadates from aqueous medium. In the present communication we report the preparation and characterisation of a few salts of $[VOF_5]^{3-}$ with various protonated nitrogeneous bases as cations. The corresponding salts with Rb^+, $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ have also been prepared.

EXPERIMENTAL

All the chemicals used were either E.Merck's G.R. or B.D.H. Analar quality. Vanadyl sulphate trihydrate was prepared by standard method [4]. $N_2H_6F_2$ was prepared by adding excess hydrofluoric acid (40 %) to a solution of hydrazine hydrate (99 %) when white crystals of $N_2H_6F_2$ appeared. Ethylene diamine difluoride was prepared by adding excess hydrofluoric acid (40 %) to a solution of ethylenediamine and then concentrating the solution in a desiccator over sulphuric acid and caustic soda when white crystals separated out. Hexamminecobalt(III) chloride and tris(ethylene diamine)cobalt(III) chloride were prepared by methods given in literature [8]. The methods of analysis of vanadium, fluorine, carbon, hydrogen and nitrogen, the measurement of conductance, magnetic moments and the recording of i.r. spectra were described previously [1]. The method of analysis of rubidium was the same as described earlièr for potassium [9].

For ion exchange studies Dowex 50(Dowex 50W-X8, analytical reagent grade of J.T.Baker Chemical Co. Phillipsberg) was packed in a polythene tube of diameter 1.5 cm and length 60 cm having an external glass tube jacket fitted with a polythene stop cock. The resin was transformed either to acid form or to sodium form by passing repeatedly a dilute solution of either HCl or NaCl respectively and finally washing with double distilled water till free from chloride.

Preparation of the salts

$Rb_3[VOF_5]$. 2.4 g RbF in 1.2 ml HF (40 %) wad added to a saturated aqeous solution of $VOSO_4.3H_2O$ (1 g). The yield was 0.8 g.

$[C_6H_9N_2]_3[VOF_5]$. This was obtained by adding a solution of 2.5 g 1,2-diamino benzene in 2.3 ml HF (40 %) to an aqueous solution of $VOSO_4.3H_2O$ (1 g). The yield was 0.8 g.

$[CH_6N_3]_3[VOF_5]$. This was obtained as above by taking 4.2 g guanidine carbonate instead of 1,2-diamino benzene. The yield was 0.8 g.

$[C_2H_{10}N_2]_3[VOF_5]_2$. A saturated aqueous solution of 2.0 g ethylene diamine difluoride was added to a saturated aqueous solution of $VOSO_4 \cdot 3H_2O$ (1 g). The yield was 0.7 g.

$[Co(NH_3)_6][VOF_5]$. This was obtained on mixing 1.0 g $VOSO_4 \cdot 3H_2O$ in 40 % HF (2.3 ml) and 2.5 g $[Co(NH_3)_6]Cl_3$ in saturated aqueous solution. The yield was 0.4 g.

$[Co(en)_3](VOF_5)$. The method of preparation was the same as above except that $[Co(NH_3)_6]Cl_3$ was replaced by $[Co(en)_3]Cl_3$ (3.2 g). The yield was 0.4 g.

In all these cases the compounds precipitated out immediately on mixing.

$(N_2H_6)_3[VOF_5]_2$. This was obtained on concentrating at room temperature a mixture of an aqueous solution of 1.7 g $N_2H_6F_2$ and an aqueous solution of $VOSO_4 \cdot 3H_2O$ (1 g). The yield was 0.4 g.

All the salts were separated by filtration and dried by pressing between filter papers. Then they were kept in a desiccator over sulphuric acid and caustic soda.

RESULTS AND DISCUSSIONS

All the salts are stable in air and are blue in colour except the salts with $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ which are yellowish green. They are soluble in water and in dilute hydrofluoric acid. Rb^+, $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$ salts are insoluble in common organic solvents like ethanol and acetone while the other salts are soluble in ethanol. The molecular conductance of freshly prepared aqueous solution (1×10^{-3} M) of the rubidium salt is 390 $ohm^{-1} mole^{-1} cm^2$ at 32°C which is in agreement with that expected for an 1:3 electrolyte. The effective magnetic moments of all the salts (Table 1) correspond with the spin-only value for a single electron.

The i.r. spectra of the salts with rubidium, ethylene diamine, guanidine and $[Co(NH_3)_6]^{3+}$ show very strong terminal V=O bands between 910 and 965 cm^{-1} (Table 2). The bands between

TABLE 1

Analytica data* and magnetic moments of the compounds at 35°C

Compounds	%V	%F	%N	%C	%H	μ_{eff}, BM
$Rb_3[VOF_5]$	12.1 (12.2)	22.8 (22.7)	62.0^a (61.3)^a			1.74
$(enH_2)_3[VOF_5]_2$	20.1 (20.0)	37.6 (37.7)	16.9 (16.7)	14.2 (14.1)	6.0 (5.9)	1.78**
$(N_2H_6)_3[VOF_5]_2$	23.8 (23.9)	45.0 (44.6)	20.0 (19.8)			1.77**
$(guanH)_3[VOF_5]$	14.9 (14.9)	27.8 (27.8)	37.1 (36.8)	10.4 (10.5)	2.8 (2.6)	1.76
$(LH)_3[VOF_5]$	10.7 (10.6)	19.8 (19.7)	17.3 (17.1)	44.5 (44.2)	5.4 (5.5)	1.78
$[Co(NH_3)_6][VOF_5]$	15.9 (15.8)	29.4 (29.4)	26.2 (26.0)			1.80
$[Co(en)_3][VOF_5]$	12.9 (12.7)	23.8 (23.7)	21.0 (20.9)			1.79

*vlues in the parenthesis are the calculated ones.
**calculated on the basis of one vanadium atom.
a=percent rubidium.
Abbreviations: en = ethylene diamine; guan = guanidine;
L = 1,2-diamino benzene.

TABLE 2

Infrared spectral bands of the compounds in nujol

Compounds	Band positions (ν, cm^{-1})
$Rb_3[VOF_5]$	1170m b, 965vs, 945s, 730m, 600m, 500s b, 510vs, 415m.
$(guanH)_3[VOF_5]$	3420vs b, 1655vs b, 1110s, 910vs, 745s, 620s b, 490m, 445s.
$(enH_2)_3[VOF_5]_2$	3450s b, 3200s b, 2000w, 1655m b, 1610s, 1520s b, 1360m, 1325m, 1085s, 1035s, 1010s, 940vs, 920sh, 790m, 740m b, 640m b, 590m b, 500vs.
$[Co(NH_3)_6][VOF_5]$	3310s b, 2720w b, 2610w b, 1600w, 1340s, 910s, 890m b, 810w, 475s.

730 and 400 cm^{-1} in the spectrum of the rubidium salt may be assigned as ν(V-F) bands. The assignment of these bands in the spectra of the other salts is difficult due to the strong absorption of the cations in this region.

On passing dilute silutions (about 5x10^{-3} M) of the potassium and rubidium salts through a column of cation exchange resin (hydrogen or sodium form) it was found that the ion $[VOF_5]^{3-}$ breaks up completely. The effluent contained all fluoride but no vanadium. The vanadium was kept adsorbed on the top of the column as $VO_2 \cdot xH_2O$, which could be finally eluted out completely with dilute HCl. The decomposition of the complex ion probably takes place as follows:

$$\text{A)}\quad M_3[VOF_5] \xrightarrow[\text{of resin}]{H^+\text{ form}} H_3[VOF_5] \quad (M = K \text{ or } Rb)$$

$$H_3[VOF_5] + H_2O \longrightarrow VO_2 + 5HF$$

$$\text{B)}\quad M_3[VOF_5] \xrightarrow[\text{of resin}]{Na^+\text{ form}} Na_3[VOF_5]$$

$$Na_3[VOF_5] + H_2O \longrightarrow VO_2 + 3NaF + 2HF$$

$$2HF \xrightarrow[\text{of resin}]{Na^+\text{ form}} 2NaF$$

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