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SHORT COMMUNICATION

# Studies on Oxohydroxofluorovanadates(IV)

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In continuation of our work on the oxofluorovanadates(IV) [1], we report here the isolation and characterisation of two salts of a new type, $(LH)_2\left[VO(OH)F_3\right]$, where L = pyridine and 2-picoline. These were prepared by using the same method [1] as was used for the preparation of the salts of the type $LH\left[VOF_3(H_2O)\right]$, except that a smaller amount of hydrofluoric acid (relative to the base) was used for the preparation of the $(LH)_2\left[VO(OH)F_3\right]$ type of salts. It appears that $\left[VO(OH)F_3\right]^{2-}$ which is initially formed on the addition of small amount of hydrofluoric acid to $VOSO_4$, is changed to $\left[VOF_3(H_2O)\right]^-$ on further addition of the acid.

$$\left[VO(OH)F_3\right]^{2-} + H^+ \longrightarrow \left[VOF_3(H_2O)\right]^-$$

Both the salts are stable when dry. They are blue crystalline substances and highly soluble in water. They are also soluble in dilute hydrofluoric acid but insoluble in common organic solvents. The molecular conductances in very dilute aqueous solutions of the salts indicate that the complex ion decomposes appreciably in dilute solution. The magnetic moments (Table 1) of the salts agree with the spin-only value for a single d electron.

The i.r. spectra (Table 1) of both the salts give a strong and broad band around 3300 $cm^{-1}$, which may be assigned as $\nu$(O-H). The presence or absence of water in the salts cannot be concluded from the spectra, since the cations give strong absorptions at about 1600 $cm^{-1}$. Both the spectra display strong terminal V=O band at 965 $cm^{-1}$. The other bands in the spectra from 1600 to 750 $cm^{-1}$ are due to the cations [2, 3]. It is difficult to

assign $\nu$(V-F) bands, since the spectra of the cations also give several bands [2, 3] between 750 to 400 $cm^{-1}$.

The TGA curves of the salts show that they begin to decompose above the room temperature and the decomposition takes place in one step without the formation of any stable intermediate compound and finally vanadium pentoxide is formed around 400°C.

TABLE 1

Magnetic moments and infrared spectral bands* of the complexes

| Compound | $\mu_{eff}$ BM at 33°C | $\nu$(O-H) | $\nu$(V=O) | Other bands |
|---|---|---|---|---|
| $(pyH)_2[VO(OH)F_3]$ | 1.73 | 3300s (very broad) | 965s | 1610s, 1530vw, 1240vw, 1220s, 1155w, 1075m, 1050m, 1010w, 945sh, 880w, 760s, 685s, 640w, 500s b. |
| $(2\text{-picH})_2[VO(OH)F_3]$ | 1.72 | 3300s (very broad) | 965s | 1640sh, 1615s, 1500sh, 1235m, 1210m, 1065w b, 1030m, 870w, 810s, 720s, 550sh, 500s. |

Abbreviation : py = pyridine; pic = picoline.
*in nujol; $\nu$ in $cm^{-1}$

EXPERIMENTAL

All the chemicals used were either E. Merck's G.R. or B.D.H. Analar quality. Pyridine and 2-picoline were distilled before use. Vanadyl sulphate trihydrate was prepared by standard method [4].

The methods of elemental analysis, the measurements of conductance, magnetic moments and the recording of TGA curves and i.r. spectra were previously described [1].

$(pyH)_2[VO(OH)F_3]$ was prepared by the addition of a saturated aqueous solution of $VOSO_4.3H_2O$(1g) to a solution containing 1.9 ml pyridine and 1.3 ml hydrofluoric acid (40%). Blue crystalline compound appeared on stirring

the mixture for a few minutes. The yield was 0.6 g. Analysis : Found: V, 17.0; F, 18.9; N, 9.2; C, 40.2; H, 4.5%. $C_{10}H_{13}N_2VO_2F_3$ requires V, 16.9; F, 18.9; N, 9.3; C, 39.9; H, 4.3%.

$(2\text{-picH})_2\left[VO(OH)F_3\right]$ was prepared by the same method as that used for the pyridine salt, replacing pyridine by 2-picoline (2.3 ml). In this case also blue crystalline compound appeared on stirring the mixture. The yield was 0.6 g. Analysis: Found: V, 15.7; F, 17.3; N, 8.4; C, 44.2; H, 5.5%. $C_{12}H_{17}N_2VO_2F_3$ requires V, 15.5; F, 17.3; N, 8.5; C, 43.8; H, 5.2%.

The salts were dried by pressing between filter papers and then keeping in a desiccator over sulphuric acid and caustic soda till constant weight. No pure compound could be isolated by the above method with bases like 2,6-lutidine, 2,2'-bipyridyl and 1,10-phenanthroline.

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