The trend observed in $T\Delta S^{\ddagger}$ versus σ curve can be explained by considering the solvation of the activated complex. The activated complex is more polar in the case of 2-ethylfluorene resulting in a large decrease in entropy. The electron withdrawing substituents render the molecule a dipole resulting in the solvation of the ground state. Thus, a smaller change in $\Delta S^{\ddagger}$ is effected.

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Oxopentafluoroniobates(V)

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The oxopentafluoroniobates (V) of the type $[(CH_3)_4N][HNbOF_5]$ and $[M(py)_4][NbOF_5]$, where M = Cu, Ni, Zn, Cd, Co and py = pyridine, have been prepared. The IR spectra and TGA data for the above compounds are reported.

A LARGE number of oxopentafluoroniobates[1,2] are known. In the present paper several new oxopentafluoroniobates of $(CH_3)_4N^+$ and $[M(py)_4]^{2+}$, where M=Cu, Ni, Zn, Cd, Co, and py=pyridine, are reported. The compounds are studied through thermogravimetry and infrared spectroscopy.

Niobium pentoxide (purity about 99·9%) obtained from the BARC was utilized in the present work. Methods for determining Nb, F and N in the compounds were as before[3]. For estimating niobium in the fluoroniobates containing Ni^{2+}, Cu^{2+} or Co^{2+} ion the sample was fumed with H_2SO_4, diluted and tartaric acid added. From the solution Ni^{2+}, Cu^{2+} or Co^{2+} were precipitated by standard methods and estimated, whilst from the filtrate niobium was precipitated as its cupferronate and estimated as Nb_2O_5. The presence of Zn and Cd along with Nb does not interfere in the precipitation of niobium as its cupferronate from the acidic oxalate solution. For determining fluorine as PbClF it was separated from Nb and the other metals by fusing the samples with K_2CO_3 and extracting with water.

Preparation of oxopentafluoroniobates — Tetramethylammonium compound was prepared as follows: $Nb\ O_5$ (2 g) was dissolved in minimum volume of HF (40%) and to it $[(CH_3)_4N]OH$ (1·4 g) acidified with HF (10%) was added. The mixture was evaporated on a water-bath to crystallization. The colourless crystals were filtered, pressed between filter papers and dried to constant weight *in vacuo* over H_2SO_4 and KOH and analysed. The compound was highly soluble in water and hydrolyse on boiling. The *p*H of its aqueous solution is ca. 3. The molar conductivity of its aqueous solution at different dilutions also indicate progressive dissociation of the complex ion with dilution.

Tetrapyridinemetal(II) *oxopentafluoroniobates* — Copper compound was prepared as follows: Nb_2O_5 (2 g) was dissolved in a minimum amount of HF (40%) and then excess pyridine was added to it. Copper carbonate (1·9 g) was suspended in pyridine (5 g) and HF (3*M*) was added till copper carbonate dissolved almost completely. The solution was filtered and then added to the niobium solution with stirring when immediately deep blue precipitate appeared. The precipitate was filtered, washed with water, filter-pressed and dried *in vacuo* over fused $CaCl_2$; yield 7·3 g.

Light blue nickel compound was prepared as above starting from its carbonate (1·8 g), Nb_2O_5 (2 g), pyridine and HF; yield 6·6 g. The cadmium compound (white polyhedra) was obtained as above by adding a solution of tetrapyridinecadmium nitrate [prepared by dissolving cadmium carbonate (2·6 g) in minimum amount of HNO_3(2N), and adding pyridine (5 g)] to a solution prepared by dissolving Nb_2O_5 (2 g) in HF (10%) and then neutralizing with pyridine. The zinc and cobalt compounds were prepared in a similar manner as the cadmium compound starting from their respective carbonates.

The analytical data are given in Table 1. The above compounds hydrolyse in water with the generation of pyridine and are insoluble in common organic solvents.

Table 1 — Analytical Data of Oxopentafluoroniobates

Compound	Found (%)				Calc. (%)			
	M(II)	N	Nb	F	M(II)	N	Nb	F
$[(CH_3)_4N][HNbOF_5]$		4·96	33·92	34·86		5·02	33·32	34·06
$[Cu(py)_4][NbOF_5]$	10·75	9·51	16·18	16·36	10·89	9·6	15·92	16·29
$[Ni(py)_4][NbOF_5]$	9·66	9·78	16·38	16·55	10·15	9·68	16·05	16·42
$[Zn(py)_4][NbOF_5]$	—	9·33	16·09	15·80	—	9·57	15·87	16·23
$[Cd(py)_4][NbOF_5]$	—	8·81	14·94	15·45	—	8·86	14·69	15·05
$[Co(py)_4][NbOF_5]$	10·32	9·62	16·39	16·17	10·18	9·68	16·05	16·42

The strong bands for Nb=O in the IR spectra were found to occur at 892-952, 918, 930-960, 935-958, and 918 cm^{-1} for the Cu, Ni, Zn, Cd and Co compounds respectively. Thus it is observed that νNb=O appears in the region, as observed[2] in the case of $M^{II}NbOF_5$, nH_2O ($M=Cu^{2+}$, Mn^{2+}, etc.). The data suggest that in the above tetrapyridinemetal compounds the $NbOF_5^{2-}$ anion remains unaltered. Due to the limitations of the instrument bands below 700 cm^{-1} could not be recorded. In

TABLE 2 — THERMAL BEHAVIOUR OF OXOPENTAFLUORONIOBATES

Compound	Decomp. temp. (°C)	Range of max. decomp. (°C)	Loss (%) observed at 500°	Theoretical loss (%) for the generation of Nb_2O_5 and $M^{II}O$
$[Cu(py)_4][NbOF_5]$	50	140-250	64·13	63·59
$[Ni(py)_4][NbOF_5]$	40	170-300	65·80	64·42
$[Zn(py)_4][NbOF_5]$	30	80-230	63·80	63·36
$[Cd(py)_4][NbOF_5]$	40	120-230	58·78	58·69
$[Co(py)_4][NbOF_5]$	40	150-240	63·21	64·13

the case of $[N(CH_3)_4][HNbOF_5]$ strong bands appeared at 930 and 955-965 cm^{-1}.

The compounds were studied thermogravimetrically as before[4] in the region 30-500° in a manually operated thermobalance. The thermal behaviour of $[M^{II}(py)_4]NbOF_5$ showed that loss of pyridine and fluorine took place simultaneously. The formation of $M^{II}NbOF_5$ also could not be observed. The residues obtained at 500° consisted of a mixture of Nb_2O_5 and metal oxide. The salient features of the thermal data are given in Table 2. The pyrolysis of $[N(CH_3)_4][HNbOF_5]$ was slow from 90° to 300°, thereafter the compound underwent very rapid decomposition and ultimately at 450° generated pure niobium pentoxide.

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Heteropoly-niobates, -tantalates & -vanadates

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Heteropolyniobates, -tantalates and -vanadates of the compositions $K_{10}H[VNb_{12}O_{38}.]20H_2O$, $K_8H_3[VTa_{12}O_{38}].26H_2O$ and $(NH_4)_2[MoV_6O_{19}].12H_2O$ have been prepared. Analytical data agree well with the proposed molecular formulae. Cell constants and space groups have been determined from X-ray studies.

REPORTS on heteropoly salts of niobium, tantalum and vanadium are very few[1-3]. The present note deals with the preparation and characterization of some new heteropoly salts, viz. potassium vanadoniobate, potassium vanadotantalate and ammonium molybdovanadate.

Aqueous solutions of freshly prepared[4] potassium hexaniobate, $K_7HNb_6O_{19}.13H_2O$, and potassium metavanadate were mixed in the molar ratio of 12:1 and refluxed for 4 hr. The resulting solution was kept under atmospheric conditions for three days and finally crystallization induced by keeping *in vacuo* when small needle-shaped crystals separated which were recrystallized thrice from hot water (Found: K, 15·32; V, 1·97; Nb, 44·27; H, 1·59. $K_{10}H[VNb_{12}O_{38}].20H_2O$ requires K, 15·44; V, 2·01; Nb, 44·15; H, 1·61%). The formations $K_{10}H[VNb_{12}O_{38}].20H_2O$ is in accord with that suggested by Lindqvist[5] for complex heteroanion of the type $[X^{n+}Nb_{12}O_{38}]^{(16-n)-}$.

The corresponding heteropoly tantalate has also been prepared as above starting from potassium vanadate and freshly prepared potassium hexatantalate[4]. Light yellow crystals of potassium vanadotantalate obtained, were crystallized from hot water (Found: K, 8·50; V, 1·35; Ta, 60·15, H, 1·49; $K_8H_3[VTa_{12}O_{38}].26H_2O$ requires K, 8·63; V, 1·41; Ta, 60·08; H, 1·52%). The formulation of the compound is in agreement with that suggested by Lindqvist[5] for heteroanion of the type $[X^{n+}Ta_{12}O_{38}]^{(16-n)-}$. Heteropoly molybdovanadate has been prepared similarly starting from ammonium metavanadate (0·2*M*) and molybdic acid (0·05*M*) solutions. Small fibrous, silky yellowish crystals of ammonium molybdovanadate obtained were crystallized from hot water (Found: N, 2·88; H, 3·29; Mo, 10·25; V, 31·50. $(NH_4)[MoV_6O_{19}].12H_2O$ requires N, 2·92; H, 3·34; Mo, 10·01; V, 31·92%). The formulation is in accord with that suggested by Keggin[6] for complex anion of the type $[V_6O_{19}]^{8-}$.

The results of the X-ray crystal diffraction studies of the compounds are given below:

(a) $K_{10}H[VNb_{12}O_{38}].20H_2O$: $a=15·66$, $b=26·10$, $c=8·40$ Å and $\alpha=\beta=\gamma=90°$. The system is orthorhombic. Volume per unit cell = 3433°29 $Å^3$. The space group is D_{2h}^2-P_{nnn}. Number of molecules per unit cell = 2. The observed density =2·46 gl^{-1}.

(b) $K_8H_3[VTa_{12}O_{38}].26H_2O$: $a=16·56$, $b=35·12$, $c=14·72$ Å and $\alpha=\beta=\gamma=90°$. The system is orthorhombic. Volume per unit cell = 8560·96 $Å^3$. The space group is I_{41}/a. Number of molecules per unit cell = 4. The observed density = 2·79 gl^{-1}.

(c) $(NH_4)_2[MoV_6O_{19}].12H_2O$: $a=9·62\pm0·02$, $b=16·25\pm0·02$, $c=6·24\pm0·02$ Å, $\alpha=\beta=\gamma=90°$. The system is orthorhombic. Volume per unit cell = 975·46 $Å^3$. The space group is D_{2h}^2-P_{nnn}. Number of molecules per unit cell = 2. The observed density = 3·240 gcc^{-1} against the calculated density of 3·259 gcc^{-1}.

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