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FLUORO- AND OXO-FLUOROZIRCONATES

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SUMMARY

The preparations of $(BH_2)[ZrF_6].mH_2O$, where B = ethylenediamine (m=0) and biguanide (m=1), $(BH)_2[ZrF_6].nH_2O$, where B = guanidine (n=1), pyridine (n=0), $(BH)[ZrF_5].H_2O$, where B = α-, β- and γ-picoline, $(BH_2)[ZrOF_3]_2.xH_2O$, where B = ethylenediamine (x=5), propylene-1,2-diamine (x=3), N,N'-dimethylethylenediamine (x=3), $M^I[ZrOF_3].1.5\ H_2O$, where M^I = alkali metals, $(N_2H_5)[Zr_2O_2F_5].4H_2O$ and $(BH_2)[ZrOF_4]$, where B = 1,10-phenanthroline and 2,2'-bipyridyl are described. The compounds were characterised by chemical analysis, TGA, IR spectroscopy and x-ray powder photography. $(pyH)_2[ZrF_6]$ (py = pyridine) is unstable and undergoes slow decomposition on keeping in air. On isothermal heating at 120°C it yields $(py\ H)[ZrF_5]$. At 180°C $(\alpha\text{-pic H})[ZrF_5].H_2O$ (α-pic = α-picoline) yields $(\alpha\text{-pic H})[Zr_2F_9]$. $K[ZrOF_3].1.5\ H_2O$ yields $K[ZrOF_3].0.5H_2O$ and the anhydrous compound successively at 130°C and 225°C. The corresponding anhydrous cesium compound is produced at 220°C. IR spectra suggest the presence of Zr–O–Zr chains in the oxofluoro-compounds. From the various types of studies it appears that the oxofluorozirconates contain only a fraction of water as Zr–OH group.

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INTRODUCTION

A literature survey shows previous description of many fluorozirconates [1-4] and a few oxofluorozirconates of alkali metals [5-10]. Whilst the previous workers prepared the oxofluorozirconates through hydrolysis of hexa- or hepta-fluorozirconate [5-7] or through high temperature reactions of ZrO_2 with a fluoride [8] or fluoroborate [9], the present work involves the isolation of alkali metal and cationic organic base oxofluorozirconates primarily through controlled hydrolysis of zirconium fluoride solution. Several new fluorozirconates of organic base cations are also described.

EXPERIMENTAL

'Zirconium fluoride solution' was prepared by digesting hydrated zirconium oxide with HF (10%) solution on a water-bath having the hydrated oxide in excess, followed by cooling and filtration. On analysis of the filtrate zirconium and fluorine were found to be present in it in the ratio 1:4. The fluoride content of the compounds was determined gravimetrically as PbClF [11]. Zirconium was estimated gravimetrically as ZrO_2 [12] and alkali metals as their sulphates [11]. Nitrogen was determined by Dumas' semi-micro method. Analytical results are reported in Table 1.

TGA data were recorded using a manually operated thermobalance by heating the compounds at a rate of 2°C/min. In the case of alkali metal compounds, TGA and DTA data were recorded using a Shimadzu DT-30 thermal analyser in a dynamic atmosphere of nitrogen. The sample was heated in a platinum crucible at a rate of 10°C/min. with inert alumina as reference. IR spectra were recorded in KBr discs on a Perkin-Elmer spectrophotometer in the range 400 to 4000 cm^{-1}. Powder X-ray diffraction photographs of oxofluorozirconates were taken in a Philips, PW 1130/00 generator using Ni-filtered Cu-K_α radiation.

Fluorozirconates

1. Pyridinium hexafluorozirconates, $(py\ H)_2[ZrF_6]$: Hydrated zirconium oxide, precipitated from an aqueous solution of zirconium nitrate (4.4 g) by adding ammonia solution, was washed with hot water and dissolved in 4.0 ml HF (40%) and diluted with 50 ml water. Pyridine was then added in excess to the solution, which was evaporated on a water-bath to crystallisation. The crystals were filtered, pressed between filter papers and dried in air.

2. α-picolinium, β-picolinium and γ-picolinium pentafluorozirconates having the same general formula $(pic\ H)[ZrF_5].H_2O$ and ethylenediaminium hexafluorozirconate, $(EnH_2)[ZrF_6]$, were obtained in the above manner by adding calculated amounts of the amine acidified with HF(20%) to fluorozirconic acid solution obtained as in (1) above. The crystals were dried over KOH in a desiccator.

3. Guanidinium hexafluorozirconate, $(gu\ H)_2[ZrF_6].H_2O$ and biguanidinium hexafluorozirconate, $(bigu\ H_2)[ZrF_6].H_2O$ were obtained similarly by mixing calculated amounts of fluorozirconic acid solution prepared as above with guanidinium carbonate and biguanide sulphate both acidified with HF (20%).

Ethylenediaminium and guanidinium hexafluorozirconates have been previously prepared [1,2] starting from $H_2ZrF_6.2H_2O$. The pyridinium compound slowly decomposes in air, but the other compounds are stable and showed no loss in weight even on keeping over P_2O_5 in vacuo.

Oxofluorozirconates

1. 1,10-phenanthrolinium oxotetrafluorozirconate, $(1,10\text{-phen}\ H_2)[ZrOF_4]$, was obtained as above by evaporating a mixture prepared from calculated amounts of 1,10-phenanthroline and hydrated zirconium oxide both dissolved in minimum amounts of HF.

2. 2,2'-bipyridyl oxotetrafluorozirconate, $(2,2'\text{-bipy}\ H_2)$-$[ZrOF_4]$: 2,2'-bipyridyl (0.8 g) was dissolved in alcohol (5 ml) and the alcoholic solution was added with stirring to 'zirconium fluoride solution' (22 ml) containing 0.45 g of Zr. The small amount of precipitate which appeared slowly was filtered off and neglected. The filtrate was evaporated in a desiccator when needle-shaped colourless crystals appeared. These were **filtered**, washed successively with small

amounts of cold water and alcohol, and dried in a desiccator containing fused $CaCl_2$.

3. Hydrazinium dioxopentafluorodizirconate, $(N_2H_5)[Zr_2O_2F_5].4H_2O$, was obtained as a precipitate on adding a solution of hydrazine hydrate (0.3 ml into 1.5 ml water) to 'zirconium fluoride solution' (18 ml containing 0.45 g Zr) with mechanical stirring. The compound was filtered, and dried as above.

4. Ethylenediaminium oxotrifluorozirconate, $(\mathrm{en}\ H_2)[ZrOF_3]_2.5H_2O$, propylene-1,2-diaminium oxotrifluorozirconate $(\mathrm{pn'}\ H_2)[ZrOF_3]_2.3H_2O$, propylene-1,3-diaminium oxotrifluorozirconate, $(\mathrm{pn}\ H_2)[ZrOF_3]_2.3H_2O$ and N,N'-dimethylethylenediaminium oxotrifluorozirconate, $(\mathrm{N,N'\text{-}dimen}\ H_2)$-$[ZrOF_3]_2.3H_2O$, were obtained as precipitates in the same manner as the hydrazinium compound using about 0.5 ml of the corresponding amine and 'zirconium fluoride solution' (18 ml) containing 0.45 g Zr.

Preparative study of the systems, zirconium fluoride - CH_3COOM^I (where M^I = Na, K, Rb and Cs) at controlled pH

A detailed study was made with four systems, viz., zirconium fluoride with (i) sodium acetate, (ii) potassium acetate, (iii) rubidium acetate and (iv) cesium acetate. Rubidium and cesium acetates were obtained by dissolving the respective carbonates in acetic acid (1:1). The reactions of 'zirconium fluoride solution' with alkali metal acetates were carried out at 1:1, 1:2 and 1:4 molar ratios. The metal acetate solution was added to calculated amount of 'zirconium fluoride solution' with constant stirring by a magnetic stirrer when a white precipitate was obtained. The pH of the mixture was recorded after the precipitation. The precipitate was filtered, washed successively with small quantities of water and alcohol,pressed between filter papers and dried over KOH to constant weight.

Based on this preparative study of different systems products were obtained whose composition corresponded or nearly corresponded to oxotrifluorozirconates. For sodium, potassium and rubidium compounds the products were obtained at pH values 4.1 to 4.4 on mixing zirconium fluoride : metal acetate in the ratio 1:2, whilst the cesium compound was obtained at pH 5.2 on mixing zirconium fluoride : cesium acetate in the ratio 1:4. Since the method of preparation is the same for the alkali metal compounds only that for the potassium compound is given below.

Potassium fluorozirconate, $K[ZrOF_3].1.5H_2O$: A solution (15 ml) of potassium acetate (2 g) was added dropwise to 'zirconium fluoride solution' (27 ml) containing 0.91 g Zr with stirring to give a precipitate. The mixture was allowed to settle. The compound was filtered,washed successively with small amounts of water and alcohol, pressed between filter papers and dried over KOH.

The oxofluorozirconates are insoluble in common organic solvents. They are stable in air but hydrolyse in water. The hydrated compounds do not dehydrate on keeping over P_2O_5 *in vacuo*.

RESULTS AND DISCUSSION

The decomposition temperatures of the compounds as observed through their TGA studies are recorded in Table 1. On the basis of TGA results the following compounds were obtained through isothermal heating of the compounds.

$$(\text{py H})_2[\text{ZrF}_6] \xrightarrow{120^\circ} \text{py H}[\text{ZrF}_5]$$

$$\alpha\text{-pic H}[\text{ZrF}_5]\cdot\text{H}_2\text{O} \xrightarrow{180^\circ} \alpha\text{-pic H}[\text{Zr}_2\text{F}_9]$$

No other intermediate was noticed by TGA and isothermal heating of the fluoro- and oxofluorozirconates of the organic base cations. The analyses of the residues obtained at around 450°C suggest them to be mixtures of fluorides and oxides of zirconium.

TGA for the potassium compound (Table 2) shows its stability upto 90°C and above that it loses weight showing stable regions for intermediates at 130-160°C and at 220-260°C. DTA indicates two endotherms showing completion of the stepwise decompositions at 130° and 220°C. The cesium compound starts losing weight at 60°C and a horizontal in TGA is observed at 220°C supported by an endotherm in DTA curve. Exotherms are observed at 350°C and 280°C for K-compound and Cs-compound respectively indicating the evolution of new structures for the two

TABLE 1

Analytical and IR data of fluoro- and oxofluorozirconates including decomposition temperatures

Compounds	Found(Calcd.)(%)			Zr-F (cm^{-1})	Zr-O (cm^{-1})	Decomposition temperature (oC)
	N/M	Zr	F			
$[\mathrm{enH_2}][\mathrm{ZrF_6}]$	10.33 (10.47)	34.20 (34.12)	42.10 (42.64)	450(s,b)	-	210
$[\mathrm{guH}]_2[\mathrm{ZrF_6}].\mathrm{H_2O}$	24.78 (24.46)	26.23 (26.56)	33.14 (33.20)	450-510(s,b)	-	230
$[\mathrm{biguH_2}][\mathrm{ZrF_6}].\mathrm{H_2O}$	21.13 (21.46)	27.87 (27.96)	34.69 (34.95)	450(w) & 480(m)	-	220
$[\mathrm{pyH}]_2[\mathrm{ZrF_6}]$	7.51 (7.66)	25.28 (24.96)	30.95 (31.20)	-	-	-
$[\mathrm{pyH}][\mathrm{ZrF_5}]$	5.19 (5.26)	34.27 (34.25)	35.69 (35.67)	440(m) & 500(s)	-	-
$[\alpha\text{-picH}][\mathrm{ZrF_5}].\mathrm{H_2O}$	4.67 (4.69)	30.52 (30.57)	32.13 (31.84)	460(w) & 500(s)	-	110
$[\alpha\text{-picH}][\mathrm{Zr_2F_9}]$	3.26 (3.13)	40.36 (40.76)	38.46 (38.21)	440(w) & 470(w)	-	-
$[\beta\text{-picH}][\mathrm{ZrF_5}].\mathrm{H_2O}$	4.67 (4.69)	30.40 (30.57)	32.23 (31.84)	455(w) & 500(s)	-	100
$[\gamma\text{-picH}][\mathrm{ZrF_5}].\mathrm{H_2O}$	4.71 (4.69)	30.35 (30.57)	31.61 (31.84)	475(m) & 505(m)	-	120
$[1,10\text{-phenH_2}][\mathrm{ZrOF_4}]$	7.22 (7.30)	23.56 (23.79)	19.80 (19.82)	460(m)	850(s)	100
$[2,2'\text{- bipyH_2}][\mathrm{ZrOF_4}]$	8.29 (8.20)	26.70 (26.72)	22.19 (22.26)	Below 400		80
$[\mathrm{enH_2}][\mathrm{ZrOF_3}]_2.5\mathrm{H_2O}$	5.82 (5.83)	37.99 (37.96)	23.41 (23.72)	425(m) & 510(w)	830(s)	50

$[pn'H_2][ZrOF_3]_2 \cdot 3H_2O$	6.06 (6.11)	40.11 (39.78)	24.45 (24.86)	420(s) & 500(m)	830(s)	110
$[pn\ H_2][ZrOF_3]_2 \cdot 3H_2O$	6.19 (6.11)	40.24 (39.78)	25.20 (24.86)	425(s) & 500(m)	830(s)	90
$[N,N'\text{-dimen}H_2][ZrOF_3]_2 \cdot 3H_2O$	5.84 (5.92)	38.43 (38.60)	24.41 (24.12)	410(s,b) & 510(s)	830(s)	120
$[N_2H_5][Zr_2O_2F_5] \cdot 4H_2O$	6.63 (6.76)	44.25 (44.02)	23.13 (22.92)	430(m)	830(s)	90
$K[ZrOF_3] \cdot 1.5H_2O$	16.72 (16.97)	39.50 (39.61)	24.39 (24.75)	430(s)	830(s)	90
$Cs[ZrOF_3] \cdot 1.5H_2O$	39.92 (41.00)	30.50 (28.14)	17.42 (17.59)	430(s)	840(s)	60
$K[ZrOF_3] \cdot 0.5H_2O$	18.52 (18.41)	42.41 (42.96)	27.09 (26.85)	435(s) & 510(w,b)	835(s)	
$K[ZrOF_3]$	20.52 (19.23)	45.06 (44.85)	29.51 (28.03)	440(s) & 500(s,b)	840(s)	
$Cs[ZrOF_3]$	43.19 (44.73)	32.92 (30.70)	19.70 (19.18)	440(s) & 520(s)	845(s)	

s = strong, m = medium, w = weak, b = broad.

TABLE 2

Results of TGA and DTA for potassium and cesium oxofluorozirconates

Compound	TGA	Temp.(^oC)	DTA	Temp.(^oC)
$K[ZrOF_3].1.5H_2O$	Intermediate at	130 to 160	Endotherm	130
	- do -	220 to 260	- do -	220
			Exotherm	350
$Cs[ZrOF_3].1.5H_2O$	- do -	220 to 260	Endotherm	220
			Exotherm	280

compounds. Kolditz and Feltz [5] reported partial loss of water and also HF in the region 140-200°C for the K-compound. The present authors did not find any loss of HF even up to 220°C in agreement with the results of Sheka et al. [7].

On the basis of these studies isothermal heating of the compounds were carried out and the products analysed. The results agree with the following scheme :

$$K[\,ZrOF_3\,].1.5H_2O \xrightarrow{130^{\circ}} K[\,ZrOF_3\,].0.5H_2O \xrightarrow{225^{\circ}} K[\,ZrOF_3\,]$$

$$Cs[\,ZrOF_3\,].1.5H_2O \xrightarrow{220^{\circ}} Cs[\,ZrOF_3\,]$$

IR spectra of all the compounds described above show strong absorption bands in the region 390-530 cm^{-1} due to Zr-F stretching vibrations [13]. The protonated organic base compounds show typical N–H frequencies in the region 3000-3500, 1540-1650, and 1390-1490 cm^{-1} [14]. The spectra of the hydrated compounds also show bands in the region 3115-3500 and 1600-1650 cm^{-1} due to symmetric and antisymmetric OH stretchings and HOH bending respectively [14]. Superimposition of these bands with those of N–H frequencies probably occurs.

The oxofluoro compounds show intense narrow absorption bands in the region 830-850 cm^{-1} which may be due to Zr = O or Zr–O–Zr bonds or to the surface OH group [15,16]. The presence of Zr–OH group could not be established with certainty since the characteristic band for M–OH was not observed in the region 1000-1150 cm^{-1} in any of the IR spectra recorded for the oxofluoro compounds [14]. The close similarity of IR bands of oxofluorozirconates to those of ZrO_2 in the region 400-500 cm^{-1} suggests the presence of Zr–O–Zr bonds in the former compounds; but in this region bands due to Zr-F also appear. Superimposition of bands due to both types of bonds as stated above is very likely. The ir bands in this region of th dehydrated products of potassium and cesium compounds of oxofluorozirconates obtained at 225° and zirconium oxide resemble each other closely.

A comparison of X-ray diffraction data of $KZrOF_3$, $1.5H_2O$ and $KZrOF_3$ (obtained by dehydration at 225°C) shows partial breaking up of the structure of the former on dehydration.

The retention of 0.5 mole H_2O at 130-140°C in potassium compound suggests the presence of strongly bound residual water. Hence it is very likely that this amount of water is present in a polymer as Zr–OH. Various data as reported above suggest the oxofluorozirconates to be polymers.

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