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Fluoro Complexes of Hexavalent Uranium.
IX. Complexes of Dioxouranium(VI) Containing Fluoride and Acetate

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The mixed fluoro acetato complexes of dioxouranium(VI), viz., $K_2[UO_2F_2(CH_3COO)_2]$, $Cs_3[(UO_2)_2F_3(CH_3COO)_4]$ *and* $(NH_4)_3[(UO_2)_2F_4(CH_3COO)_3]$ *were prepared by crystallising solutions containing* UO_2F_2 *and the alkali acetates. Recrystallisation of the potassium and ammonium salts gave* $M[UO_2F(CH_3COO)_2]$ $(M = K$ *and* $NH_4)$*. A third ammonium salt,* viz., $NH_4[(UO_2)_2F_4(CH_3COO)]$ *was obtained by heating* $(NH_4)_3[(UO_2)_2F_4(CH_3COO)_3]$ *at 150–160 °C. The conductivity of the dilute solutions of the compounds indicates appreciable dissociation of the complex ions. The i.r. spectra of the complexes suggest that the acetate ion is present as a bidentate or bridging group. The lattice parameters of the ammonium and potassium salts have been determined.*

Introduction

In continuation to our work [1–4] on the mixed ligand fluoro complexes of the UO_2^{2+} ion we present in this communication the isolation and characterisation of a few uranyl complexes containing fluoride and acetate. The fluoro complexes of UO_2^{2+} have been thoroughly studied because of their high stability and practical uses. Acetato complexes of UO_2^{2+} have also received considerable attention. However, studies on the complexes of UO_2^{2+} containing both fluoride and acetate are very scanty. Only one paper [5] reporting the preparation of $M[UO_2F(CH_3COO)_2]$ $(M = K$ and $NH_4)$ and $(CN_3H_6)_2[UO_2F_3(CH_3COO)(H_2O)]$ has appeared. The properties or the structures of the complexes have not been studied. The potassium and ammonium salts were prepared by adding alkali fluoride to a solution of uranyl acetate containing acetic acid. We have, however, obtained mixed fluoro acetato complexes of other types by introducing alkali acetate to uranyl fluoride.

Experimental

Uranyl nitrate hexahydrate, hydrogen peroxide, potassium acetate and ammonium acetate were of BDH or E. Merck Analar or G.R. quality. Preparation of the acid, $H[UO_2F_3]\cdot H_2O$ starting from $UO_2(NO_3)_2\cdot 6H_2O$ has been described in our earlier publications [1, 6]. Uranyl fluoride was prepared by heating $H[UO_2F_3]\cdot H_2O$ in a platinum crucible at 150 °C to a constant weight. Caesium acetate was prepared by adding slight excess of acetic acid to caesium carbonate (E. Merck G.R. quality) followed by complete evaporation and drying in a desiccator over caustic soda.

Analyses

Methods of analysis of uranium, alkali metals and fluorine were described in our previous papers [1, 2]. Uranium content of the ammonium salts was also determined by igniting the salts and weighing as U_3O_8. Nitrogen was analysed by Kjeldahl's method. Total fluoride and acetate content was determined by passing the salt solutions through a column of cation exchange resin (Dowex 50-X8, A.R. grade of J. T. Baker Chemical Co., Phillipsberg) in hydrogen form and titrating the effluent with standard alkali solution using phenolphthalein as indicator. Uranyl ion remained fixed on the resin. Analyses of carbon and hydrogen were done by Mikroanalytisches Laboratorium, Beller, Göttingen.

Physical Measurements

Recording of the thermograms and the conductivity of solutions and the determination of lattice parameters of the salts from X-ray powder diffraction data were described in our earlier publications [1, 2]. Infrared spectra were recorded in potassium bromide pellet in the range of 4000–650 cm^{-1} using a Perkin-Elmer spectrophotometer (No. 257).

Preparation of the Complexes

$(NH_4)_3[(UO_2)_2F_4(CH_3COO)_3]$. A concentrated solution of 1.5 g (4.9 mmol) of UO_2F_2 was mixed with a concentrated solution of 1.2 g (14.7 mmol) of ammonium acetate with continuous stirring in a polythene beaker. Crystals appeared after 5 minutes of stirring. The yield was 1.4 g.

TABLE I. Analytical Data* of the Complexes.

Compound	U(%)	F(%)	Total anion** per U atom	Alkali metal or N(%)	C(%)	H(%)	Molecular conductance*** (ohm^{-1} mol^{-1} cm^2)
$(NH_4)_3[(UO_2)_2F_4(CH_3COO)_3]$	56.2 (56.2)	9.2 (9.0)	3.5 (3.5)	5.1 (5.0)	9.0 (8.5)	2.5 (2.5)	630
$(NH_4)[UO_2F(CH_3COO)_2]$	56.0 (56.0)	4.4 (4.5)	3.0 (3.0)	3.4 (3.3)			290
$(NH_4)[(UO_2)_2F_4(CH_3COO)]$	69.0 (68.7)	10.5 (10.9)	2.5 (2.5)	2.1 (2.0)			405
$K_2[UO_2F_2(CH_3COO_2)]$	47.0 (47.2)	7.5 (7.5)	3.9 (4.0)	16.0 (15.5)	9.4 (9.5)	1.2 (1.2)	265
$K[UO_2F(CH_3COO)_2]$	53.1 (53.3)	4.6 (4.3)	3.0 (3.0)	8.8 (8.7)			260
$Cs_3[(UO_2)_2F_3(CH_3COO)_4]$	38.2 (38.6)	4.6 (4.6)	3.4 (3.5)	32.0 (32.3)	8.1 (7.8)	1.1 (1.0)	

*The values in parenthesis are the calculated ones. **Total fluoride and acetate. ***1 × 10^{-3} *M* aqueous solution at 25 °C.

$K_2[UO_2F_2(CH_3COO)_2]$ *and* $Cs_3[(UO_2)_2F_3(CH_3COO)_4]$

These were prepared by a method similar to the above replacing ammonium acetate with appropriate amounts of potassium and caesium acetates. Crystals appeared immediately on stirring. The yields were 1.6 g and 1.2 g respectively.

$NH_4[UO_2F(CH_3COO)_2]$ *and* $K[UO_2F(CH_3COO)_2]$

These were prepared by slow evaporation of concentrated solutions of $(NH_4)_3[(UO_2)_2F_4(CH_3COO)_3]$ and $K_2[UO_2F_2(CH_3COO)_2]$ in a desiccator over concentrated sulphuric acid. Starting from 1.0 g of the parent compound the yields were about 0.3 g.

$(NH_4)[(UO_2)_2F_4(CH_3COO)]$

The compound was obtained by heating $(NH_4)_3[(UO_2)_2F_4(CH_3COO)_3]$ at 150–160 °C to constant weight.

No pure rubidium compound could be isolated by the above method. Crystallisation of UO_2F_2 and alkali acetate solutions in 1:1 ratio also did not give any pure compound. All the compounds were separated by filtration and dried by pressing between filter papers and then keeping in a desiccator over concentrated sulphuric acid. The analytical data of the compounds are given in Table I.

Results and Discussion

The salts are yellow crystalline substances, stable in air and soluble in water. The conductivity of dilute solutions (1 × 10^{-3} *M*) of the compounds is rather high (Table I) indicating considerable dissociation of the complex ions.

The TGA curve of $(NH_4)_3[(UO_2)_2F_4(CH_3COO)_3]$ indicated that it begins to decompose from about 130 °C. The thermogram gave two horizontals stretching from 190 to 250 °C and 290 to 400 °C. The losses in weight at these two stages were 18.7 and 26.6%, which correspond with the formation of $NH_4[(UO_2)_2F_4(CH_3COO)]$ and UO_2F_2 respectively (loss calc. 18.2 and 27.2% respectively). U_3O_8 was finally obtained around 600 °C (loss found 33.6; calc. 33.7%). Isothermal heating of $(NH_4)_3[(UO_2)_2F_4(CH_3COO)_3]$ at 150–160 °C gave a loss of 18.3% and the residue analysed as $NH_4[(UO_2)_2F_4(CH_3COO)]$.

The i.r. spectral band positions of the complexes are recorded in Table II. The uranyl (UO_2) stretching frequency in the complexes appears between 940 and 840 cm^{-1}. The antisymmetrical UO_2 band is, however, overlapped with the ν(C–C) band of acetate which appears at 924 cm^{-1} in sodium acetate [7]. In a few complexes the symmetrical UO_2 band appears as a very weak one while in others it appears as a medium or strong intensity band at about 850 cm^{-1}. Acetate ion has very weak absorption in this region. Interesting features in the spectra lie in the region of 1560 to 1400 cm^{-1}. The antisymmetrical COO band appears as a very strong one around 1520 cm^{-1} clearly indicating that the acetate ion is not present as a unidentate ligand. In complexes containing unidentate acetate this band is shifted to high frequency (1650–1590 cm^{-1}) [8, 9]. A distinction

TABLE II. IR Spectral Bands of the Complexes (ν, cm^{-1}).

Compound	$\nu(UO_2)$	$\nu_{as}(COO)$	$\nu_s(COO) + \delta(CH_3)$	$\delta(COO)$	Other bands
$K_2[UO_2F_2(CH_3COO)_2]$	930vs, 870s	1565sh, 1540vs, 1505sh	1405s, 1460vs	680s	3350m(br), 2900vw, 1120vw, 1050vw, 1020vw, 955sh
$K[UO_2F(CH_3COO)_2]$	915vs, 840vw	1555sh, 1520vs, 1500sh	1400s, 1450vs	675s	3390m(br), 2900vw, 1620m, 1045vw, 1010w, 945sh
$(NH_4)_3[(UO_2)_2F_4(CH_3COO)_3]$	920vs, 880m, 840vw	1560sh, 1535vs, 1505sh	1395vs, 1445vs	680s	3400s(br), 3120vs, 1620m, 1045w, 1015w, 950m
$(NH_4)[UO_2F(CH_3COO)_2]$	930vs, 850vw	1565sh, 1540vs, 1510sh	1405vs, 1465vs	685s	3450br, 3280br, 3140vs, 2900w, 2820w, 1630m, 1055w, 1020w, 955sh
$(NH_4)[(UO_2)_2F_4(CH_3COO)]$	930vs, 850vw	1560sh, 1530vs, 1510sh	1400vs, 1460vs	685s	3560m, 3150vs, 2900w, 2840w, 1730w(br), 1615m, 1060w, 1020w, 950sh
$Cs_3[(UO_2)_2F_3(CH_3COO)_4]$	920vs, 865m	1555sh, 1530vs, 1550sh	1400s, 1450vs	675s	3360m(br), 2900vw, 1600m(br), 1450vs, 1140w, 1040w, 1010w, 940sh

TABLE III. Crystallographic Data of the Complexes.

Compound	Crystal system	Z	Lattice parameter	Calculated density (g/cm^3)	Observed density (g/cm^3)
$(NH_4)_3[(UO_2)_2F_4(CH_3COO)_3]$	Orthorhombic	1	$a = 11.2$ $b = 8.2$ $c = 5.3$ A	2.90	2.79
$NH_4[UO_2F(CH_3COO)_2]$	Orthorhombic	2	$a = 10.0$ $b = 6.8$ $c = 11.2$ A	1.86	2.08
$NH_4[(UO_2)_2F_4(CH_3COO)]$	Orthorhombic	1	$a = 6.8$ $b = 7.9$ $c = 10.0$ A	2.14	2.31
$K_2[UO_2F_2(CH_3COO)_2]$	Hexagonal	4	$a = b = 10.6$ $c = 13.0$ A	2.64	2.84

between bidentate and bridging coordination of acetate is difficult from i.r. spectra. In the ammonium salt the problem is rendered all the more difficult because of the appearance of the very strong intensity ν_4 band of NH_4^+ at about 1400 cm^{-1} where the symmetrical COO band of acetate ion in sodium acetate also appears [7]. In addition, the correct assignment of the symmetrical COO band is somewhat difficult, because the CH_3 deformation band (which is however, weak) appears close to the symmetrical COO band (COO at 1414; CH_3 at 1430 and 1443 cm^{-1}) [7, 9]. It has been stated [9] that the separation between the two ν(COO) frequencies is smaller (compared to that in sodium acetate in which it is about 160 cm^{-1}) in bidentate (chelate) acetate, whereas in the complexes containing bridging acetate the two COO frequencies are close to the free ion values. The separation of the two COO frequencies in the present complexes is about 80 cm^{-1} (if the 1450 cm^{-1} band is taken as the symmetrical COO band), while it is of the order of 130 cm^{-1}, if the 1400 cm^{-1} band is taken as the symmetrical COO band. It appears that the complexes contain acetate as bidentate chelating group. The acetate ion is present as a bidentate group in $Na[UO_2(CH_3COO)_3]$ [10] the COO frequencies in which are reported [11] to occur at 1537 and 1472 cm^{-1}. The complexes $(NH_4)_3[(UO_2)_2F_4(CH_3COO)_3]$ and $NH_4[(UO_2)_2F_4(CH_3COO)]$ containing 1.5 and 0.5 acetate group per uranium atom may contain bridging acetate. The spectra of the complexes show medium intensity bands at about 3400 and 1620 cm^{-1} indicating the presence of water. The potassium and the caesium salts suffered practically no loss in weight on heating at 110 °C which shows that the water came from potassium bromide used in recording the spectra.

The salts $(NH_4)_3[(UO_2)_2F_4(CH_3COO)_3]$, $NH_4[(UO_2)_2F_4(CH_3COO)]$, $NH_4[UO_2F(CH_3COO)_2]$ and $K_2[UO_2F_2(CH_3COO)_2]$ gave well defined X-ray powder diffraction spectra. The crystallographic data are given in Table III.

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