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X-Ray Powder Diffraction and Thermal Studies on Some Uranium(III) Compounds

A. CHADHA, S. SAMPATH and D. M. CHACKRABURTTY

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay-400 085, India

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X-ray powder diffraction studies of uranium(III) formate, uranium(III) sulphate and double sulphates of uranium(III) with ammonium, rubidium and caesium reveal a striking similarity of uranium(III) and the corresponding cerium(III) compounds.

The mode of thermal decomposition of the uranium(III) compounds in oxidising and reducing atmospheres is reported; two new anhydrous uranium(III) compounds $(NH_4)U(SO_4)_2$ and $RbU(SO_4)_2$ could be obtained.

Introduction

The trivalent oxidation state which is characteristic of lanthanides and transplutonium elements has been rarely encountered in uranium except the hydrides and halides [1]. This is essentially because of oxidation of uranium(III) by air and water. More recently, however, two ingenious methods have been developed for preparation of uranium(III) compounds. In the first method, reduction of uranium(IV) by liquid zinc amalgam in non-aqueous condition has been used by Drozdzynski and co-workers to obtain uranium(III) formate and anhydrous uranium(III) chlorocomplexes of type M_2UCl_5 and MU_2Cl_7 (M = NH_4, K or Rb) and UPO_4 [2–4]. Uranium(III) formate is reported to be trigonal like lanthanide formates and belong to rhombohedral system with space group *R3m* [2]. In the other method, electrolytic reduction of aqueous uranium(VI) solution at low temperatures has been used by Barnard *et al.* to get hydrated sulphates, double sulphates and also double chlorides of uranium(III) [5, 6]. Using the latter method, attempts to get anhydrous uranium(III) compounds by vacuum heating have not been successful. The compounds were characterised by magnetic and spectroscopic measurements. However, no structural data is available on these compounds.

In this paper, X-ray diffraction and thermal studies of following compounds of uranium(III) are reported:

(i) $U(HCOO)_3$
(ii) $U_2(SO_4)_3 \cdot 8H_2O$
(iii) $(NH_4)U(SO_4)_2 \cdot 4H_2O$
(iv) $RbU(SO_4)_2 \cdot 4H_2O$
(v) $CsU(SO_4)_2 \cdot 5.5H_2O$

TABLE I. Chemical Analysis and Thermogravimetric Data on Uranium(III) Compounds.

Compound	Uranium(%)		Sulphate (%)		Carbon(%)		Hydrogen(%)		% Wt. loss found at 200 °C in H_2	% Wt. loss expected for complete dehydration
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.		
$U(HCOO)_3$	63.51	63.81	–	–	9.35	9.65	1.17	0.81	–	–
$U_2(SO_4)_3 \cdot 8H_2O$	52.1	52.4	31.4	31.7	–	–	–	–	8.54	15.86
$(NH_4)U(SO_4)_2 \cdot 4H_2O$	45.7	45.8	36.4	36.9	–	–	–	–	14.9	13.85
$RbU(SO_4)_2 \cdot 4H_2O$	40.2	40.9	32.5	32.7	–	–	–	–	12.25	12.79
$CsU(SO_4)_2 \cdot 5.5H_2O$	35.6	35.9	28.7	29.0	–	–	–	–	7.0	14.95
$NH_4U(SO_4)_2$	53.25	53.12	42.92	42.85	–	–	–	–	–	–
$RbU(SO_4)_2$	46.32	46.17	46.32	46.17	–	–	–	–	–	–

TABLE II. Observed and Calculated d Spacings (A) and Observed Relative Intensities for $U(HCOO)_3$, $U_2(SO_4)_3 \cdot 8H_2O$ and $MU(SO_4)_2 \cdot nH_2O$ Complexes.

$U(HCOO)_3$				$U_2(SO_4)_3 \cdot 8H_2O$				$(NH_4)U(SO_4)_2 \cdot 4H_2O$				$RbU(SO_4)_2 \cdot 4H_2O$				$CsU(SO_4)_2 \cdot 5.5H_2O$			
hkl	d_o	d_c	I/I_o	*hkl*	d_o	d_c	I/I_o	*hkl*	d_o	d_c	I/I_o	*hkl*	d_o	d_c	I/I_o	*hkl*	d_o	d_c	I/I_o
110	5.340	5.340	90	112	5.418	5.402	92	100	6.617	6.621	17	100	6.607	6.610	10	111	9.686	9.533	20
101	3.754	3.756	50	200	4.988	4.965	13	021	6.417	6.417	100	021	6.417	6.417	85	020	9.398	9.446	45
021	3.079	3.072	62	020	4.796	4.785	13	110	6.254	6.255	9	110	6.259	6.245	7	102	6.662	6.685	20
220	2.671	2.670	100	021	4.622	4.614	8	120	5.444	5.436	6	$\bar{1}11$	5.353	5.371	10	112	6.338	6.305	95
131	2.181	2.176	50	004	4.349	4.350	63	$\bar{1}21$	4.832	4.830	24	040	4.763	4.765	55	220		6.303	
140	2.017	2.018	53	114	3.681	3.678	13	111		4.820		130	4.589	4.581	20	222	4.778	4.765	50
321	1.886	1.885	38	023		3.691		040	4.760	4.761	45	121	4.422	4.411	10	032		4.763	
330	1.781	1.780	24	220	3.461	3.446	17	121	4.405	4.414	12	002	4.339	4.340	30	321	4.592	4.596	15
051	1.690	1.687	12	204	3.271	3.272	13	012	4.230	4.234	8	$\bar{1}31$	4.191	4.200	35	302	4.418	4.460	60
312	1.609	1.604	30	024	3.220	3.219	50	131	3.900	3.918	5	022	3.952	3.950	15	123	4.185	4.183	70
600	1.541	1.542	24	115	3.102	3.106	21	200	3.317	3.311	14	131	3.879	3.917	15	223	3.865	3.845	35
520	1.478	1.481	24	223	2.944	2.962	39	210	3.278	3.262	21	$\bar{1}02$		3.850		033	3.826	3.844	45
431	1.428	1.426	9	132	2.872	2.867	34	042	3.220	3.208	73				10	004	3.623	3.640	20
				224	2.697	2.701	42	060	3.178	3.174	11	051	3.496	3.490	100	104	3.549	3.560	20
				133		2.691		$\bar{2}11$		3.182		141	3.417	3.441	25	114	3.500	3.497	40
				116	2.666	2.673	100	132	3.030	3.027	8	102		3.441		214	3.292	3.293	60
				332	2.221	2.221	26	151		3.026		200	3.307	3.305	30	501		3.296	
				420	2.204	2.204	26	$\bar{1}42$	2.986	2.995	26	122	3.255	3.236	55	511	3.231	3.248	35
				008	2.170	2.175	21	211	2.948	2.940	10	042	3.204	3.209	35	224	3.163	3.150	60
				240	2.156	2.156	17	142	2.790	2.790	15	060	3.178	3.177	70	034		3.151	
				404		2.156		023	2.770	2.770	14	$\bar{2}11$		3.177		053	2.985	2.981	95
				316	2.125	2.127	17	152	2.702	2.709	11	151	3.042	3.026	15	005	2.902	2.912	15
				136	2.094	2.097	29	$\bar{1}52$	2.567	2.555	5	132		3.026		062		2.890	
				118	2.070	2.074	8	113	2.527	2.519	7	$\bar{1}42$	2.986	2.994	70	162	2.851	2.849	25
				208	1.989	1.992	21	241		2.523		061		2.983		600	2.810	2.821	60
				028	1.977	1.980	29	043	2.473	2.474	5	211	2.952	2.935	10	205	2.746	2.754	50
				511	1.933	1.933	13	212		2.470		160	2.854	2.863	15	611		2.740	
				512	1.899	1.898	13	171	2.380	2.387	27	142	2.805	2.790	15	070	2.698	2.699	25
				152	1.836	1.837	26	133	2.353	2.359	3	$\bar{1}61$	2.763	2.763	50	523	2.666	2.664	35
				336	1.799	1.801	13	$\bar{2}52$	2.265	2.258	4	240	2.724	2.716	70	621		2.657	
				154	1.719	1.725	8	$\bar{1}72$	2.216	2.222	11	$\bar{1}52$	2.698	2.709	35	622	2.535	2.534	30
				227	1.683	1.686	34	300	2.201	2.207	4	$\bar{1}23$	2.658	2.667	5	072		2.531	
				600	1.654	1.655	8	252		2.207		241	2.525	2.521	40	514	2.455	2.458	20
				155		1.654		004	2.175	2.172	4	123	2.453	2.454	20	444	2.377	2.382	100
				408	1.633	1.636	8	181	2.149	2.148	38	$\bar{1}71$		2.448		552		2.382	
				516	1.614	1.615	4	$\bar{1}53$	2.096	2.091	3	$\bar{1}62$		2.450		633	2.280	2.274	20
				156	1.578	1.577	8	$\bar{2}62$		2.101	3	171	2.385	2.389	55	604	2.233	2.230	15
				604	1.545	1.547	13					080		2.382		651		2.234	
				248	1.529	1.531	4					133	2.360	2.358	10	236	2.191	2.188	15
												162	2.335	2.334	5	515		2.195	

081	2.300	2.297	10	652	2.157	2.159	75
053		2.306		525	2.145	2.150	70
$\bar{1}53$	2.243	2.245	10	246	2.088	2.091	70
143		2.241					
063	2.143	2.139	95				
$\bar{1}04$		2.141					

It also includes the isolation of anhydrous $(NH_4)U(SO_4)_2$ and $RbU(SO_4)_2$ compounds for the first time, from their respective hydrated salts.

Experimental

All preparations were carried out in a glass apparatus with provisions for precipitation, filtration and drying in inert atmosphere. Uranium(III) formate was prepared by non aqueous method [2]. Uranium tetrachloride was obtained by passing argon saturated with carbon tetrachloride vapours over uranium dioxide at 480 °C. The dark green uranium tetrachloride was dissolved in anhydrous formic acid and reduced with liquid zinc amalgam. The olive green solid obtained corresponded to the composition $U(HCOO)_3$.

Attempts made to prepare uranium(III) acetate by a similar method were not successful. Uranium tetrachloride solutions in glacial acetic acid on reduction with liquid zinc amalgam gave intense red solutions characteristic of uranium(III). However, precipitation could not be carried out without oxidation of uranium(III).

Uranium(III) sulphate, $U_2(SO_4)_3 \cdot 8H_2O$ was obtained by electrolytic reduction of uranyl sulphate (10 g in 100 ml of 1*M* sulphuric acid) at about 10 °C. The precipitation of uranium(III) sulphate from the cold aqueous uranium(III) solution was carried out with alcohol.

The double sulphates were obtained by addition of equimolar quantities of respective ammonium, rubidium or caesium sulphate to the uranium(III) sulphate solution obtained as above.

Table I gives the chemical analysis data for uranium, carbon and hydrogen in uranium(III) formate and uranium and sulphate in the sulphates and double sulphates of uranium(III). Total uranium was determined gravimetrically as U_3O_8 after ignition of ammonium diuranate; sulphate was estimated as $BaSO_4$; carbon and hydrogen were determined by burning the sample in oxygen and estimating CO_2 and H_2O evolved by absorption in ascarite and anhydrous copper sulphate respectively.

The X-ray powder diffraction patterns of the compounds were obtained by using Siemen's X-ray diffractometer (Cuk_α radiation = 1.5418 Å). The slides were prepared and coated with Bostikote to prevent surface oxidation. The density of the compounds was determined by pyknometric method using xylene.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out by using Mettler Thermal Analyser. The products obtained by thermal decomposition in air, argon and hydrogen were characterized using X-ray, infrared and chemical methods.

TABLE III. Structural Data on Uranium(III) Compounds.

No.	Compound	Crystal System	Lattice Parameters (A)	No. of Molecules in Unit Cell (*Z*)	Density Observed (g/cm^3)	Density Calculated (g/cm^3)
1.	$U(HCOO)_3$	Hexagonal	$a = 10.68$ $c = 4.11$	3	4.4	4.6
		Rhombohedral	$a = 6.32$ $\alpha = 115°26'$	1		
2	$U_2(SO_4)_3 \cdot 8H_2O$	Orthorhombic	$a = 9.93$ $b = 9.57$ $c = 17.40$	4	3.4	3.7
3	$(NH_4)U(SO_4)_2 \cdot 4H_2O$	Monoclinic	$a = 6.67$ $b = 19.04$ $c = 8.75$ $\beta = 97°$	4	3.0	3.1
4	$RbU(SO_4)_2 \cdot 4H_2O$	Monoclinic	$a = 6.66$ $b = 19.06$ $c = 8.75$ $\beta = 97°$	4.	3.2	3.5
5	$CsU(SO_4)_2 \cdot 5.5H_2O$	Orthorhombic	$a = 16.92$ $b = 18.89$ $c = 14.56$	8	3.7	3.7

The infrared spectra were taken using Perkin-Elmer Spectrophotometer in the range (650 cm^{-1}–4000 cm^{-1}).

Results and Discussion

(A) X-Ray Diffraction Studies

The observed and calculated *d* spacings and observed intensities of powder diffraction lines have been obtained and are presented in Table II. The patterns were indexed using Hesse–Lipson and Buergers methods [7]. In Table III are reported the crystal class with lattice parameters and number of molecules in the unit cell of each compound. The calculated and measured densities are also given.

X-ray diffraction data shows that uranium(III) formate is similar to cerium(III) formate [8, 9] (unit cell values of cerous formate $a = 10.67$ Å, $c = 4.08$ Å; hexagonal) and belongs to the space group C^5_{3v}–$R3m$ with one molecule per unit cell. In analogy with corresponding cerium salt, this compound has a 9 fold coordination of the carboxyl oxygens about the uranium atom, six oxygen atoms forming the trigonal prism and other three oxygen atoms equidistant from the uranium atom. It was found that the X-ray lattice parameter data of uranium(III) sulphate, $U_2(SO_4)_3 \cdot 8H_2O$ is similar to that of cerium(III) sulphate octahydrate, $Ce_2(SO_4)_3 \cdot 8H_2O$ and has a space group $Cmca$–D^{18}_{2h} with 4 molecules per unit cell [10]. $Ce_2(SO_4)_3 \cdot 9H_2O$ on the other hand is reported to be hexagonal [10]. This further confirms that the uranium(III) sulphate prepared by us has the composition, $U_2(SO_4)_3 \cdot 8H_2O$. The very close similarities of lattice parameters of the uranium(III) compounds with the corresponding cerium(III) compounds [9, 10] are in conformity with closeness of the ionic radii of Ce^{3+} with U^{3+} (Ionic radii of Ce^{3+} = 1.03 Å and of U^{3+} = 1.03 Å) [11].

Hydrated ammonium uranium(III) sulphate and hydrated rubidium uranium(III) sulphate are indexed on the monoclinic system with 4 molecules per unit cell and cell constant data have similarity with the data on ammonium cerium(III) sulphate $(NH_4)Ce(SO_4)_2 \cdot 4H_2O$ [12] and ammonium neodymium sulphate $(NH_4)Nd(SO_4)_2 \cdot 4H_2O$ [13]. However, caesium uranium(III) sulphate $CsU(SO_4)_2 \cdot 5.5H_2O$ is indexed on the orthorhombic crystal system and contains 8 molecules in one unit cell. The differences in the structures and compositions of the caesium compound from the corresponding rubidium and ammonium compounds could be attributed to the differences in the ionic radii (Cs^+ = 1.69 Å Rb^+ = 1.48 Å NH_4^+ = 1.43 Å) [14].

Barnard and co-workers have given a composition $(NH_4)U(SO_4)_2 \cdot 4.5H_2O$ for the ammonium salt whereas from our X-ray data and comparison with the corresponding cerium and neodymium salts

[12, 13] it appears that the salt may be better represented as $NH_4U(SO_4)_2 \cdot 4H_2O$.

(B) Thermal Studies

Uranium(III) formate and uranium(III) sulphate were found to give U_3O_8 in air at 800 °C. The sulphate decomposed in air *viz.*,

$$U_2(SO_4)_3 \cdot 8H_2O \xrightarrow{350\ ^\circ C} U_2(OH_2)(SO_4)_3 \xrightarrow{600\ ^\circ C} UO_2SO_4 \xrightarrow{800\ ^\circ C} U_3O_8$$

The decomposition of ammonium uranium(III) sulphate in air was found to be similar to that of uranium(III) sulphate *i.e.*, at 650 °C, uranyl sulphate was formed, and U_3O_8 was the final product at 900 °C. Caesium uranium(III) sulphate in air at 650 °C decomposed into $Cs_2(UO_2)_2(SO_4)_3$ as confirmed by X-ray and thermogravimetry [15]; and above 1000 °C, $Cs_2U_2O_7$ was formed [16]. In argon atmosphere at 900 °C caesium salt gave a mixture of $Cs_2U_4O_{12}$ and UO_2 and gave UO_2 as the final product at temperatures greater than 950 °C. The decomposition of rubidium uranium(III) sulphate was found to be incomplete even on heating in air at 950 °C. But in argon, it gave $Rb_2U_2O_7$ [17] at 900 °C as evident from TGA and X-ray observations.

In hydrogen atmosphere at 200 °C ammonium uranium(III) sulphate was completely dehydrated, without the oxidation of uranium(III), forming anhydrous $(NH_4)U(SO_4)_2$ as confirmed by infrared and thermogravimetry and chemical analysis. On heating for 25 hrs in hydrogen, the product was still noncrystalline. Rubidium uranium(III) sulphate also gave at 200 °C in hydrogen atmosphere anhydrous $RbU(SO_4)_2$. Results of chemical analysis of the two anhydrous salts are given in Table I. Both the anhydrous compounds on treatment with concentrated hydrochloric acid gave an intense red colour which is characteristic of uranium(III). On the other hand, partial dehydration was observed with the caesium salt on being heated at 200 °C in hydrogen without the oxidation of uranium(III). The presence of water in the heated caesium salt was confirmed by infrared.

Uranium(III) sulphate $U_2(SO_4)_3 \cdot 8H_2O$, on being heated at 200 °C in hydrogen atmosphere, was partially dehydrated, without oxidation of uranium(III).

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