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X-RAY AND THERMAL STUDIES ON URANYL ACETATES OF ZINC, MAGNESIUM AND NICKEL

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Thermal decomposition of metal uranyl acetates is one of the best ways of preparation of uranates in crystalline form at low temperatures. Acetates of the type $M(UO_2)_2(OAc)_6 \cdot 7H_2O$ (M = Zn(II), Mg(II) and Ni(II) were prepared and characterised. Their X-ray powder diffraction analysis showed that they all belong to the orthorhombic crystal class.

The thermal decomposition of acetates in air goes through the reduction of uranium(VI) to uranium(IV) during acetate decomposition followed by reoxidation by oxygen. Zinc uranylacetate gave on thermal decomposition ZnU_3O_{10}, the nickel salt gave NiU_3O_{10} and the magnesium salt gave a mixture of $MgUO_4$ and MgU_3O_{10}. The thermal decomposition of acetates in helium led to reduction of uranium(VI) to uranium(IV) with the formation of UO_2. No lower valent uranates could be identified.

In uranium-metal-oxygen systems, the uranates are prepared by one of three methods: 1) heating of oxides of uranium with metal oxides or carbonates, 2) precipitation from uranyl solution with metal ions as hydroxides followed by heating, and 3) ignition of metal uranyl double salts. The last method has the advantage that compounds of definite composition can be prepared and purified and depending on the compound selected, heating can lead to a single phase without any unreacted metal or uranium oxides. Thus uranates are obtained in pure crystalline form at relatively low temperatures.

Double acetates of uranium with metal ions are one of the best sources for the preparation of uranates because of their low decomposition temperatures (300–600°). The preparation and some physicochemical studies of uranium(VI) with Zn(II), Mg(II), and Ni(II) have been reported [1] but their X-ray and thermal data are not available. In this paper we report the preparation, characterisation and thermal behaviour of some double acetates $M(UO_2)_2(CH_3COO)_6 \cdot 7H_2O$ (M = Zn, Mg and Ni).

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Experimental

The three complexes, namely $Zn(UO_2)_2(OAc)_6 \cdot 7H_2O$, $Mg(UO_2)_2(OAc)_6 \cdot 7H_2O$ and $Ni(UO_2)_2(OAc)_6 \cdot 7H_2O$ (OAc = CH_3COO) were prepared following the general method given by Hoekstra and Katz [2]. Instead of uranyl acetate, UO_3 obtained by heating uranyl nitrate at 400° was used. The acetates of Zn, Mg and Ni used were BDH quality chemicals. The UO_3 and corresponding metal acetates were mixed in a molar ratio of 2 : 1 and dissolved in 50% glacial acetic acid and evaporated to dryness. The complexes were recrystallised by dissolving the solids in 50% glacial acetic acid and slow evaporation of the solutions until a sufficient amount of crystals was obtained. The crystals were filtered, washed with acetic acid and dried with acetone. The uranium content was determined by using the modified Davies–Gray method [3]. The carbon content of the complexes was determined by decomposition of the complexes in oxygen at 900° and absorption of the CO_2 liberated in ascarite [4]. The number of water molecules was confirmed by thermogravimetric analysis.

Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) of the samples were carried out in a Mettler Thermoanalyser TA–1. Measurements were carried out with approximately 100 mg of sample in flowing dry air or helium gas at 100 ml/min. The balance was normally operated with a linearly increasing furnace temperature of 10 deg/min to a maximum temperature of 1000°. X-ray powder diffraction patterns (XRD) of the samples were taken by a Siemens X-ray diffractometer using Cu–K_α radiation (λ = 1.5418 Å).

Results and discussion

The results of chemical analysis of the double acetates prepared are given in Table 1. The compounds have been reported in literature to be orthorhombic from optical microscopy but no X-ray data have been reported in A.S.T.M. The X-ray data obtained for these compounds could be indexed on orthorhombic systems. The

Table 1 Analytical results for double acetates

Sr No	Chemical composition	Uranium, %		Carbon, %		Water, %	
		calc.	found	calc.	found	calc.	found
1	$Zn(UO_2)_2(CH_3COO)_6 \cdot 7H_2O$	43.7	44.8	13.49	13.54	11.0	11.6
2	$Mg(UO_2)_2(CH_3COO)_6 \cdot 7H_2O$	45.7	46.0	14.15	14.03	11.5	12.0
3	$Ni(UO_2)_2(CH_3COO)_6 \cdot 7H_2O$	45.0	44.6	13.66	13.58	10.8	11.7

indexed data of the zinc uranyl acetate, magnesium uranyl acetate and nickel uranyl acetate are given in Tables 2, 3 and 4, respectively. The orthorhombic cell parameters are in agreement with axial ratios reported [1].

The TG, DTA curves of the three double acetates obtained in air are shown in Fig. 1. The loss of water of crystallisation was complete at 200° and was accompanied by an endothermic DTA peak between 100–200°. The number of water molecules was calculated from the mass change observed in the TG curve. In all cases it was found to be 7. The anhydrous metal uranyl acetates start decomposing above 300°. The decomposition in air is accompanied by an exothermic DTA peak due to oxidation of organic matter. A slight mass gain observed in the TG and the DTG curves and another exothermic DTA peak around 400° follow the acetate decomposition. This could be explained on the basis of oxidation of U(IV) formed by the decomposition of the acetates. The final products of decomposition were identified by means of X-ray diffraction patterns to be uranates in which uranium is present as U(VI).

In the case of zinc uranyl acetate and nickel uranyl acetate, the products obtained were the triuranates, ZnU_3O_{10} [5] and NiU_3O_{10} [6] respectively. No other X-ray

Table 2 X-ray data for $Zn(UO_2)_2(OAc)_6 \cdot 7H_2O$
Orthorhombic, $a = 13.260$ Å, $b = 15.399$ Å, $c = 14.840$ Å, $\lambda = 1.5418$ Å

$1/d^2$, obs.	$1/d^2$, calc.	*hkl*	I/I_0
0.02203	0.02238	012	30
0.02274	0.02255	120	60
0.02290	0.02275	200	5
0.02352	0.02385	102	5
0.02662	0.02696	210	5
0.02740	0.02729	201	50
0.02784	0.02806	112	100
0.03163	0.03151	211	20
0.04107	0.04090	202	5
	0.04087	003	
0.04560	0.04513	212	5
0.04826	0.04818	131	10
0.05150	0.05118	300	20
0.05960	0.05994	311	10
0.06210	0.06180	132	15
0.06734	0.06747	040	20
0.07304	0.07315	140	15
0.07829	0.07834	104	5
0.08490	0.08451	133	5
0.09070	0.09099	400	15

Table 3 X-ray data for $Mg(UO_2)_2(OAc)_6 \cdot 7H_2O$
Orthorhombic, $a = 13.222$ Å, $b = 15.376$ Å, $c = 15.285$ Å, $\lambda = 1.5418$ Å

$1/d^2$, obs.	$1/d^2$, calc.	hkl	I/I_0
0.01691	0.01690	020	30
0.02119	0.02120	021	40
0.02289	0.02288	200	50
0.02679	0.02692	121	100
	0.02711	210	
0.03100	0.03140	211	20
0.03984	0.04000	202	20
0.04432	0.04380	130	20
	0.04408	221	
0.04873	0.04847	113	20
0.05696	0.05692	222	10
0.06127	0.06095	230	40
	0.06091	132	
0.06540	0.06523	231	60
0.07230	0.07190	041	50
0.10680	0.10655	034	5
0.11190	0.11220	134	20
0.12410	0.12390	025	10
0.13250	0.13290	251	5
0.15900	0.15920	440	5
0.17480	0.17460	045	5

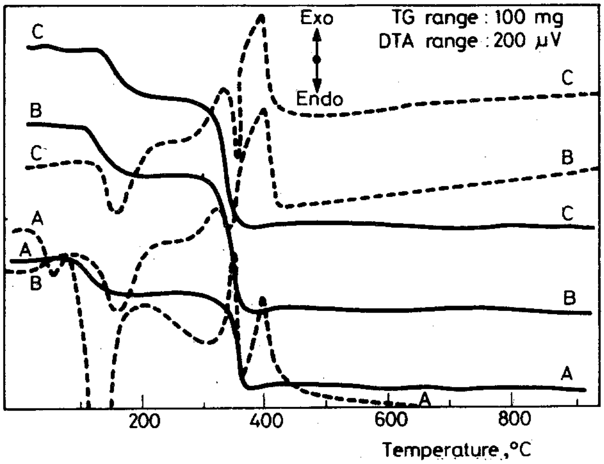

Fig. 1 TG and DTA curves of $M(UO_2)_2(CH_3COO)_6 \cdot 7H_2O$ in air TG range: 100 mg; DTA range: 200 µV. A: $Zn(UO_2)_2(CH_3COO)_6 \cdot 7H_2O$ (104.7 mg); B: $Mg(UO_2)_2(CH_3COO)_6 \cdot 7H_2O$ (152.6 mg); C: $Ni(UO_2)_2(CH_3COO)_6 \cdot 7H_2O$ (125.5 mg)

Table 4 X-ray data for $Ni(UO_2)_2(OAc)_6 \cdot 7H_2O$
Orthorhombic, $a = 13.292$ Å, $b = 15.303$ Å, $c = 14.571$ Å, $\lambda = 1.5418$ Å

$1/d^2$, obs.	$1/d^2$, calc.	*hkl*	I/I_0
0.01724	0.01708	020	50
0.02160	0.02179	021	40
0.02250	0.02264	200	100
0.02318	0.02311	012	70
0.02687	0.02691	210	70
0.02747	0.02735	201	100
0.02856	0.02877	112	20
0.03178	0.03162	211	40
0.04091	0.04148	202	5
0.04385	0.04409	130	7
0.04489	0.04443	221	25
0.04875	0.04880	131	7
0.05094	0.05094	300	15
0.05875	0.05856	222	10
0.06082	0.06107	230	15
0.06237	0.06293	132	40
0.06802	0.06802	320	70
0.07328	0.07303	041	15

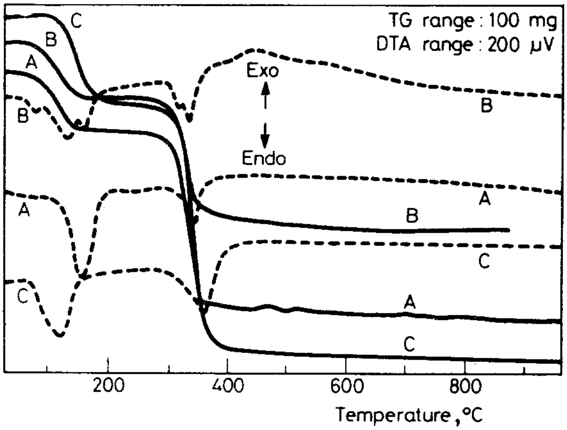

Fig. 2 TG and DTA curves of $M(UO_2)_2(CH_3COO)_6 \cdot 7H_2O$ ih helium. TG range: 100 mg; DTA range: 200 µV ; A: $Zn(UO_2)_2(CH_3COO)_6 \cdot 7H_2O$ (149.3 mg); B: $Mg(UO_2)_2(CH_3COO)_6 \cdot 7H_2O$ (127.7 mg); C: $Ni(UO_2)_2(CH_3COO)_6 \cdot 7H_2O$ (209.4 mg)

lines could be detected although the metal oxides ZnO and NiO are expected to be present on the basis of material balance in the decomposition scheme:

$$M(UO_2)_2(OAc)_6 \cdot 7H_2O \rightarrow M(UO_2)_2(OAc)_6 \rightarrow 2/3\, MU_3O_{10} + 1/3\, MO$$

This is possible because the amount of metal oxides formed was less than 5 weight% and hence could not be detected in the X-ray patterns. The product of decomposition of magnesium uranyl acetate on the other hand was a mixture of $MgUO_4$ [7] and MgU_3O_{10} [5]. Hoekstra and Katz [2] had earlier observed that magnesium diuranate prepared for the study of thermal decomposition was actually a mixture of $MgUO_4$ and MgU_3O_{10} on the basis of X-ray crystallographic data. It follows therefore that the decomposition of magnesium uranyl acetate follows the sequence:

$$2Mg(UO_2)_2(OAc)_6 \cdot 7H_2O \rightarrow 2Mg(UO_2)_2(OAc)_6 \rightarrow MgU_3O_{10} + MgUO_4$$

The thermal decomposition of these complexes has also been studied in inert helium atmosphere. The thermal curves are shown in Fig. 2. As in the case of air, the loss of water of crystallisation was complete at around 200°. An endothermic peak was present in the DTA curve. The anhydrous acetates decompose above 300° and unlike the decomposition in air, the decomposition was associated with endothermic DTA peaks. The final products isolated at 800° gave X-ray patterns of UO_2 only. Thus in helium atmosphere the acetate decomposition causes the reduction of U(VI) to U(IV) and since no mixed oxides of U(IV) with Zn(II), Mg(II) and Ni(II) are stable, UO_2 remains as the final product.

Conclusion

1) The thermal decomposition of double acetates is an easy way to prepare mixed oxides in a highly crystalline form at low temperature. Our results showed that the following mixed oxides were obtained in highly crystalline form: ZnU_3O_{10}, MgU_3O_{10}, $MgUO_4$ and NiU_3O_{10}.

2) The thermal decomposition in inert atmosphere led to reduction of U(VI) to U(IV) but did not give any lower valent uranates showing that they are not stable.

3) X-ray powder diffraction patterns of double acetates of zinc, magnesium and nickel showed that they all belonged to the orthorhombic system. This can be explained by the similarity of the ionic radii of Zn(II), Mg(II) and Ni(II).

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References

1 I. I. Chernyaev, Complex Compounds of Uranium (English translation), Israel program for scientific translation (1966), pp. 101–102.
2 H. R. Hoekstra and J. J. Katz, J. Am. Chem. Soc., 74 (1952) 1683.
3 A. R. Eberle, M. V. Lerner, C. G. Goldbeck and C. J. Rodden, NBL Report 252 (1970).
4 R. Belcher and C. E. Spooner, J. Chem. Soc. (1943) 313.
5 E. A. Ippolitova et al., Radiokhimiya, 6 (1959) 660.
6 L. M. Kovba, Vestn. Mosk. Univ., 21 (1966) 29.
7 A. P. Young, Science, 153 (1966) 1380.

Zusammenfassung — Thermische Zersetzung von Metalluranylazetaten ist eine der geeignetsten Methoden zur Darstellung kristalliner Uranate bei niedrigen Temperaturen. Azetate des Types $M(UO_2)_2(OAc)_6 \cdot 7H_2O$ mit M = Zn(II), Mg(II) und Ni(II) wurden hergestellt und beschrieben. Eine Pulverdiffraktionsanalyse zeigte, daß alle der orthorhombischen Kristallklasse angehören. Der thermische Zerfall der Azetate in Luft vollzieht sich während des Azetatzerfalls über die Reduktion von Uran(VI) zu Uran(IV) bis zu einer anschließenden Reoxydation durch Sauerstoff. Bei der thermischen Zersetzung liefert Zinkuranylazetat ZnU_3O_{10}, das Nickelsalz liefert NiU_3O_{10} und das Magnesiumsalz ein Gemisch aus $MgUO_4$ und MgU_3O_{10}. Der thermische Zerfall der Azetate in Helium führt zur Reduktion von Uran(VI) zu Uran(IV) unter Bildung von UO_3. Uranate mit niedrigerer Wertigkeit konnten nicht identifiziert werden.

Резюме — Термическое разложение металлуранил ацетатов является одним из наилучших способов низкотемпературного получения уранатов в кристаллической форме. С этой целью получены и охарактеризованы ацетаты типа $M(UO_2)_2(OAc)_6 \cdot 7H_2O$, где M = цинк, магний и никель. Порошковый рентгенодифракционный анализ показал, что все соединения относятся к орторомбической сингонии. Термическое разложение ацетатов в атмосфере воздуха протекает через стадию восстановления шестивалентного урана до четырехвалентного с последующим окислением его вновь до шестивалентного кислородом, образующимса при разложении ацетата. При термическом разложении цинковой соли уранилацетата образуется ZnU_3O_{10}, никелевой соли — NiU_3O_{10}, а при разложении магниевой соли образуется смесь $MgUO_4$ и MgU_3O_{10}. Термическое разложение ацетатов в гелиевой атмосфере приводило к восстановлению шестивалентного урана до четырехвалентного с образованием двуокиси урана. Уранаты более низкой валентности не были идентифицированы.