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FORMATION OF URANIUM MIXED OXIDES FROM THERMAL DECOMPOSITION OF URANYL PROPIONATE COMPLEXES

V. GONZÁLEZ, R. M. ROJAS and J. BERMÚDEZ

Instituto de Química Inorgánica „Elhúyar" del C. S. I. C. Facultad de Ciencias Químicas, Universidad de Madrid, Ciudad Universitaria, Madrid 3. Spain

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Four new derivatives of uranium with propionic acid, ammonium and various divalent cations have been synthesized, whose general formula corresponds to $NH_4M[UO_2(C_2H_5COO)_3]_3nH_2O$, ($M = Mn^{++}$, Co^{++}, Ni^{++} and Zn^{++}). These compounds have been studied by X-ray diffraction, differential thermal and thermogravimetric analysis, so as to identify the different solid phases isolated during heat treatment. The existence of a new double oxide of uranium and cobalt with fluorite type structure has also been shown.

The literature contains information on manganese, cobalt, nickel and zinc triuranates, MU_3O_{10} [1–7]. In all these papers, the triuranates are obtained by solid-state reactions, using as starting materials mixtures of uranium oxide U_3O_8, and the corresponding metallic oxides or carbonates; they can also be prepared by hydrothermal synthesis at high temperature and pressure. Bearing in mind that the most advantageous uranium: metal ratio to obtain these triuranates is 3 : 1, new ammonium uranyl propionate complexes with Mn, Co, Ni and Zn of the general formula $MNH_4[UO_2(C_2H_5COO)_3]_3nH_2O$ were synthesized. In the present paper it is shown that the triuranates are easily obtained by the pyrolysis of the complexes. Their thermal behaviour is investigated by DTA and TG; X-ray diffraction has been employed to identify the intermediate decomposition products.

Experimental

Apparatus

Differential thermal analysis and thermogravimetric analysis were performed in a static air atmosphere, using Deltatherm Model D-2000 equipment. α-Al_2O_3 reference material, Pt/Pt–Rh thermocouples and a heating rate of 10°/min were used for all experiments. The sample weights for DTA and TG studies were 20–30 mg and 6–8 mg, respectively. X-ray diffraction data were obtained with a Philips Model 1310 unit, using both camera (114.83 mm diameter) and diffractometer techniques (Ni-filtered, CuK_α radiation).

X-ray fluorescence analysis was carried out with a Philips Model 1540 spectrometer, using a silver anode X-ray tube. A Pye-Unicam SP-90 Series 2 atomic absorption spectrophotometer and a Coleman Model 33 microcombustion analyzer, were also used for analysis.

Synthesis of the compounds

The compounds were obtained by mixing aqueous solutions of uranyl propionate with metallic and ammonium propionates in the molar ration U : M : NH_4 = = 3 : 1 : 1. The suggested overall reaction scheme for the formation of the compounds is as follows:

$$3\,UO_2(C_2H_5COO)_2 2\,H_2O + M(C_2H_5COO)_2 + NH_4C_2H_5COO \xrightarrow{H_2O}$$
$$\rightarrow MNH_4[UO_2(C_2H_5COO)_3]_3 nH_2O$$

After prolonged standing of the resulting solutions, the complexes were isolated as well-formed crystals.

The air-dried salts were analyzed for uranium, divalent metals, carbon, hydrogen and nitrogen. Uranium content was determined by X-ray fluorescence, divalent

Table 1

Interplanar spacings, *d*, and relative intensities, *I*, for the X-ray powder patterns of $NH_4Mn\ [UO_2(C_2H_5COOO)_3]_3 \cdot 6\ H_2O$ and $NH_4Co\ [UO_2H_5COO)_3]_3 \cdot 6\ H_2O$

$NH_4Mn[UO_2(C_2H_5COO)_3]_3 \cdot \cdot 6\ H_2O$		$NH_4Co[UO_2(C_2H_5COO)_3]_3 \cdot \cdot 6H_2O$	
d Å	*I*	*d*, Å	*I*
8.29	14	8.25	7
7.97	22	7.92	20
7.56	35	7.43	12
7.24	21	7.22	23
7.02	100	6.98	90
6.83	75	6.75	45
6.50	87	6.37	100
6.36	98	6.20	25
5.92	35	5.26	34
5.30	42	5.05	25
5.11	14	4.95	27
5.05	24	4.87	11
4.90	26	4.65	6
4.54	12	4.51	7
4.35	26	4.35	3
4.22	20	4.30	23
4.15	8	4.19	15
4.08	20	4.14	8
4.04	13	4.06	30
3.96	23	3.95	25
3.88	33	3.87	23
3.85	9	3.75	16
3.78	9	3.70	42
3.70	43	3.58	15
3.60	37	3.49	34
3.51	45	3.39	12
		3.24	4

metals by atomic absorption spectrophotometry, and carbon, hydrogen and nitrogen by the microcombustion method. The results of the analysis are given below:

Calculated for $MnNH_4[UO_2(C_2H_5COO)_3]_3 6 H_2O$ (%): C 19.66; H 3.70; N 0.85; U 43.32; Mn 3.30. Found (%): C 19.60; H 3.58; N 0.86; U 43.47; Mn 3.35.
Calculated for $CoNH_4[UO_2(C_2H_5COO)_3]_3 6 H_2O$ (%): C 19.61; H 3.69; N 0.84; U 43.22; Co 3.57. Found (%): C 19.64; H 3.62; N 0.85; U 43.49; Co 3.61.
Calculated for $NiNH_4[UO_2(C_2H_5COO)_3]_3 7 H_2O$ (%): C 19.40; H 3.77; N 0.83; U 42.76; Ni 3.51. Found (%): C 19.48; H 3.68; N 0.85; U 42.90; Ni 3.35.
Calculated for $ZnNH_4[UO_2(C_2H_5COO)_3]_3 8 H_2O$ (%): C 19.12; H 3.83; N 0.82; U 42.27; Zn 3.86. Found (%): C 19.19; H 3.96; N 0.83; U 42.27; Zn 3.96.

The interplanar spacings and relative intensities of the X-ray powder patterns of these compounds are reported in Tables 1 and 2.

Table 2

Interplanar spacings, *d* and relative intensities, *I* for the X-ray powder patterns of $NH_4Ni\ [UO_2(C_2H_5COO)_3]_3 \cdot 7\ H_2O$ and $NH_4Zn\ [UO_2(C_2H_5COO)_3]_3 \cdot 8\ H_2O$

$NH_4Ni[UO_2(C_2H_5COO)_3]_3 \cdot 7\ H_2O$		$NH_4Zn[UO_2(C_2H_5COO)_3]_3 \cdot 8\ H_2O$	
d, Å	*I*	*d*, Å	*I*
8.22	10	8.30	4
7.88	32	7.93	9
7.40	20	7.45	6
7.19	18	6.97	100
6.94	87	6.75	18
6.73	84	6.50	18
6.41	100	6.33	29
6.36	93	6.23	10
6.23	35	5.26	7
5.26	32	5.09	9
5.07	28	4.94	6
4.94	35	4.29	6
4.88	29	4.21	9
4.81	8	4.14	5
4.55	15	4.06	8
4.49	17	3.96	8
4.27	3	3.87	7
4.20	28	3.83	8
4.14	22	3.74	2
4.09	25	3.70	7
4.05	15	3.66	6
3.95	20	3.57	5
3.85	38	3.49	45
3.55	13	3.24	3
3.52	36	2.83	3
3.47	20	2.76	10
3.37	24		

Results and discussion

DTA and TG curves of the compounds are given in Figs 1–3. Tables 3 and 4 show in detail the interpretation given to the observed thermal effects.

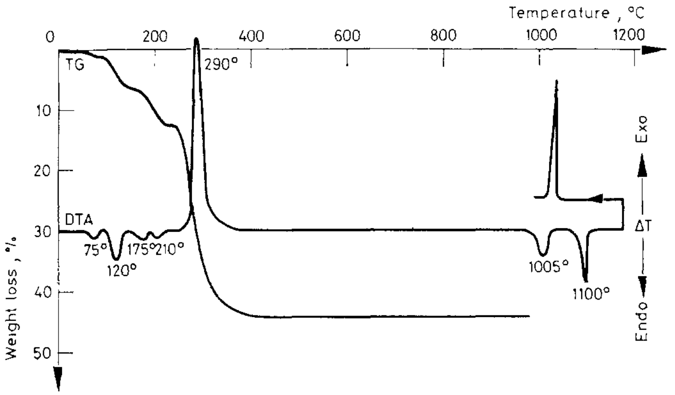

Fig. 1. DTA and TG curves of $NH_4Mn[UO_2(C_2H_5COO)_3]_3 \cdot 6\ H_2O$

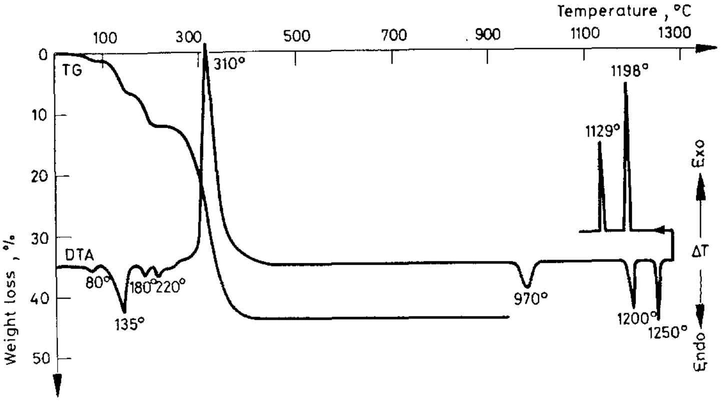

Fig. 2. DTA and TG curves of $NH_4Co[UO_2(C_2H_5COO)_3]_3 \cdot 6\ H_2O$

Ammonium manganese and ammonium cobalt uranyl propionates

Both compounds dehydrate in two successive steps; the anhydrous complexes decompose between 150 and 230° with the elimination of one molecule of ammonium propionate. An exothermic decomposition of the residual products takes place at about 245°, giving as residues MnU_3O_{10} and CoU_3O_{10}, as indicated by their X-ray powder diffraction patterns in the temperature range 450–950°. Both manganese and cobalt triuranates decompose at 980°, to a mixture of $MnUO_4$ or $CoUO_4$ and U_3O_8.

Table 3

Thermal behaviour of manganese and cobalt ammonium uranyl propionates

Compound	Thermal effect, T °C	Reaction	Weight loss, %	
			Calc.	Found
$NH_4Mn\ [UO_2(C_2H_5COO)_3]_3 \cdot 6\ H_2O$	50— 80	Removal of 1 water molecule	1.08	1.04
	90— 140	Removal of 5 water molecules	5.46	5.46
	150— 230	Removal of ammonium propionate molecule	5.52	5.47
	245— 385	Removal of the remainder organic matter to yield MnU_3O_{10}	31.55	31.49
	980—1020	Decomposition of MnU_3O_{10}		
	180—1103	Formation of MnU_2O_6		
$NH_4Co\ [UO_2(C_2H_5COO)_3]_3 \cdot 6\ H_2O$	70— 90	Removal of 1 water molecule	1.09	1.07
	90— 150	Removal of 5 water molecules	5.44	5.43
	160— 230	Removal of ammonium propionate molecule	5.50	5.57
	255— 400	Removal of the remainder organic matter to yield CoU_3O_{10}	31.49	31.90
	980—1020	Decomposition of CoU_3O_{10}		
	1186—1209	Formation of $Co_3U_2O_8$		
	1236—1254	Formation of CoU_2O_6		

The endothermic reversible effect observed at 1100° in the DTA curve of ammonium manganese uranyl propionate is attributed to the reaction between $MnUO_4$ and U_3O_8 to give manganese diuranate with a fluorite type structure [8]; the excess of uranium is in the form of U_3O_8.

In the case of the mixture $CoUO_4$ and U_3O_8, the decomposition of cobalt monouranate to $Co_3U_2O_8$ produces the endothermic effect observed at 1200°. The reflections corresponding to the hexagonal form of CoU_2O_6 that, according to Bacmann [9], is also formed when $CoUO_4$ decomposes, has not been detected in the X-ray diagrams.

Table 4

Thermal behaviour of nickel and zinc ammonium uranyl propionates

Compound	Thermal effect, T °C	Reaction	Weight loss, %	
			Calc.	Found
$NH_4Ni[UO_2(C_2H_5COO)_3]_3 \cdot 7\ H_2O$	75– 100	Removal of 1 water molecule	1.08	1.03
	110– 150	Removal of 6 water molecules	6.46	6.50
	160– 240	Removal of ammonium propionate molecule	5.45	5.49
	250– 325	Removal of the remainder organic matter to yield NiU_3O_{10}	31.14	30.77
	970–1010	Decomposition of NiU_3O_{10}	0.96	1.10
$NH_4Zn[UO_2(C_2H_5COO)_3]_3 \cdot 8\ H_2O$	70– 85	Removal of 1 water molecule	1.06	1.07
	90– 150	Removal of 7 water molecules	7.43	7.52
	160– 250	Removal of ammonium propionate molecule	5.37	5.36
	255– 375	Removal of the remainder organic matter to yield ZnU_3O_{10}	30.69	30.26
	970–1020	Decomposition of ZnU_3O_{10}	0.95	0.95

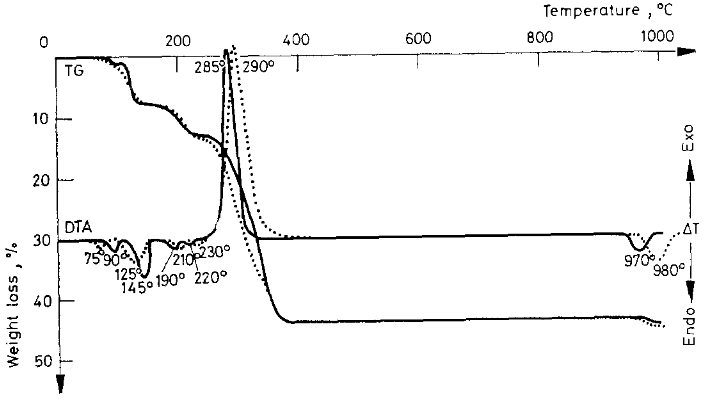

Fig. 3. DTA and TG curves of $NH_4Ni[UO_2(C_2H_5COO)_3]_3 \cdot 7\ H_2O$ (——), and $NH_4Zn[UO_2(C_2H_5COO)_3]_3 \cdot 8\ H_2O$ (. . . .)

At 1250°, $Co_3U_2O_8$ reacts with the stoichiometric quantity of the residual uranium oxide U_3O_8, and the compound obtained at 1300° corresponds to the cubic disordered form of CoU_2O_6, as shown by its X-ray diffraction pattern [10].

Ammonium nickel and ammonium zinc uranyl propionates

The thermal behaviours of nickel and zinc ammonium uranyl propionates follow very similar courses, as shown in their DTA and TG curves in Fig. 3. They lose one water molecule without modifying their X-ray powder patterns. The second endothermic effects for the zinc and nickel compounds are attributed to the evolution of six and seven water molecules, respectively. The anhydrous compounds lose one molecule of ammonium propionate, and after the pyrolysis reaction the residues isolated correspond to NiU_3O_{10} and ZnU_3O_{10}, respectively. The last endothermic effects observed in both DTA curves correspond to the decomposition of these triuranates to give a mixture of U_3O_8 and the metallic oxides, NiO and ZnO, which are stable up to the maximum temperature reached.

As can be seen, the formation of the metallic triuranates occurs more directly and at considerably lower temperatures than those generally used by other authors. This fact could be due both to the correct U/M ratio in the starting compounds and the greater reactivity of the intermediate uranium and metallic oxides, formed probably after the pyrolysis of the complexes, thereby reducing the diffusion problems at the molecular level.

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Résumé — Quatre nouveaux dérivés de l'uranium avec l'acide propionique, l'ammonium et divers cations bivalents ont été synthétisés. Leur formule générale correspond à $NH_4M[UO_2(C_2H_5COO)_3]_3\ nH_2O$, ($M = Mn^{++}$, Co^{++}, Ni^{++} et Zn^{++}). Ces composés ont été examinés par diffraction des rayons X ainsi que par analyses thermique et thermogravimétrique afin d'identifier les différentes phases solides isolées pendant leur traitement thermique. L'existence d'un nouvel oxyde double d'uranium et de cobalt de structure type fluorine est également démontrée.

ZUSAMMENFASSUNG — Vier neue Derivate des Urans mit Propionsäure, Ammonium und verschiedenen zweiwertigen Kationen wurden synthetisiert. Die allgemeine Formel ist: $NH_4M[UO_2(C_2H_5COO)_3]_3nH_2O$, ($M = Mn^{++}$, Co^{++}, Ni^{++} und Zn^{++}). Diese Verbindungen wurden durch Röntgendiffraktion, Differentialthermoanalyse und thermogravimetrische Analyse untersucht um die während der Wärmebehandlung isolierten verschiedenen Festphasen zu identifizieren. Die Existenz eines neuen Doppeloxides von Uran und Cobalt mit einer Struktur von Fluorit-Typ wurde ebenfalls nachgewiesen.

Резюме — Синтезированы четыре новых производных урана с пропионовой кислотой, аммонием и с различными двухвалентными катионами с общей формулой $NH_4M[UO_2(C_2H_5COO)_3]_3 \cdot nH_2O$, где $M = Mn^{++}$, Co^{++}, Ni^{++} и Zn^{++}. Соединения были изучены с помощью рентгено-диффракционного анализа, дифференциального термического и термогравиметрического анализа, с тем чтобы идентифицировать различные твердые фазы, выделенные во время тепловой обработки. Доказано существование новой двойной окиси урана и кобальта с флюоритной структурой.