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SYNTHESIS, CHARACTERIZATION AND THERMAL DECOMPOSITION OF URANYL PROPIONATE COMPLEXES WITH Zn, Mn, Ni and Co

M. M. ESPIGARES,* J. B. POLONIO and E. G. RIOS

Instituto de Quimica Inorganica "Eluyar" C. S. I. C. Madrid, España
** Junta de Energia Nuclear, Madrid, España.*

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Uranyl propionate complexes of Zn(II), Mn(II), Ni(II) and Co(II), of the general formula $M[(C_2H_5COO)_3UO_2]_2 \cdot nH_2O$, have been synthesized and studied by differential thermal analysis, thermogravimetry and X-ray diffraction.

The resulting products of pyrolysis have been identified as the corresponding metal diuranates $U_3O_{10}M$.

Several investigations on the preparation and properties of the uranyl propionate compounds with alkaline metals have been published. E. Rimbach [1] reported the preparation of potassium uranyl propionate in 1904. Papers published later [2, 3] describe the preparation of complexes of uranyl propionates with rubidium, caesium, ammonium and potassium giving X-ray data.

In recent year considerable attention has been directed to the study of uranyl propionate complexes with lithium and sodium [4, 5].

Studies of uranyl propionate complexes with other metals have not appeared in the literature. This paper describes the synthesis, characterisation and thermal behaviour of the uranyl propionate complexes with Zn(II), Mn(II), Ni(II) and Co(II). The paper also describes studies of the products of pyrolysis using X-ray diffraction. The presence of the resulting triuranates has been confirmed by the preparation of the stoichiometric mixtures.

Experimental

Reagents and apparatus

All the syntheses were carried out with analytical grade reagents.

Thermogravimetric (TG) and differential thermal analysis (DTA) curves were recorded with a Deltatherm Model D-3000 apparatus in static air atmosphere; the heating rate for both TG and DTA experiments was 5°/min.

X-ray patterns were obtained with a Philips Model 1310/00 diffractometer using Ni-filtered, Cu K_α radiation. A 114.83 powder camera was also used for identification purposes. The metals, M(II), were analysed with a Beckman Model 440 atomic absorption spectrophotometer.

Synthesis and analysis

The general method of preparation involved the reaction, in aqueous propionic acid solution, of uranyl propionate with the respective metal propionate. The metal propionate were obtained by the reaction of the metal carbonate with propionic acid. Uranyl propionate and metal propionate solutions in the U : M molar ratio 2 : 1 were mixed; the mixture was concentrated by warming at about 70°. After cooling and prolonged standing of the resulting solution well-formed crystals were obtained.

The general method of synthesis takes place according the following scheme:

$$2[UO_2(C_2H_5COO)_2] + M[(C_2H_5COO)_2] \rightarrow M[(C_2H_5COO)_3UO_2]_2 \cdot nH_2O$$

The resulting crystals were filtered off, washed with a small portion of cold water and dried by sucking air through the filter. All the salts can be recrystallized from a dilute solution of propionic acid.

The zinc and manganese uranyl propionate crystals are greenish-yellow and the nickel and cobalt ones are pale-green and amber, respectively.

The compounds were analyzed for uranium, M(II), carbon and hydrogen. Uranium was determined after reduction to U(IV) and subsequent titration with ceric sulphate. The divalent metals were analysed by atomic absorption spectroscopy, after extraction of uranium with trioctylphosphine oxide (TOPO) [6] or by ion exchange [7].

The results of the analyses are given below:

Calculated for $Zn[(C_2H_5COO)_3UO_2]_2 \cdot 6H_2O$
% Carbon 18.76, % Hydrogen 3.12, % Uranium 45.63, % Zinc 6.2

Experimental
% Carbon 18.93, % Hydrogen 3.32, % Uranium 45.48, % Zinc 5.9

Calculated for $Mn[(C_2H_5COO)_3UO_2]_2 \cdot 7H_2O$
% Carbon 18.92, % Hydrogen 3.15, % Uranium 46.07, % Manganese 5.30

Experimental
% Carbon 19.00, % Hydrogen 3.40, % Uranium 46.23, % Manganese 5.10

Calculated for $Ni[(C_2H_5COO)_3UO_2]_2 \cdot 8H_2O$
% Carbon 18.87, % Hydrogen 3.14, % Uranium 45.80, % Nickel 5.66

Experimental
% Carbon 18.79, % Hydrogen 3.11, % Uranium 45.75, % Nickel 5.62

Calculated for $Co[(C_2H_5COO)_3UO_2]_2 \cdot 7H_2O$
% Carbon 18.86, % Hydrogen 3.13, % Uranium 45.90, % Cobalt 5.67

Experimental
% Carbon 18.83, % Hydrogen 3.08, % Uranium 45.83, % Cobalt 5.67

Results and discussion

Thermal analysis curves of the compounds are given in Figs 1 and 2. Table 1 shows the interpretation given to the observed thermal effects.

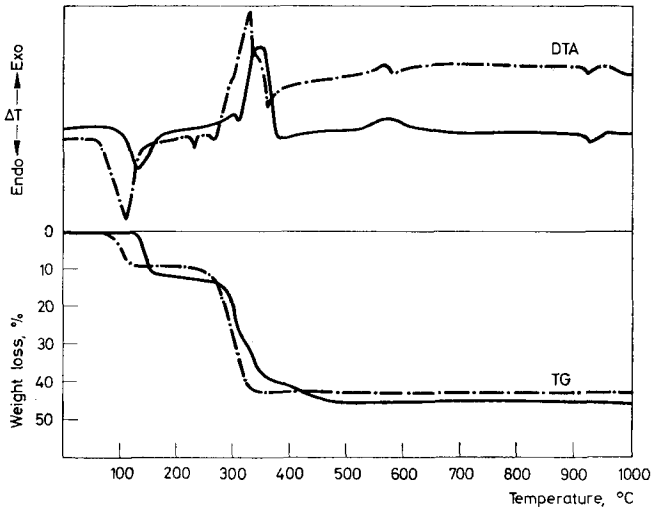

Fig. 1. DTA and TG curves of $Zn[(C_2H_5COO)_3UO_2]_2 \cdot 6H_2O$ (—.—.—), and of $Ni[(C_2H_5COO)_3UO_2]_2 \cdot 8H_2O$ (— — —)

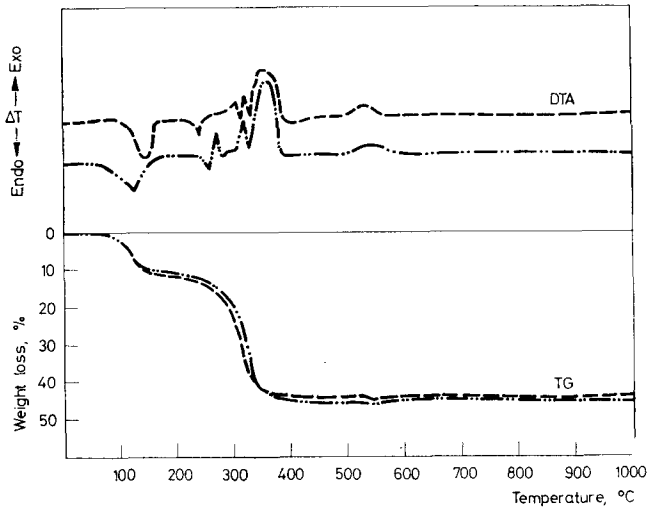

Fig. 2. DTA and TG curves of $Mn[(C_2H_5COO)_3UO_2]_2 \cdot 7H_2O$ (—..—..—), and of $Co[(C_2H_5COO)_3UO_2]_2 \cdot 7H_2O$ (— — —)

Table 1

Thermal behaviour of the metal uranyl propionate compounds

Compound	Thermal effect (T °C)	Transformation	Weight loss (%)	
			calculated	found
$Zn[(C_2H_5COO)_3UO_2]_2 \cdot 6H_2O$	70–140	Dehydration	9.38	9.00
	250	Melting		
	260–380	Removal of organic matter	34.30	34.20
	~550	Formation of $ZnU_3O_{10}+ZnO$		
	~961	Decomposition to form $U_3O_8 + ZnO$ *		
$Mn[(C_2H_5COO)_3UO_2]_2 \cdot 7H_2O$	80–180	Dehydration	10.80	10.27
	265	Melting		
	270–380	Removal of organic matter	33.73	34.81
	500–600	Formation of $MnU_3O_{10}+MnO$		
$Ni[(C_2H_5COO)_3UO_2]_2 \cdot 8H_2O$	120–170	Dehydration	12.20	12.70
	270–380	Removal of organic matter	33.00	32.90
	500–600	Formation of $NiU_3O_{10}+NiO$		
	900	Decomposition to form $U_3O_8 + NiO$ *		
$Co[(C_2H_5COO)_3UO_2]_2 \cdot 7H_2O$	100–170	Dehydration	10.83	10.72
	250	Melting		
	280–400	Removal of organic matter	33.54	33.72
	500–600	Formation of $CoU_3O_{10}+CoO$		
	1000	Formation of $CoUO_4+U_3O_8$		

* Not observable — The decompositions have been confirmed by X-ray.

The first endothermic peak and weight loss are attributed to the stoichiometric water removal from all the compounds. X-ray studies show that the crystalline structures of the initial hydrated compounds and the anhydrous ones are equal.

The second endothermic effect observed for the zinc, manganese and cobalt compounds is due to the melting of the products. The accurately melting points have been determined. According to our observations, the nickel compound did not show a melting point.

The thermal effects and the corresponding weight losses observed in the temperature range 260–400° are due to the pyrolysis of the compounds and removal of the organic matter. The decomposition occurs inmediatly after the melting. The X-ray diffraction patterns of the products in the temperature range 400–500° are typical of amorphous substances.

The weak exothermic effect for all compounds at about 550° is due to the formation of crystalline substances, stable up to 900°. These substances have been identified as the corresponding metal triuranates.

Table 2

Interplanar spacings, d (Å), and relative intensities, I, for the X-ray powder patterns of U_3O_{10}(Zn, Mn, Ni,) and $CoUO_4$

ZnU_3O_{10}		MnU_3O_{10}		NiU_3O_{10}		$CoUO_4$	
d	I	d	I	d	I	d	I
5.14	8	5.11	7	5.12	12	4.59	60
4.13*	63	4.70	22	4.74	12	4.14*	81
3.43*	8	4.13	60	4.06	57	3.47	23
3.29	100	3.47	8	3.87	8	3.42*	86
2.97	6	3.35	21	3.38	15	3.35*	52
2.64*	8	3.30	25	3.28	100	2.24	98
2.62*	6	3.27	100	3.02	10	2.76	100
2.57	67	2.80	40	2.96	10	2.67	25
2.37	6	2.56	52	2.55	50	2.63*	73
2.08	8	2.42	10	2.37	8	2.60*	45
2.06	17	2.35	8	2.08	12	2.37	40
1.98	6	2.06	21	2.02	18	2.29	30
1.89	25	1.95	8	1.97	10	2.12	34
1.76	8	1.89	23	1.89	25	2.10	25
1.74	27	1.81	14	1.74	10	2.02	22
1.72	20	1.79	13	1.71	27	1.99*	27
1.64	13	1.74	21	1.63	15	1.95*	23
1.52	12	1.71	14	1.59	8	1.82	23
		1.63	10	1.52	12	1.80*	35
		1.52	8			1.77	25
		1.43	6			1.74	20
						1.65*	28
						1.60	22
						1.58*	17
						1.55*	24
						1.47	20
						1.42	23

X: U_3O_8 reflexions

The results of the analyses of the compounds after heating at 800° are given below.

Calculated for $ZnU_3O_{10} + ZnO$
% Uranium 72.88, % Zinc 9.99

Experimental
% Uranium 72.24, % Zinc 9.63

Calculated for $MnU_3O_{10} + MnO$
% Uranium 74.04, % Manganese 8.53

Experimental
% Uranium 73.65, % Manganese 8.12

Calculated for $NiU_3O_{10} + NiO$
% Uranium 73.60, % Nickel 9.00

Experimental
% Uranium 72.57, % Nickel 8.29

Calculated for $CoU_3O_{10} + CoO$
% Uranium 73.57, % Cobalt 9.10

Experimental
% Uranium 72.36, % Cobalt 8.70

The interplanar spacings and relative intensities of the X-ray powder patterns for these triuranates are reported in (Table 2).

The nickel and zinc triuranates decomposed at temperatures of about 900° and 961° respectively yielding U_3O_8 and MO as shown by X-ray diffraction patterns.

The formation of these triuranates was confirmed by air heating, at 800–900°, of the mixtures of the metal carbonate and U_3O_8 in the ratio U : M, 2 : 1 in accordance with similar methods reported in the literature for the preparation of certain uranates [8. 9].

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RÉSUMÉ — On a synthétisé puis étudié par ATD, TG et diffraction des rayons X les complexes d'uranylpropionate de Zn(II), Mn(II), Ni(II) et Co(II), de formule générale $M[(C_2H_5COO)_3UO_2]_2 \cdot nH_2O$. Les produits de la pyrolyse ont été identifiés comme étant les triuranates des métaux correspondants, de formule MU_3O_{10}.

ZUSAMMENFASSUNG — Der allgemeinen Formel $M[(C_2H_5COO)_3UO_2]_2 \cdot nH_2O$ entsprechende Uranylpropionat-Komplexe von Zn(II), Mn(II), Ni(II) und Co(II) wurden synthetisiert und mittels Differentialthermoanalyse, Thermogravimetrie und Röntgendiffraktion untersucht.

Die entstandenen Pyrolyseprodukte wurden als die entsprechenden Metall-Triuranate der Formel MU_3O_{10} identifiziert.

Резюме — Уранилпропионатные комплексы Zn(II), Mn(II), Ni(II) и Co(II) общей формулы $M[(C_2H_5COO)_3.UO_2]_2 \cdot nH_2O$ были синтезированы и изучены с помощью дифференциального термического анализа, термогравиметрического анализа и диффракции рентгеновых лучей. Образующиеся продукты пиролиза были идентифицированы как диуранаты соответствующих металлов общей формулы MU_3O_{10}.