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.

(Received April 26, 1974; in revised form June 10, 1974)

Uranyl propionate complexes of Zn(II), Mn(II), Ni(II) and Co(II), of the general formula M[(C\textsubscript{3}H\textsubscript{5}COO)\textsubscript{3}UO\textsubscript{2}]\textsubscript{n}·nH\textsubscript{2}O, 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\textsubscript{3}O\textsubscript{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\textsubscript{\alpha} 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°C. 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 analyzed 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

*J. Thermal Anal.* 8, 1975