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Compounds of Thorium and Quadrivalent Uranium with Benzoylacetone and Dibenzoylmethane

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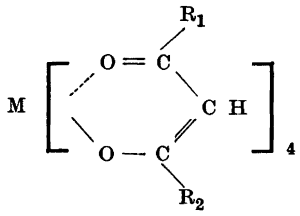
Partly for some attempts to obtain a Szilard-Chalmers concentration of thorium, partly for a magnetochemical investigation, it was of interest to prepare the six complex compounds



where M = Th or U^{IV} and R_1, R_2 = CH_3 or C_6H_5.

A good method used for the preparation of thoriumacetylacetonate is the one described in *Inorganic Syntheses* [1]. Uranium(IV)acetylacetonate was prepared according to Biltz and Clinch [2], with some small modifications.

It does not appear that the other compounds, included in the above formula, have been reported in the literature. This paper describes the preparation of these chelate compounds and some of their properties.

The thorium compounds were prepared by treating a solution of benzoylacetone or dibenzoylmethane in ether, with a solution of thorium nitrate in water, and adding ammonia until the mixture had about pH 7. The uranium compounds could not conveniently be prepared in that way, on account of the rapid oxidation of the quadrivalent uranium. It was, however, possible to synthetize them in a hot, saturated, alkaline solution of diketone in water to which an uranium solution was added. The work with the uranium compounds in solution was carried out in nitrogen atmosphere.

EXPERIMENTAL

Preparation of the diketones *. Acetylacetone and dibenzoylmethane were prepared according to methods given in *Org. Syntheses* [3, 4]. Benzoylacetonate was prepared by condensation of acetylacetate with acetophenone according to Fischer [5].

Preparation of the uranium(IV)solution. Uranium(IV)solution was prepared by electrolytic reduction of uranyl chloride in hydrochloric acid solution, according to a modification of a method described by Rosenheim and Loebel [6]. In order to obtain the reduction to quadrivalent state of uranium it was, however, not necessary to exclude air from the reduction vessel. However, for preservation, the uranium(IV)solution was kept in nitrogen atmosphere.

Analysis of thorium and uranium. The complex compounds were decomposed by strong nitric acid. After evaporation up to dryness the residue was ignited over the blast to constant weight. Thus thorium was determined as ThO_2 and uranium as U_3O_8.

In order to determine the concentration of quadrivalent uranium in the uranium solutions, titration with permanganate was used [7].

Thorium benzoylacetonate

27 g of benzoylacetone was dissolved in 250 ml ether and the solution was added to a solution of 17 g $Th(NO_3)_4$, $4HO_2$ in 40 ml of water. The solutions were shaken after each addition of small portions of 4 *N* ammonia until the complex salt precipitated. 4 *N* ammonia was then added drop by drop until the mixture just became alkaline. When the ether layer had been poured off, the precipitated thorium benzoylacetonate was filtered off on a Büchner funnel, washed with a small portion of ether, and after that with hot water.

When the precipitate had been dried in a vacuum desiccator, it was recrystallized from benzene. M. p. 212—213° C (dec). Yield 18.6 g (69 %).

$C_{40}H_{36}O_8Th$ (876.8)	Calc.	C	54,79	H	4.14	Th	26.47
	Found	»	54.38	»	4.14	»	26.46

Thoriumbenzoylacetonate constitutes a pale-yellow powder, insoluble in water, acetone, ethanol and ether, slightly soluble in benzene, toluene (about 0.4 g/l), aniline and pyridine (about 1 g/l).

Thorium dibenzoylmethane

10 g of dibenzoylmethane was dissolved in 50 ml ether. This solution was added to a solution of 5 g $Th(NO_3)_4$, $4H_2O$ in 15 ml of water. The complex compound was then prepared in the same manner as the benzoylacetonate. Excess of ammonia was avoided. An excess could conveniently be counteracted by a small portion of acetic acid.

The precipitate was recrystallized from benzene. M. p. about 196° C (dec). Yield 5.1 g (49 %).

$C_{60}H_{44}O_8Th$ (1125.1)	Calc.	C	64.04	H	3.94	Th	20.63
	Found	»	64.01	»	3.98	»	20.51

* These preparations were carried out by Mr. K. Halvarson, whom I wish to thank.

Thorium dibenzoylmethane forms yellow crystals, insoluble in water and ethanol, soluble in acetone, ether, benzene (about 50 g/l) and toluene, very soluble in pyridine.

Uranium(IV)acetylacetonate

This compound was prepared according to Biltz and Clinch [2]. However, it was found to be advisable to recrystalize from ether in nitrogen atmosphere. Without this precaution the substance was easily oxidized. Its colour became yellow-green, and the analysis gave too high values of the uranium content. Also by recrystallization from toluene in air, the compound was easily oxidized.

The recrystallizations in nitrogen atmosphere were carried out in a Soxhlet apparatus, where the bulb was provided with a glass inlet tube for the gas from a nitrogen container.

The decomposition of the acetylacetonate seems to begin at about 165° C, and the melting point at about 177° C is vague. The yield of the recrystallized product was 40 %.

It is soluble in acetone, ethanol, ether, benzene, toluene (about 40 g/l) and pyridine.

Uranium(IV)benzoylacetonate

To 150 ml of a solution of UCl_4(0.20 C) and HCl(3.8 C) were added first 17 g of sodium acetate and then with rapid stirring a solution of 15 g NaOH in water. 15 g benzoylacetonate was dissolved at about 65° C in 600 ml water, containing 5 g of NaOH. The stirring was carried on and the solution added to the buffered uranium solution, which was first heated to 65° C. A dark-brown precipitate was formed, which easily clogged together and adhered to the glass walls. It was filtered off on a Büchner funnel and washed with hot water and afterwards with portions of ethanol. The precipitation and the rapid filtration was suitably carried out in air.

The substance was dried in a vacuum desiccator and then recrystallized from benzene in nitrogen atmosphere. M. p. about 210° C (dec). Yield 13.3 g (65 %).

$C_{40}H_{36}O_8U$ (882.7)·	Calc.	C	54.42	H	4.11	U 26.97
	Found	»	54.89	»	4.17	» 26.50

Uranium(IV)benzoylacetonate forms a red-brown powder insoluble in water, very slightly soluble in ethanol, ether and toluene, slightly soluble in benzene and soluble in pyridine. It is easily oxidized by air in solutions.

Uranium(IV)dibenzoylmethane

To 80 ml of a solution of UCl_4 (0.22 C) and HCl(5.1 C) were added, first 10 g of sodium acetate, and then under stirring a solution of 12 g NaOH in water. 15 g dibenzoylmethane was dissolved at about 65° C in 600 ml water containing 4 g NaOH. The preparation was then done in the same way as the preparation of the benzoylacetonate.

The compound was recrystallized from benzene in nitrogen atmosphere. M. p. 198—199° C. The decomposition begins at about 180° C. Yield: 10.4 g (55 %).

$C_{60}H_{44}O_8U$ (1131.0)	Calc.	C	63.71	H	3.92	U 21.05
	Found	»	63.71	»	3.95	» 20.86

Uranium(IV)dibenzoylmethane forms a red-brown powder, insoluble in water, slightly soluble in ethanol, soluble in acetone, ether, benzene and pyridine.

It might be possible to find addition compounds of the described thorium and uranium complex compounds with different solvents. However, attempts to prepare such compounds have not been made.

SUMMARY

Preparations of thorium benzoylacetonate, thorium dibenzoylmethane, uranium(IV)benzoylacetone and uranium(IV)dibenzoylmethane have been described. The method to prepare uranium(IV)acetylacetonate given by Biltz and Clinch has been commented.

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