Chemistry

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1962

SovietRxiv

Abstract

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On the Preparation of Mixed Oxalato-Carbonato Complex Compounds of Thorium

(Presented by Academician V. I. Spitsyn, May 11, 1962)

In recent years, in connection with the use of thorium for the production of nuclear energy, the attention of researchers to this long-known element has increased sharply. In particular, the question of complex formation by thorium is of great practical and theoretical interest. This element exhibits a strong tendency to form complex compounds with various anions. However, the literature data on complex compounds of thorium are rather scanty. It is true that in recent years reports on studies of thorium complex compounds, in particular carbonato and oxalato compounds, have begun to appear increasingly often in the literature ([1–8]).

We were unable to find in the literature data on mixed oxalato-carbonato complex compounds of thorium; there are only fragmentary indications of the good solubility of thorium oxalate in carbonate solutions. Until recently there were also no data in the literature on oxalato-carbonato compounds of tetravalent uranium. A work was published comparatively recently ([9]) reporting the preparation of oxalato-carbonato complexes of tetravalent uranium. As for tetravalent plutonium, a series of mixed oxalato-carbonato complex compounds with different numbers of oxalato and carbonato groups had been obtained for it considerably earlier ([10]).

Experimental Part

To obtain mixed oxalato-carbonato complex compounds of thorium, we used thorium oxalate and sodium and potassium carbonates as starting materials. When these reagents interact in water, readily soluble complex compounds are formed.

Oxalato-carbonato complexes of thorium with sodium in the outer sphere. To carry out the syntheses, we took the starting substances in definite molar ratios and, depending on the ratio of the reagents, obtained products of one composition or another.

Thus, at the molar ratio
$Th(C_2O_4)_2 \cdot 6H_2O : Na_2CO_3 = 1 : 5$, we took, in one series of experiments, 3 g

of thorium oxalate, 3.1 g of sodium carbonate, and 50 ml of water. The interaction proceeded at room temperature. The resulting solution of the complex compound was poured into the same or a somewhat larger volume of ethyl alcohol. A white, finely crystalline precipitate separated. It was filtered off, washed with alcohol, dried in air at room temperature, and then analyzed. The analysis gave:

	Th	H_2O	C_2O_4''	CO_2
In percent	20.94	17.69	17.31	15.50
By ratio	1	11	2.1	3.9

Thus, the composition of the substance obtained may be expressed by the formula $Na_8Th(C_2O_4)_2(CO_3)_4 \cdot 11H_2O$.

Wishing to clarify the question of the influence of the concentration of the reagents on the composition of the complex formed, in the second series of experiments, with the same amounts of thorium oxalate and sodium carbonate (ratio 1 : 5), we took half as much water, i.e., 25 ml. The composition of the product isolated in this case differs only in its water content.

In analysis of the air-dry substance it was found:

	Th	H_2O	C_2O_4''	CO_2
In percent	22.52	16.61	15.82	16.76
By ratio	1	9.5	1.85	3.98

The composition of the substance obtained may be expressed by the formula $Na_8Th(C_2O_4)_2(CO_3)_4 \cdot 9.5H_2O$. The syntheses were reproduced several times, and the composition of the products obtained was the same each time; only the water content in the product sometimes varied. Under the microscope the substance obtained appears homogeneous, but its crystals are so small that it is not possible to determine their refractive indices. To obtain larger crystals, we attempted to isolate this complex by slow crystallization from an aqueous solution. As usual, 3 g of thorium oxalate were treated with a solution of soda (3.1 g in 25 ml of water), and the resulting solution of the complex was left to evaporate at room temperature until the greater part of the substance had crystallized. The crystals that separated were carefully suction-filtered on a Büchner funnel, dried in air, and analyzed. These experiments showed that from the aqueous solution a substance of the same composition separates —$Na_8Th(C_2O_4)_2(CO_3)_4 \cdot 9$–$10.5H_2O$.

The substance obtained consists of plate-like crystals with refractive indices $N_g = 1.500$; $N_m = 1.489$; $N_p = 1.483$. The water in the isolated complex proves to be water of crystallization; it is completely lost at a temperature of 105–110°.

When thorium oxalate and sodium carbonate interact in a molar ratio of 1 : 6, a complex of another composition is formed. By pouring into alcohol, a substance was isolated containing

	Th	H_2O	C_2O_4''	CO_2
In percent	19.51	16.84	15.65	18.14
By ratio	1	11	2.1	4.9

This composition of the substance corresponds to the formula $Na_{10}Th(C_2O_4)_2(CO_3)_5 \cdot 11H_2O$. Under the microscope the substance obtained appears homogeneous. The refractive indices of the crystals are $N_g = 1.502$; $N_m = 1.489$; $N_p = 1.473$. At the same molar ratio of the reagents, from an aqueous solution, by evaporation at room temperature, a substance of a different composition precipitates first. On its analysis it was found:

	Th	H_2O	C_2O_4''	CO_2
In percent	22.58	19.86	8.54	20.78
By ratio	1	11.3	0.99	4.85

This corresponds to the formula $Na_8Th(C_2O_4)(CO_3)_5 \cdot 11H_2O$. Under the microscope the crystals of this substance have the form of long thin rods. The refractive indices of the crystals are $N_g = 1.556$; $N_p = 1.440$. After separation of this substance, after some time a second phase separates from the mother liquor, which consists mainly of sodium oxalate.

On the basis of this example it may be supposed that the complex isolated in the solid state is not identical with the complex present in solution, and that the composition of the isolated complex depends on the method of isolation.

Thorium oxalato-carbonato complexes with potassium in the outer sphere. Starting from the ratio

$Th(C_2O_4)_2 \cdot 6H_2O : K_2CO_3 = 1 : 4$; 3 g of thorium oxalate, 3.2 g of potassium carbonate, and 50 ml of water were taken. As a result of their interaction at room temperature, a clear colorless solution was formed. This solution was poured into alcohol with thorough stirring. Two liquid layers were thereby obtained: the upper one—turbid and occupying the greater part of the volume—and the lower one—of small volume, consisting of a heavy syrup-like liquid. The layers were separated from one another, and the lower layer was treated several times with alcohol until it crystallized.

The substance obtained was dried in air, ground to a powder, and analyzed. Its analysis gave the following figures:

	Th	H_2O	C_2O_4''	CO_2
In percent	27.25	12.46	12.26	16.79
By ratio	1	5.9	1.2	3.2

Thus, the composition of the substance obtained may be expressed by the formula $K_4Th(C_2O_4)(CO_3)_3 \cdot 6H_2O$.

Syntheses were carried out in a similar manner at a molar ratio of the reacting substances of 1 : 6. In these cases the isolated complexes contained one additional carbonate group; their composition was expressed by the formula $K_6Th(C_2O_4)(CO_3)_4 \cdot 6$—$8H_2O$.

As is evident from the data presented, all the isolated complexes contain a smaller number of carbonate groups than they should if all of the carbonate introduced were consumed in the formation of the complex. In addition, attention is drawn to the fact that, at the same ratio of the reacting substances (1 : 6), in the case of the interaction of thorium oxalate with Na_2CO_3, complexes of more complex composition are isolated than in the case of interaction with K_2CO_3.

It is possible that both types of complexes have a more complex composition in solution, and that in the course of isolation in the solid state they undergo certain changes; moreover, these changes affect the sodium complexes to a lesser extent, since the sodium complexes, when treated with alcohol, are immediately isolated in crystalline form, whereas the potassium complexes change more, since they are subjected to prolonged treatment with alcohol in order to be isolated in crystalline form.

Analyses of the substances obtained were carried out by known methods. Thorium was precipitated as thorium oxalate and ignited to the dioxide; the oxalate ion was determined by titration with a potassium permanganate solution; for determination of the carbonate ion, a weighed portion of the complex was decomposed with acid and the evolved CO_2 was absorbed by Ascarite. Water was determined from the loss in weight after keeping the substance in a drying oven at a temperature of 110—150°.

In aqueous solutions all the substances obtained are readily hydrolyzed. The study of the properties of the compounds obtained is continuing.

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Received
9 V 1962

REFERENCES

1. I. I. Chernyaev, V. A. Golovnya, A. K. Molodkin, ZhNKh, 3, No. 12, 2671 (1957).

2. B. Frank, Ann. Univ. M. Curie-Sklodowska, AA-II, 47, 1956 (1958), cited in RZhKhim., No. 14, 48993 (1959).
3. I. I. Chernyaev, V. A. Golovnya, A. K. Molodkin, ZhNKh, 6, 2, 394 (1961).
4. I. I. Chernyaev, A. K. Molodkin, ZhNKh, 6, 4, 809 (1961).
5. K. N. N. Kutur, Proc. Indian Acad. Sci., A, 47, No. 6, 373 (1958).
6. Monisha Bose, D. M. Chowdhury, J. Indian Chem. Soc., 32, 673 (1955).
7. N. P. Luzhnaya, I. S. Kovaleva, ZhNKh, 6, 6 (1961).
8. M. Boutelsky, H. A. J. Ben-Bassat, Bull. Soc. Chim. France, No. 2, 233 (1958).
9. V. A. Golovnya, G. T. Bolotova, ZhNKh, 6, 11, 2488 (1961).
10. A. D. Gelman, L. M. Zaitsev, ZhNKh, 3, 7, 1555 (1958).

Note: Figure translations are in progress. See original paper for figures.