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Abstract

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ON THE PREPARATION OF OXALATO-SULFITE AND SULFITE COMPLEX COMPOUNDS OF THORIUM AND URANIUM (IV)

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Researchers' interest in thorium and uranium compounds has greatly increased in recent years in connection with the use of these elements for the production of nuclear energy. In particular, the question of complex formation by these elements with oxalate and sulfite ions is of great practical and theoretical interest. It is known that when an alkali-metal sulfite or sulfur dioxide is dissolved in a solution of a thorium salt, a white precipitate is formed, corresponding to the composition $Th(SO_3)_2 \cdot H_2O$ ([1–4]). This precipitate is somewhat soluble in an excess of alkali-metal sulfites, with formation of complex compounds. Grossman ([4]) reports compounds of composition $2K_2SO_3 \cdot Th(OH)_2(SO_3) \cdot 10H_2O$ and $2Na_2SO_3 \cdot Th_2(OH)_2(SO_3)_3 \cdot xH_2O$. For uranium, the normal salt $U(SO_3)_2$ is still unknown. Rosenheim and Kelmy ([5]) described the preparation of complex compounds of composition: $(NH_4)_4[U(SO_3)_4]$, $Na_6[U_2(SO_3)_7] \cdot 2H_2O$, $K_6[U_2(SO_3)_7] \cdot 12H_2O$, $CN_3H_6[U(SO_3)_2OH] \cdot 2H_2O$. These compounds were obtained by the interaction of salts of tetravalent uranium with sulfites of alkali metals, ammonium, or guanidine. The same work gives a method for obtaining the salt $(NH_4)_4[Th(SO_3)_4] \cdot 6H_2O$. This exhausts the information available to us in the literature on sulfite compounds of thorium and uranium (IV). There is no information at all in the literature on mixed oxalato-sulfite compounds of these elements.

The aim of our work was the isolation and investigation of hitherto unknown complex compounds of thorium and uranium (IV) with oxalate and sulfite ions.

The starting substances for the synthesis of mixed complex thorium compounds were thorium oxalate and sodium sulfite. At room temperature, thorium oxalate dissolves fairly well in concentrated sodium sulfite solutions, which indicates the formation of complex compounds. When the resulting solution is poured into alcohol, the complex separates as a heavy syrup-like mass which, upon repeated treatment with alcohol, is converted into a white crystalline substance.

Analyses established that the isolated complexes are mixed oxalato-sulfites, and their composition can be expressed by the general formula $Na_{2n}[Th(C_2O_4)_2(SO_3)_n] \cdot x\ H_2O$. As our experiments showed, the number of sulfite groups in the complex depends on the molar ratio in which the starting substances are taken, and also on their concentration. We carried out two series of experiments. In the first series, for 3 g of thorium oxalate we took the corresponding weighed amount of sodium sulfite and, in all cases, a constant volume of water—25 ml. Under these conditions, at a molar ratio of the starting substances of 1 : 4, the precipitated complex has the composition $Na_6[Th(C_2O_4)_2(SO_3)_3] \cdot 5{-}6H_2O$. On analysis it was found:

	Th	C_2O_4	SO_3	Na	H_2O
In %	24.42	18.96	25.0	15.76	10.54
By ratio	1	2	2.9	6.5	5.5

At the molar ratio
$Th(C_2O_4)_2 \cdot 6H_2O : Na_2SO_3 = 1 : 5$ the composition of the isolated complex corresponds to the formula
$Na_8[Th(C_2O_4)_2(SO_3)_4] \cdot 6H_2O$, which was established on the basis of analyses. The analysis gave the following figures:

	Th	C_2O_4	SO_3	Na	H_2O
In %	21.57	15.55	30.33	17.64	9.98
By ratio	1	2	4.1	7.8	6.0

As a result of the interaction of thorium oxalate and sodium sulfite, taken in the molar ratio 1 : 6, a complex of composition
$Na_{10}[Th(C_2O_4)_2(SO_3)_5] \cdot 5{-}6H_2O$ is isolated, which is confirmed by analyses:

	Th	C_2O_4	SO_3	Na	H_2O
In %	19.55	14.78	34.30	20.33	8.15
By ratio	1	2	5	10.5	5.4

In the interaction of the starting substances in ratios 1 : 7 and 1 : 8, complexes of composition
$Na_{12}[Th(C_2O_4)_2(SO_3)_6] \cdot 5{-}6H_2O$ and
$Na_{14}[Th(C_2O_4)_2(SO_3)_7] \cdot 5{-}6H_2O$, respectively, are isolated. As is evident from the data presented, under these conditions complexes are isolated that contain one sulfite group fewer than was taken according to the ratio.

In the second series of experiments, with the same quantities of the starting substances, we took 50 ml of water, i.e., reduced the concentration by half. In

these cases complexes were isolated that contained two sulfite groups fewer than had been taken according to the ratio. Thus, at a ratio of thorium oxalate to sodium sulfite = 1 : 6, a complex of composition
$Na_8[Th(C_2O_4)_2(SO_3)_4] \cdot 5H_2O$ was isolated. At ratios 1 : 7 and 1 : 8, complexes of composition
$Na_{10}[Th(C_2O_4)_2(SO_3)_5] \cdot 5H_2O$ and
$Na_{12}[Th(C_2O_4)_2(SO_3)_6] \cdot 5H_2O$, respectively, were isolated.

By similar methods, through the interaction of uranium oxalate and sodium sulfite, a series of oxalato-sulfite complex compounds of tetravalent uranium was obtained. At the ratio
$U(C_2O_4)_2 \cdot 6H_2O : Na_2SO_3 = 1 : 2$, a complex was obtained corresponding to the composition
$Na_2[U(C_2O_4)_2 \cdot SO_3(H_2O)_2] \cdot 3.5H_2O$. Analysis found:

	U	C_2O_4	SO_3	Na	H_2O
In %	37.1	26.2	12.1	7.3	10.0
By ratio	1	1.91	0.97	2.0	3.58

At the ratio
$U(C_2O_4)_2 \cdot 6H_2O : Na_2SO_3 = 1 : 3$, a substance was isolated corresponding to the composition
$Na_4[U(C_2O_4)_2(SO_3)_2] \cdot 2H_2O$, which is confirmed by analyses:

	U	C_2O_4	SO_3	Na	H_2O
In %	34.1	24.4	23.5	12.0	5.0
By ratio	1	1.95	2.07	3.7	2

If the starting substances were taken in the ratio 1 : 4, a complex of composition $Na_6[U(C_2O_4)_2(SO_3)_3] \cdot 5H_2O$ was obtained. On analysis it was found:

	U	C_2O_4	SO_3	Na	H_2O
In %	26.6	18.9	26.0	16.5	10.3
By ratio	1	1.96	2.99	6.1	4.8

Taking uranium oxalate and sodium sulfite in the ratio 1 : 5, a complex
$Na_8[U(C_2O_4)_2(SO_3)_4] \cdot 4H_2O$ was obtained, the analyses of which gave the following figures:

	U	C_2O_4	SO_3	Na	H_2O
In %	22.8	16.5	30.6	19.5	6.8
By ratio	1	1.95	3.99	8.85	4.0

At ratios of the initial substances of 1 : 6 and 1 : 8, complexes of the compositions $Na_{10}[U(C_2O_4)_2(SO_3)_5] \cdot 7.5H_2O$ and $Na_{12}[U(C_2O_4)_2(SO_3)_6] \cdot 7–8H_2O$, respectively, were obtained. Analysis of the first of these gave:

	U	C_2O_4	SO_3	Na	H_2O
In %	20.2	14.8	33.3	20.3	11.2
By ratio	1	2.0	5.0	10.3	7.4

Analysis of the second complex gave:

	U	C_2O_4	SO_3	Na	H_2O
In %	17.7	12.7	36.2	21.9	10.0
By ratio	1	1.9	6.08	12.8	7.5

For all the isolated uranium complexes, as for the thorium complexes, the presence of two oxalate groups and of a variable number of sulfite groups is characteristic; this number depends on the ratio of the starting substances and on their concentration in solution.

The complex structure of the ions $[Me(C_2O_4)_2(SO_3)_n]^{2n-}$ was confirmed by absorption on the anion exchanger AV-17, as well as by replacement of the outer-sphere cation (sodium by barium).

Assuming that the coordination number of thorium and tetravalent uranium in the complex compounds is 8, one must allow that the oxalate and sulfite groups in the isolated complexes may occupy either one or two coordination sites. As for the complex $Na_{14}[Th(C_2O_4)_2(SO_3)_7]$, something definite about its structure can be said only after additional investigation has been carried out.

In addition to mixed uranium(IV) complexes, we isolated purely sulfite complexes: $Na_6[U(SO_3)_5] \cdot nH_2O$, $Na_8[U(SO_3)_6] \cdot nH_2O$, $Na_{10}[U(SO_3)_7] \cdot nH_2O$, $Na_{12}[U(SO_3)_8] \cdot nH_2O$. To obtain them, the complex salt $K_3H_3[U(NO_3)_{10}] \cdot 3H_2O$, prepared by a previously developed method ([6]), and anhydrous sodium sulfite were used. All the isolated complexes are finely crystalline powders, which appear homogeneous under the microscope. However, it was not possible to determine the refractive indices of the crystals because of their extremely small size. The investigation is continuing.

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REFERENCES CITED

[1] Chydenius, Pogg. Ann., **119**, 43 (1863).
[2] Cleve, Bull. Soc. Chim., **21**, 115 (1874).
[3] R. Chavastelon, C. R., **130**, 781 (1900).
[4] H. Grossmann, Zs. anorg. Chem., **44**, 229 (1905).
[5] A. Rosenheim, M. Kelmy, Zs. anorg. Chem., **206**, 31 (1932).
[6] H. H. Krot, N. P. Ermolaev, A. D. Gelman, ZhNKh, **11**, 9, 2034 (1962).

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