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Abstract

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On Some Urea-Containing Complex Thorium Halides

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The existence of a large number of thorium compounds, diverse in composition, with such neutral ligands as ammonia ([1]-[3]), organic amines ([3]), and various oxygen-containing organic molecules of the ketone, aldehyde, and alcohol type, etc. ([6]), can be explained by the clearly expressed acceptor properties of the thorium atom. Compounds of this type should also include the numerous thorium hydrates. As a rule, coordination in all these compounds occurs through the free electron pair of the ligand.

It is known from the literature that urea, in the overwhelming majority of its compounds, also acts as a neutral ligand ([7]-[9]). The nature of the interaction of urea with various uranyl salts ([10], [11]) and tetravalent uranium ([12]) indicates the great reactivity of urea toward these complex-forming agents as well. The ease with which urea coordinates is explained by the presence in it of a highly polar carbonyl group and a sufficiently large dipole moment (4.56 D) ([13], [14]). In addition, the unshared pair of electrons present on nitrogen in the NH_2 group can also participate in bonding with the central atom ([15]). We have studied the nature of the interaction of several thorium salts with urea.

There is no information in the published literature on similar thorium compounds.

We have carried out the synthesis of a series of urea-containing thorium halides and have studied some of their properties. The synthesis of such compounds was conducted in methanolic solutions in order to exclude, to a considerable extent, the influence of water molecules during their formation. Table 1 gives the synthesis conditions and the results of analysis of the isolated compounds.

Table 1

$ThHal_4 : (NH_2)_2CO$ (mole : mole) in the initial solution	Compound	Thorium found, %	Thorium calc., %	Halogen found, %	Halogen calc., %	Nitrogen found, %	Nitrogen calc., %	N_p	N_m	N_g	d^{25}, g/cm^3
1 : 6	$ThCl_4 \cdot 6(NH_2)_2CO \cdot 2H_2O$	30.00	30.13	19.02	18.42	21.42	21.82				2.072
1 : 8	$ThCl_4 \cdot 8(NH_2)_2CO$	27.30	27.17	16.04	16.57	26.40	26.23	1.563	1.596	1.649	2.170
1 : 6	$ThBr_4 \cdot 6(NH_2)_2 \cdot 2H_2O$	24.59	24.95	34.70	34.38	18.06	18.08	1.625	1.646	1.656	2.44
1 : 8	$ThBr_4 \cdot 8(NH_2)_2CO$	22.26	22.49	30.54	30.99	22.01	21.71	1.595	1.632	1.661	2.31
1 : 8	$ThJ_4 \cdot 8(NH_2)_2CO$	19.32	19.02	41.30	41.62	18.17	18.37				2.42

All the compounds synthesized by us are crystalline diamagnetic substances. Their individuality was established by repeated synthesis, by crystal-optical and thermogravimetric methods, and by studying absorption in the infrared region of the spectrum.

The urea-containing thorium halides are readily soluble in water and methanol; they do not dissolve in ether, benzene, acetone, etc.

Data on the determination of molar electrical conductivity indicate their dissociation in aqueous solutions:

$$\begin{aligned} ThCl_4 \cdot 8(NH_2)_2CO \quad & \mu_{250} = 489\ \Omega^{-1} \cdot cm^2\ (pH\ 2.8), \\ ThCl_4 \cdot 6(NH_2)_2CO \cdot 2H_2O \quad & \mu_{250} = 495\ \Omega^{-1} \cdot cm^2\ (pH\ 3), \\ ThBr_4 \cdot 8(NH_2)_2CO \quad & \mu_{250} = 510\ \Omega^{-1} \cdot cm^2\ (pH\ 2.5), \\ ThBr_4 \cdot 6(NH_2)_2CO \cdot 2H_2O \quad & \mu_{250} = 495\ \Omega^{-1} \cdot cm^2\ (pH\ 3), \\ ThJ_4 \cdot 8(NH_2)_2CO \quad & \mu_{250} = 497\ \Omega^{-1} \cdot cm^2\ (pH\ 2.9). \end{aligned}$$

In anhydrous methanolic solution the compounds are more stable. The thermal stability of the compounds studied was investigated. It is characteristic that the thermal decomposition of the compounds $ThCl_4 \cdot 8(NH_2)_2CO$, $ThBr_4 \cdot 8(NH_2)_2CO$, and $ThJ_4 \cdot 8(NH_2)_2CO$ proceeds in approximately the same temperature interval (135-350°) and ends at a temperature of the order of 500-600°. The decomposition of $ThCl_4 \cdot 6(NH_2)_2CO \cdot 2H_2O$ and $ThBr_4 \cdot 6(NH_2)_2CO \cdot 2H_2O$ begins at lower temperatures, of the order of 75 and 100°, respectively. In the absorption spectra of the urea-containing thorium halides, all the frequencies of the carbonyl group of urea are observed, while the maximum frequency values in this region do not exceed 1640 cm^{-1}, which is characteristic of urea coordinated through Me—O bonds.

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

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