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Abstract

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CHEMISTRY

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STUDY OF THORIUM COMPLEX FORMATION BY METHODS OF ION EXCHANGE, INFRARED SPECTROSCOPY, AND NUCLEAR MAGNETIC RESONANCE

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Ion-exchange method. The study of complex compounds of thorium with certain organic acids is of theoretical and practical significance, since it can provide important information for the rational separation of thorium and other elements by the ion-exchange method. Although many works have appeared in this field, there are still few quantitative data on complex formation of thorium with organic acids. Taking this circumstance into account, we studied the complex formation of thorium with malic, trihydroxyglutaric, tartaric, α-hydroxyisobutyric, and mandelic acids at different concentrations of addend and pH, by the ion-exchange method. The results of our studies for the first three acids were compared with the data of O. E. Zvyagintsev and L. G. Khromenkova^(1), obtained by the conductometric method. We determined the average effective charge of the complex thorium ions with these acids by the method

Table 1

Acid	$[A^-]$, mol/l	pH	Ionic strength, μ	Instability constants by Paramonova's method	Instability constants by Fronaeus' method	Proposed composition
Malic	3.8	2	0.3	$K_1 = 7.00 \cdot 10^{-6} K_2 = 2.00 \cdot 10^{-7}$	–	$[\mathrm{Th(HA)}_n]^{3n+}[\mathrm{Th(HA)}_{2n}]^{2n+}$
Trihydroxyglutaric	7.7	2	0.3	$K_1 = 3.00 \cdot 10^{-5}$	–	$[\mathrm{Th(HA)}_n]^{3n+}$
Tartaric	9.9	2	0.3	$K_1 = 2.30 \cdot 10^{-5}$	–	$[\mathrm{Th(HA)}_n]^{3+}$
Mandelic	3.0	2.2	0.2	$K_2 = 1.14 \cdot 10^{-3} K_2 = 1.04 \cdot 10^{-5} K_3 = 1.24 \cdot 10^{-6}$	$K_1 = 1.82 \cdot 10^{-3} K_2 = 0.67 \cdot 10^{-5} K_3 = 1.92 \cdot 10^{-7}$	$[\mathrm{Th(A)}_n]^{3n+}[\mathrm{Th(A)}_{2n}]^{2n+}[\mathrm{Th(A)}_{3n}]^{n+}$
α-Hydroxyisobutyric	2.0	2.2	0.2	$K_1 = 2.74 \cdot 10^{-4} K_2 = 2.98 \cdot 10^{-6} K_3 = 8.40 \cdot 10^{-8}$	$K_1 = 3.87 \cdot 10^{-4} K_2 = 2.44 \cdot 10^{-6} K_2 = 8.34 \cdot 10^{-9}$	$[\mathrm{Th(A)}_n]^{3n+}[\mathrm{Th(A)}_{2n}]^{2n+}[\mathrm{Th(A)}_{3n}]^{n+}$

Table 2

Acid	$[A^-]$, mol/l	pH	Ionic strength, μ	Average effective charge z
Malic	$3.8 \cdot 10^{-3}$	2	0.3	+10.4
Malic	$9.2 \cdot 10^{-4}$	2	0.3	+10.3
Malic	$2.3 \cdot 10^{-4}$	2	0.3	+10.8
Malic	$3.8 \cdot 10^{-5}$	2	0.3	+4.6
Hydrochloric	10^{-1}	2	0.3	+4.2

Acid	$[A^-]$, mol/l	pH	Ionic strength, μ	Average effective charge z
Trihydroxyglutaric	$7.7 \cdot 10^{-4}$	2.8	0.3	+2.0
α-Hydroxyisobutyric	10^{-3}	2.2	0.2	+3.3
Mandelic	10^{-2}	2.2	0.2	−0.4
Mandelic	$1.42 \cdot 10^{-3}$	2.2	0.2	+3.1
Mandelic	$0.57 \cdot 10^{-4}$	2.2	0.2	+3.8

ion exchange ([2]). The values of the instability constants obtained by us are given in Table 1. The mean effective charge (Table 2) made it possible to conclude that the forms of existence of thorium complex ions in solutions of the above-mentioned acids that we proposed are justified. From Table 2 it is seen that in a solution of malic acid thorium forms polynuclear complex ions, i.e., a process of polymeric association takes place through the formation of hydrogen bridges. We did not detect a similar phenomenon in solution for the other thorium complex ions studied.

Infrared spectroscopy method. To study the structure of thorium complex compounds by the IR spectroscopy method, we synthesized in an acidic medium a series of thorium complexes with malic, trihydroxyglutaric, α-oxyisobutyric, mandelic, acetic, thiosalicylic, and p-aminosalicylic acids. Analyses for the content of C, H, H_2O, and ThO_2 made it possible to assign to these thorium complex compounds the following structural formulas, given in Table 3.

Table 3

ThO_2, g calculated	ThO_2, g found	Thorium compound	Proposed formula
0.1300	0.1240	Malate	$[ThA_2] \cdot 1{-}2H_2O$
0.0194	0.0191	Trioxiglutarate	$[ThA_2] \cdot H_2O$
0.1520	0.1500	Mandelate	$[ThA_4] \cdot xH_2O$
0.1250	0.1230	α-Oxyisobutyrate	$[ThA_4] \cdot xH_2O$
0.1268	0.0270	Acetate	$[Th(OH)_2A_2] \cdot H_2O$
0.0390	0.0391	Thiosalicylate	$[Th_2(OH)_2A_3] \cdot H_2O$
–	–	p-Aminosalicylate	$[Th(OH)_3A] \cdot 3H_2O$

We recorded the infrared spectra of the listed compounds on an IKS-14 spectrometer with LiF, NaCl, and KBr prisms, in hexachlorobutadiene for the LiF

region and in vaseline oil for the NaCl region. Interpretation of the IR spectra shows that thorium in these compounds is bound mainly to the addend through the carboxyl group, and not to the oxy group of these oxy acids.

In the case of thorium *p*-aminosalicylate, thorium is also coordinatively bound to the amino group. In thorium thiosalicylate, thorium is bound, in addition to the carboxyl group, also to the thio group (SH). Study of the IR spectrum of thorium acetate shows that, in the formation of this compound, polymeric association occurs as a result of the formation of hydrogen bonds. We established the formation of intermolecular hydrogen bonds also in the compounds of thorium malate, trioxiglutarate, and mandelate. The X-ray diffraction patterns obtained for these compounds establish that thorium thiosalicylate, *p*-aminosalicylate, and malate are X-ray-amorphous substances.

Nuclear magnetic resonance. The nuclear magnetic resonance spectra were recorded on a medium-resolution spectrograph at the Institute of Atomic Physics (Bucharest)* at $B = 1175$ gauss and frequency $\nu = 5$ MHz for proton resonance. We studied thorium acetate, and, for comparison of the data obtained, we also studied the proton resonance of magnesium acetate. The obtained derivative curves of proton resonance show that for thorium acetate the mean width (δH) is equal to 0.7485 gauss, and for magnesium acetate 5.250 gauss. To determine the second moment, a calculation was carried out on the basis that the obtained proton-resonance curves are well described by a Gaussian function

$$f(H) \sim Fe^{-\frac{(H-H_0)^2}{2\beta^2}}.$$

* The authors consider it their pleasant duty to express gratitude to Marti Weiner and Adrian Valeriu for valuable assistance in recording the resonance spectra.

From the formula

$$\Delta H_2^2 = \frac{\int_{-\infty}^{\infty} f(H)(H-H_0)^2\,dH}{\int_{-\infty}^{\infty} f(H)\,dH}$$

we found from the experimental data that, for thorium acetate, $\Delta H_2^2 = 0.14$ G^2, and for magnesium acetate, 6.89 G^2. The decrease in the value of the second moment for thorium acetate to $\Delta H_2^2 = 0.14$ indicates the presence of a process of polymeric association in this compound.

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