Precipitation of Thorium or Uranium(VI) Complex Ion with Cobalt(III) or Chromium(III) Complex Cation, (II)

Precipitation of Thorium and Uranium(VI) Sulfito Complex Ions

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The precipitations of thorium and uranium(VI) sulfito complex ions with hexammine cobalt(III) chloride as the precipitant have been studied. The orange-colored uranium(VI) precipitate obtained is \( \left[ \text{Co(NH}_3\right]_6\text{UO}_2\text{(SO}_3\text{)}_3\text{]Cl}_2\text{H}_2\text{O} \), which is in the form of square bipyramid, about 4 \( \mu \text{m} \) across in a cubic symmetry of the diamond type with \( a=10.40 \) \( \text{Å} \). It decomposes to an oxide mixture of \( \text{Co}_3\text{O}_4 \) and \( \text{U}_3\text{O}_8 \) above 850°C in the air through a sulfate mixture of \( \text{CoSO}_4 \) and \( \text{UO}_2\text{SO}_4 \).

Composition of the thorium precipitate varies with the precipitation conditions. Therefore, it is considered that the thorium precipitate contains thorium hydroxide and basic thorium sulfite.

**KEYWORDS:** precipitation, thorium sulfito complex ion, uranium(VI) sulfito complex ion, hexammine cobalt(III) cation, ammonium sulfites, cobalt(II) sulfate, uranium(VI) sulfate, thermogravimetric analysis, differential thermal analysis

I. INTRODUCTION

The ability of sulfite ion to form complexes with metal cation is reported to be higher than that of sulfate or oxalate ion\(^{(1)}\). Sulfite compounds of thorium and uranium(VI) were prepared and studied by spectrophotometric, IR and NMR spectroscopic and thermoanalytical methods in U.S.S.R.\(^{(2)}\)\(^{–}\)\(^{(5)}\). It was shown that sulfite ions are present as a bidentate ligand and sulfito complexes of thorium and uranium(VI) ions are nearer to the carbonato complexes than to the sulfato or oxalato complexes. It is thus possible that thorium and uranium(VI) sulfito complex ions are precipitated from ammonium sulfite solution with hexammine cobalt(III) ion similarly to the case of carbonato complex ions\(^{(6)}\).

The present work was carried out to see any possibility of the formation of sulfito complex compounds of thorium and uranium(VI) ions with hexammine cobalt(III) ion. Hexaurea chromium(III) ion was not used, because it precipitates as the sulfite under the experimental conditions.

Sulfite ion is used as a reductant of uranium(VI) to uranium(IV) in the acidic medium\(^{(7)}\). In the preliminary experiment, however, it was confirmed that hexammine cobalt(III) and uranium(VI) ions were not reduced in ammonium sulfite solution.

II. EXPERIMENTAL

1. Reagents Used

Thorium and uranium(VI) salts were purified by ion exchange and solvent extraction\(^{(8)}\).

The stock solutions of thorium and uranium(VI) were prepared by the procedure reported previously\(^{(9)}\). Concentrations of the stock solutions were 14.7 mgTh/ml in 0.5 N HCl and 10.6 mgU/ml in 0.5 N HCl.

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Commercial reagent grade ammonium sulfite was used without purification. Concentration of the ammonium sulfite stock solution was 2.5 M.

The precipitant, i.e. hexammine cobalt(III) chloride ([Co(NH₃)₆]Cl₃) was prepared by Biltz's method (10). Concentration of the precipitant stock solution was 0.2 M.

All other reagents used were of analytical grade.

2. Precipitation Conditions
Experiments were all carried out with total volume 1 ml at room temperature (25±3°C). One-tenth milliliter of thorium uranium(VI) stock solution was added to 0.3~0.7 ml of ammonium sulfite stock solution. The solution was adjusted to a suitable volume by addition of distilled water. And, to it was gradually added 0.1~4.4 ml of the precipitant stock solution. Thus, the precipitate was produced as a function of ammonium sulfite and precipitant concentrations.

The solution with the precipitate was stood for one day. The concentration of a metal ion in the supernatant was determined by spectrophotometry (11)(12).

3. Chemical Analyses
The precipitate was filtered out with a sintered glass filter (G-4) and washed with distilled water until the washings became colorless. It was then dried in the air for several days.

The dried precipitate was dissolved in dilute hydrochloric acid containing iodine. The content of hexammine cobalt(III) ion was determined by spectrophotometry at 475 nm (13). The content of sulfite ion was determined by titration using iodine (14). Content of the metal ion was determined by the method just described (11)(12).

4. Thermal Analyses
Thermogravimetric and differential thermal analyses were made by using a Rigaku Denki Model 8902 instrument. A portion of the dried precipitate was transferred to a microcrucible and heated at a rate of 20°C/min in air.

Solubility measurement and crystallographic analyses of the precipitate were made by the methods reported previously (15).

III. RESULTS AND DISCUSSION
In the present study the concentration of sulfite was above 0.75 M. Therefore, most of thorium or uranium(VI) ions are considered to exist in the chemical species of [Th(SO₃)₄]⁴⁻ or [UO₂(SO₄)₃]⁴⁻ by comparing the ability of complex formation of sulfite ion with that of carbonate or oxalate ion, although there is no quantitative data (15). The transparent solution of sulfito complex ion was not obtained below 0.5 M ammonium sulfite because of the formation of thorium hydroxide.

Orange-colored precipitate was produced in addition of the precipitant stock solution to the thorium or uranium(VI) sulfito complex ion solution. Figure 1 shows precipitation behavior of thorium and uranium(VI) sulfito complex ions with hexammine cobalt(III) cation.
complex ions. The concentration of thorium ion in the supernatant decreases monotonously with precipitant concentration and increases with sulfite concentration. The concentration of uranium(VI) ion in the supernatant decreases with precipitant concentration, but it is almost constant with sulfite concentration of 0.75~1.75 M.

Composition of the thorium precipitate varies with the precipitate conditions as shown in Table 1; thorium content of the precipitate decreases with increasing sulfite and decreasing precipitant concentrations. However, composition of the uranium(VI) precipitate is constant independent of the precipitation conditions; it corresponds to $[\text{Co(NH}_3\text{)_6}]^{2+}$.[UO$_4$(SO$_3$)$_3$]$_3$$\text{H}_2\text{O}$ (Found: Co(NH$_3$)$_6$ 25.3, U 27.8, SO$_3$ 26.9; Calcd.: Co(NH$_3$)$_6$ 25.1, U 27.8, SO$_3$ 28.0 %). Solubility of the uranium(VI) precipitate in water is 1.75 mgU/100 gH$_2$O at 25±2°C.

These results may be considered as follows. Thorium and uranium(VI) sulfito complex ions are not so stable as carbonato complex ions$^{(1)}$. The thorium precipitate contains thorium hydroxide or basic thorium sulfite, or both. In addition of the precipitant, a part of the sulfite ion is used to form outer-sphere complex ion, $[\text{Co(NH}_3\text{)_6}]\text{SO}_3^-$ therefore, low concentration of the precipitant leads to small precipitation yield, and high concentration of the precipitant leads to the ease in formation of thorium hydroxo species. The thorium precipitate of which the composition is not known acts as a nucleus for thorium hydroxide and basic thorium sulfite precipitation. Sulfite ions act as bidentate ligands in the uranium(VI) precipitate and six coordination sites of uranium(VI) ion are occupied by three sulfite ions. Consequently, formation of higher complex $[\text{UO}_4(\text{SO}_3)_n]^ {2n-4}^-$ ($n\geq4$) is difficult.

Figure 2 shows thermoanalytical results of the uranium(VI) sulfito complex precipitate together with those of uranium(VI) sulfato complex precipitate. High-temperature endothermic peaks are observed at 760, 820 and 848°C, respectively. Also from thermogravi-

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>Precipitation condition</th>
<th>Analyses (%)</th>
<th>Composition$^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH$_3$)$_2$SO$_3$ concn. (M)</td>
<td>[Co(NH$_3$)$_6$]Cl$_3$ concn. (M)</td>
<td>[Co(NH$_3$)$_6$] Th SO$_3$</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>1.0</td>
<td>0.02</td>
<td>16.2 22.2 25.5</td>
</tr>
<tr>
<td>2.</td>
<td>1.0</td>
<td>0.04</td>
<td>16.0 22.7 24.4</td>
</tr>
<tr>
<td>3.</td>
<td>1.0</td>
<td>0.06</td>
<td>15.6 24.2 23.7</td>
</tr>
<tr>
<td>4.</td>
<td>1.0</td>
<td>0.08</td>
<td>14.1 25.3 21.6</td>
</tr>
<tr>
<td>5.</td>
<td>1.75</td>
<td>0.04</td>
<td>17.0 21.9 27.1</td>
</tr>
</tbody>
</table>

$^\dagger$ Composition represents molar ratios of components in the precipitate calculated on the basis of the chemical analysis data.

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Fig. 2 Thermogravimetric analysis and differential thermal analysis curves of uranium(VI) precipitate
are assigned to enantiotropic phase transition of \( \text{UO}_2\text{SO}_4 \), decomposition of \( \text{UO}_2\text{SO}_4 \) to \( \text{U}_3\text{O}_8 \), and finally, decomposition of \( \text{CoSO}_4 \) to \( \text{Co}_8\text{O}_4 \) \cite{15}--\cite{17}. The sulfite ion is thus oxidized to sulfate ion, giving a mixture of cobalt(II) and uranium(VI) sulfates. A large endothermic peak is observed at 232°C for the sulfito complex precipitate and at 288°C for the sulfato complex precipitate. This is assigned to decomposition of hexammine cobalt(III) ion. At low temperature, the decomposition possibly takes place in the sulfito complex precipitate because of the reducing property of sulfite ion. Two small endothermic peaks, possibly assigned to decomposition of double sulfate \( (\text{NH}_4)_2\text{Co(SO}_4)_2 \) to \( \text{CoSO}_4 \), appear only in the sulfato complex precipitate at 384 and 420°C. This means that the sulfito complex precipitate decomposes directly to a mixture of cobalt(II) and uranium(VI) sulfates at these temperature. The thermogravimetric curve also supports this phenomenon.

A scanning electron micrograph of the uranium(VI) sulfito complex precipitate is shown in Photo. 1. The crystal is in the form of square bipyramid, about 4 \( \mu \text{m} \) across, in a cubic symmetry of the diamond type with \( a=10.40 \text{ Å} \).

Therefore, the present precipitate system will be useful for study of uranium(VI) recovery from the sulfite solution.

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*Photo. 1* Photograph of uranium(VI) sulfito complex precipitate

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1 \( \mu \text{m} \)