Determination of Hexamminecobalt(III)-, Monochloropentamminecobalt(III)- and Cobalt(II)- Ions in their Mixture by the Isotope Dilution Method

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Received April 26, 1966

A simple and rapid method was investigated for the determination of $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and Co^{2+} ions in their mixture by the aid of the direct isotope dilution method. $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion was separated in the form of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 2\text{CdCl}_2 \cdot 3\text{H}_2\text{O}$ by treating with the equal volume of 10% CdCl_2 solution. $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ion was separated in the form of the $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ precipitate by adding conc. HCl to 1.5 N acidity. Co^{2+} ion was separated from the cation-exchanger bed column by eluting with 1 N HCl . The determinations of several to several tens mg of these ions are possible within $\pm 3\%$ error.

The simple procedures for the preparation of ^{60}Co -labelled $[\text{Co}^(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Co}^*(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ by the radiosynthetic method are also given.*

Introduction

It is often difficult to attain quantitative separation of complex ions from one another when they resemble each other in their chemical properties. In such situations, however, the determination of each ion is still possible by the aid of the isotope dilution method, when only a part of the ion in question can be separated with the satisfactory chemical purity. The authors reported in the previous paper¹⁾ the determination of the radiochemical yield of ^{60}Co found in the $[\text{Co}^*(\text{NH}_3)_5\text{Cl}]^{2+}$ form or in the Co^{2+} form, which was produced by the recoil effect in the neutron-irradiated hexamminecobalt(III) chloride $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, with the aid of the reversed dilution method. In this paper, the determination of inactive $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and Co^{2+} ions in their mixture by the direct isotope dilution method has been tried. The determination of these ions is often necessitated in the solution chemical or radiation chemical studies of such complex compounds.

Experimental

1. Materials

Cobalt(II) chloride: $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ of the reagent grade was used without any further

purification.

Monochloropentamminecobalt(III) chloride:

$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was prepared starting from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ by the method of Hynes and others²⁾.

Hexamminecobalt(III) chloride: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ was prepared starting from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ by the method written in the Brauer's Handbuch³⁾.

Radioactive cobalt: The ^{60}Co processed radioisotope in the chemical form of CoCl_2 supplied by ORNL was used.

^{60}Co -labelled hexamminecobalt(III) chloride:

$[\text{Co}^*(\text{NH}_3)_6]\text{Cl}_3$ was prepared as follows: 0.1 g $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ was irradiated with neutron by the JRR-1 reactor (neutron flux: $3 \times 10^{11} \text{ n/cm}^2 \cdot \text{sec}$) for 5 hr. Several percent of the ^{60}Co activity thus formed was found in the $[\text{Co}^*(\text{NH}_3)_5\text{Cl}]^{2+}$ form and about 60% in the Co^{2+} form. To purify $[\text{Co}^*(\text{NH}_3)_6]\text{Cl}_3$, the irradiated $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ was dissolved in water. 10 mg each of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and CoCl_2 were added to the solution as the scavenger or the hold-back carrier, and then $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was precipitated by adding HCl until the acidity of the solution became 1.5 N. After

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centrifuging, the supernatant was treated with the equal volume of conc. HCl and several ml of ethyl alcohol to precipitate $[\text{Co}^*(\text{NH}_3)_6]\text{Cl}_3$. The precipitate was centrifuged and then dissolved in water again. 10 mg each of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and CoCl_2 were added to this solution again, and the above-mentioned scavenging and precipitation were repeated several times yielding radiochemically pure $[\text{Co}^*(\text{NH}_3)_6]\text{Cl}_3$. The labelled complex salt was stored in the solid state and dissolved before use.

^{60}Co -labelled monochloropentamminecobalt (III) chloride: 0.1 g $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was irradiated in the JRR-1 reactor for 5 hr. About 3% and 50% of the ^{60}Co activities thus formed were found in the $[\text{Co}^*(\text{NH}_3)_6]^{3+}$ and Co^{2+} forms, respectively. The purification was carried out as follows: The irradiated $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was dissolved in water. 10 mg each of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and CoCl_2 were added as the hold-back carriers. $[\text{Co}^*(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was then precipitated by adding HCl to 1.5 N acidity. The precipitate was then dissolved in water again and the above-mentioned procedure was repeated several times. The purified $[\text{Co}^*(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was stored in the solid state and the spike solution was prepared before use.

2. Apparatus

The radioactivity was measured in a well-type scintillation counter (NaI crystal, $1\frac{3}{4}$ in $\times$ 2 in) connected with a single-channel pulse-height analyser.

The optical density of the solution of each cobalt compound was measured with the Hitachi EPU-2 spectrophotometer.

3. Procedure for the determination of $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion

Add 5 ml of radioactive $[\text{Co}^*(\text{NH}_3)_6]\text{Cl}_3$ solution (total activity A_1 : $\sim 10,000$ cpm, total amount W_1 : 1–10 mg $[\text{Co}(\text{NH}_3)_6]^{3+}$) to the sample solution containing 2–30 mg of $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion. Precipitate $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 2\text{CdCl}_2 \cdot 3\text{H}_2\text{O}$ by adding the equal volume of 10% CdCl_2 solution. After centrifuging, dissolve the precipitate in 10 ml of water, and then reprecipitate by adding 10 ml of 10% CdCl_2 solution. Dissolve the precipitate in 6 ml of

water. Pipette 5 ml of the solution in a polyethylene counting tube. Measure the radioactivity (A_2) and then the optical density (D_2) of the solution at 480 m μ .

On the other hand, measure the radioactivity (A_1) and the optical density (D_1) with 5 ml of the radioactive $[\text{Co}^*(\text{NH}_3)_6]\text{Cl}_3$ solution.

From these experimental data, the amount of $[\text{Co}(\text{NH}_3)_6]^{3+}$ in the sample solution (W_x) can be calculated according to the following formula:

$$W_x = \left(-\frac{A_1}{\frac{5D_1}{A_2}} - 1 \right) \cdot W_1 = \left(\frac{A_1}{A_2} \cdot \frac{D_2}{D_1} - 1 \right) \cdot W_1$$

When the sample solution contains a large amount of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ in it (> 1 mg/ml), the sample is first treated with conc. HCl to 1.5 N acidity to precipitate the bulk of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. With the supernatant, the separation of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ is carried out according to the above-mentioned procedure.

4. Procedure for the determination of

$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ion

Add 5 ml of radioactive $[\text{Co}^*(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ solution (total activity A_1 : $\sim 10,000$ cpm, total amount W_1 : 1–10 mg $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$) to the sample solution containing 3–40 mg of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ion. Add conc. HCl to 1.5 N acidity to precipitate $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. After centrifuging, dissolve the precipitate in 10 ml of water, and then reprecipitate $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ by adding 1.5 ml of conc. HCl. Dissolve the precipitate in 5–6 ml of water. Take 5 ml of the solution in a counting tube. Measure the activity (A_2) and then the optical density (D_2) of the solution at 362 m μ .

On the other hand, measure the activity (A_1) and the optical density (D_1) with 5 ml of the radioactive $[\text{Co}^*(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ solution.

The amount of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ion in the sample solution (W_x) is then calculated according to the following formula:

$$W_x = \left(\frac{A_1}{A_2} \cdot \frac{D_2}{D_1} - 1 \right) \cdot W_1$$

5. Procedure for the determination of Co^{2+} ion

Add 5 ml of radioactive Co^*Cl_2 solution (total activity A_1 : $\sim 10,000$ cpm, total amount W_1 : 1–10 mg Co^{2+}) to the sample solution

containing 10 ~ 50 mg of Co^{2+} . Transfer the solution to the cation-exchanger bed column (Diaion SK #1, 100~200 mesh, HR-form, 0.9cm ϕ $\times$ 5cm). Elute Co^{2+} by passing 1 N HCl through the resin bed. Take 5 ml of the most coloured part of the eluate in a counting tube. Measure the activity (A_2) and then the optical density (D_2).

On the other hand, take 5 ml of the radioactive Co^*Cl_2 solution in a 25 ml volumetric flask. Add 5 ml of 2 N HCl and dilute the solution to the mark with 1 N HCl. Take 5 ml of the solution in a counting tube and measure the activity (A_1) and the optical density (D_1).

The amount of Co^{2+} in the sample solution (W_x) is then calculated according to the following formula:

$$W_x = \left(\frac{A_1}{A_2} \cdot \frac{D_2}{D_1} - 1 \right) \cdot W_1$$

Results and discussion

1. Determination of $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion

An essential condition for the above mentioned procedure for the determination is that the chemical purity of the separated $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ fraction is high enough. This was easily checked by the following tracer method: A mixture of 10 mg each of inactive $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, labelled $[\text{Co}^*(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and radioactive Co^*Cl_2 was treated with the equal volume of 10% CdCl_2 solution to precipitate $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 2\text{CdCl}_2 \cdot 3\text{H}_2\text{O}$. After reprecipitation, the precipitate was dissolved in water and its activity was measured. It was shown that the activity of $[\text{Co}^*(\text{NH}_3)_5\text{Cl}]^{2+}$ and/or Co^{*2+} entering the $[\text{Co}(\text{NH}_3)_6]^{3+}$ fraction was small enough to be neglected.

The analytical results obtained with the

Table 1. Determination of $[\text{Co}(\text{NH}_3)_6]^{3+}$ ion. (In the presence of 10 mg of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and 20 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$)

$[\text{Co}(\text{NH}_3)_6]^{3+}$ taken (mg)	$[\text{Co}(\text{NH}_3)_6]^{3+}$ found (mg)	error (%)
0.87	0.93	+ 6.9
1.74	1.74	$\pm$ 0.0
2.61	2.69	+ 3.1
3.48	3.42	- 1.7

mixtures of 10 mg of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, 20 mg of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and the various amounts of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ are shown in Table 1.

2. Determination of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ion

The chemical purity of the $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ separated according to the above-mentioned procedure was first checked by the tracer method: To a mixture of 10 mg each of labelled $[\text{Co}^*(\text{NH}_3)_6]\text{Cl}_3$, inactive $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and radioactive Co^*Cl_2 was added conc. HCl to 1.5N acidity. After reprecipitation, the activity of the resulting precipitate was measured. It was shown that the contamination by $[\text{Co}^*(\text{NH}_3)_6]\text{Cl}_3$ and Co^*Cl_2 activity was negligible.

The results of the determination of the various amounts of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in the presence of 60 mg each of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are shown in Table 2.

Table 2. Determination of $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ion. (In the presence of 60 mg each of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$)

$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ taken (mg)	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ found (mg)	error (%)
4.44	4.43	- 0.2
6.66	6.90	+ 3.6
8.88	8.82	- 0.7

3. Determination of Co^{2+} ion

The separation of the Co^{2+} fraction in a sufficiently high chemical purity was ascertained by the tracer method with a mixture of labelled $[\text{Co}^*(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}^*(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and inactive CoCl_2 .

The results of the determination of Co^{2+} ion in the presence of 60 mg each of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ are shown in Table 3.

Table 3. Determination of Co^{2+} ion. (In the presence of 60 mg each of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$)

Co^{2+} taken (mg)	Co^{2+} found (mg)	error (%)
9.7	9.9	+ 2.1
19.5	20.0	+ 2.6
29.2	28.8	- 1.4
38.9	38.9	$\pm$ 0.0
48.8	49.8	+ 2.0

4. Determination of $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and Co^{2+} in the same sample

Three portions of the sample solution were taken, and each portion was subjected to the determination of each ion according to the above-mentioned procedure. An example for the mixture of several tens mg of each ion is listed in Table 4.

Table 4. Determination of $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and Co^{2+}

ion	amount taken (mg)	amount found (mg)	error (%)
$[\text{Co}(\text{NH}_3)_6]^{3+}$	27.6	28.3	+ 2.5
$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$	30.9	31.5	+ 1.9
Co^{2+}	114	112	- 1.8

Thus, the determinations of several to several tens mg of $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and Co^{2+} ions are possible within $\pm 3\%$ error.

要 旨

同位体希釈法によるヘキサアンミンコバルト(Ⅲ)イオン、モノクロロペンタアンミンコバルト(Ⅲ)イオンならびにコバルト(Ⅱ)イオンの定量

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同位体希釈法を用い, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ならびに Co^{2+} の混合物について, それぞれのイオンを定量する方法を研究した。 $[\text{Co}(\text{NH}_3)_6]^{3+}$ 部分は, ラベルつき化合物 $[\text{Co}^*(\text{NH}_3)_6]\text{Cl}_3$ の一定量を添加したのち, CdCl_2 溶液を加えて $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \cdot 2\text{CdCl}_2 \cdot 3\text{H}_2\text{O}$ の形で沈殿, 分離し, その比放射能を測定することにより定量した。 $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ 部分は, ラベルつき化合物 $[\text{Co}^*(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ の一定量を加えたのち, 濃塩酸を酸性度が 1.5 N になるまで加えて, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ の形で沈殿させ, 分離した。 Co^{2+} イオンは, 試料溶液の一部を陽イオン交換樹脂のカラムに通して陽イオンをいったん樹脂層に付着させたのち, 1 N 塩酸で溶離して分離した。この方法により, 数ミリグラムないし数十ミリグラム程度のこれらのイオンを, $\pm 3\%$ 以内の誤差で定量することが可能である。

なお, 放射合成法により, $[\text{Co}^*(\text{NH}_3)_6]\text{Cl}_3$ ならびに $[\text{Co}^*(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ を簡単に調製する方法を考案した。

The method has an advantage in the fact that it requires no quantitative separation of each ion. It is suitable for the simple and rapid determination of these ions in their mixture.

The authors wish to express their heartfelt thanks to the members of the JRR-1 group at the Japan Atomic Energy Research Institute for the neutron irradiation. A part of the expense of this work was defrayed by a grant from the Ministry of Education of Japan, to which the authors' thanks are due.

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