The Determinations of Some Metal Ions by Using Hexamminecobalt(III) Chloride and Sodium Thiosulfate as Precipitants

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Many studies for the determinations of various metals using hexamminecobalt(III) chloride as the reagent have been reported. For example, indium has been determined gravimetrically[1,2], colorimetrically[3,4], volumetrically[3], and radiometrically[3] in the form of $[Co(NH_3)_6]InCl_6$ in a hydrochloric acid system. Moreover, thallium has been determined as $[Co(NH_3)_6]TlCl_6$[5-9], aluminum as $[Co(NH_3)_6]AlF_6$[10], gallium as $[Co(NH_3)_6]GaF_6$[11], scandium as $[Co(NH_3)_6]ScF_4$[12,13], iron as $[Co(NH_3)_6]FeF_6$[14], phosphate as $[Co(NH_3)_6]PO_4\cdot 4H_2O$[15-18], vanadate as $[Co(NH_3)_6](VO_3)_3$[19], and beryllium as $[Co(NH_3)_6][(H_2O)_2Be_2(CO_3)_2(OH)_3]\cdot 3H_2O$[20,21].

Recently Yatsimirskii and Roslyakova have studied the precipitation reactions of copper and lead, using hexamminecobalt(III) chloride and sodium thiosulfate as precipitants[22]; that is, when these reagents were added to the solutions of the metal ions mentioned above, these metals were precipitated, forming insoluble complexes such as $[Co(NH_3)_6]_5[Cu(S_2O_3)_3]_3\cdot 12H_2O$ and $[Co(NH_3)_6]_2[Pb_2(S_2O_3)_5]$; they have also developed iodometric determination methods. As one of a series of these studies, and in order to develop Yatsimirskii's method, this work was performed.

It was found in this study that silver, cadmium, mercury and bismuth were precipitated forming insoluble complex salts immediately, when hexamminecobalt(III) chloride and sodium thiosulfate solutions were added to the solutions of the metal ions mentioned above; the compositions of these complex salts, except bismuth salt were confirmed to be $[Co(NH_3)_6][Ag(S_2O_3)_2]$, $[Co(NH_3)_6]_4[Cd(S_2O_3)_3]_3\cdot 6H_2O$ and $[Co(NH_3)_6]_4[Hg(S_2O_3)_3]_3\cdot 10H_2O$ respectively. The composition of the slightly soluble complex salt which is formed by adding a hexamminecobalt(III) chloride solution to a sodium thiosulfate solution was found to be $[Co(NH_3)_6](S_2O_3)Cl\cdot H_2O$, while Rãy prepared the complex salt $[Co(NH_3)_6]S_2O_3Cl$ by the addition of ammonia to a mixed solution of cobalt(II) chloride, ammonium chloride and sodium thiosulfate in a current of air[23].

We have studied various methods of the determination of metal ions based on the formation of metal complexes; that is, we studied silver by measuring volumetrically the excess of sodium thiosulfate with a standard iodine solution, copper and mercury by weighing gravimetrically their complex salts, and mercury and lead by EDTA titration after their salts had been decomposed.

Experimental

Preparation of Hexamminecobalt(III) Chloride Thiosulfate.—To 10 ml. of a 0.1 M hexamminecobalt(III) chloride solution, an equimolar solution of sodium thiosulfate was added and stirred; after a while a precipitate was obtained. The precipitate was then filtered through a glass filter (1G No. 4), washed 2∼3 times successively with 5 ml. of distilled water, and dried on calcium chloride in a dessicator for a month.

Preparation of Silver, Cadmium and Mercury Complexes.—To the mixture of 1.0 ml. of 0.1 M metal chloride and 15 ml. of 1 M ammonium acetate solutions, 10 ml. each of 0.1 M hexamminecobalt(III) chloride and 0.1 M sodium thiosulfate solutions were added. A precipitate of the metal

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complex salt was formed immediately. The precipitate was filtered through a glass filter, washed repeatedly with 5 ml. of water and dried on calcium chloride for a month.

Analytical Methods of Complex Salts.—*Determination of the Hexamminecobalt(III) Ion.*—A known quantity of the dried precipitate was dissolved in a 10% sodium hydroxide solution and boiled untill the black brown precipitate of cobalt(III) hydroxide was obtained. The solution containing the precipitate was acidified by adding hydrochloric acid and boiled to dissolve the cobalt(III) hydroxide. After the solution had been allowed to cool the concentration of cobalt(III) ion in the solution was determined by the nitroso-R and EDTA methods. The quantity of hexamminecobalt(III) ion was calculated by making use of their factors.

Determination of the Thiosulfate Ion.—In the case of hexamminecobalt(III) chloride thiosulfate, a known quantity of the sample was dissolved in distilled water and the thiosulfate ion was determined by iodometric titration. As for the metal complexes, after the metal complex formed had been filtered off through a glass filter, the concentration of thiosulfate ion in the filtrate was determined by iodometric titration, and then the content of this ion in the complex was calculated from the difference between the total concentration of this ion and that in the filtrate.

Determination of the Chloride Ion. — After the sample had been treated with a 10% hot sodium hydroxide solution, the cobalt(III) hydroxide formed was filtered off. Then a few milliliters of 3% hydrogen peroxide were added to the filtrate, and this mixture was warmed in boiling water, to oxidize the thiosulfate to the sulfate ion or to sulfur[24]; this treatment was followed by the addition of copper(II) nitrate for the decomposition of the excess of hydrogen peroxide[25]. After the solution had been allowed to cool, the concentration of the chloride ion was determined by Mohr's method.

Determination of the Water of Crystallization.—The sample was dried again up to a constant weight on the phosphorus pentoxide under reduced pressure (below 20 mmHg), and the water content was calculated from the weight difference.

Determination of the Silver Ion.—After the sample had been decomposed by the same treatment as in the determination of the hexamminecobalt(III) ion in the complex salt, the silver hydroxide formed was filtered and dissolved again in dilute aqueous ammonia; then silver chloride was precipitated by acidifying the solution with nitric acid, and the concentration of silver ion was determined gravimetrically.

Determination of the Cadmium and Mercury Ions.—After alkali and acid treatments, these metals were determined by EDTA titration.

Procedures. — *General Procedure for the Determination of Silver by Iodometric Titration.*—To about 10 ml. of a solution containing 5∼50 mg. of silver and 15 ml. of a buffer solution, 10 ml. each of 0.1 M hexamminecobalt(III) chloride and equimolar thiosulfate solutions were added and stirred, so a precipitate of silver complex was formed immediately. After the solution had been left standing for 5 min., the precipitate was filtered through a glass filter (1G, No. 4), washed 3 times with 10 ml. of distilled water, and the filtrate and the washings were collected into a 100 ml. dry flask. The filtrate was titrated with a standard iodine solution to determine the excess of sodium thiosulfate, and the number of thiosulfate ions in the precipitate was calculated from the difference between the total thiosulfate concentration added and that in the filtrate. The concentation of silver was determined indirectly by making use of their factors.

Procedure for Determination of Copper, Mercury and Lead by the Gravimetric Method.—To a sample solution containing about 2 ml. of a 0.03∼0.1 M metal chloride solution, 15 ml. of a buffer solution and 10 ml. each of the two reagents were added; a precipitate of the metal complex was then formed. After the solution had been left standing for about 15 min., the precipitate was filtered through a weighed glass filter (1G No. 4) and washed with distilled water and then with alcohol and ether. It was dried in an air bath at 50°C for 3 hr. and weighed after cooling.

Procedure for the Determination of Mercury and Lead by EDTA Titration.—A precipitate formed by the same procedure as in the gravimetric method was filtered through filter paper (Toyo-roshi 5C) and washed with distilled water, transferred to the beaker, and decomposed with the alkali and acid treatments previously mentioned; then the concentration of metal ions was determined by EDTA titration.

Results and Discussion

Stability of Sodium Thiosulfate in Solutions of Various pH Values from 1 to 10.5.—In this study, the most important finding was that the hexamminecobalt(III) chloride and sodium thiosulfate used as precipitants were stable under the experimental conditions. It is well known that hexamminecobalt(III) chloride is very stable in solutions over this pH range. Sodium thiosulfate, on the other hand, was unstable in solutions with pH values below 4 and decomposed, separating out sulfur, but it was stable in solutions with pH values above 5; therefore, the experiment could not be done below this pH value.

Effect of the Ammonium Acetate Solution Added.—When a 0.1 M sodium thiosulfate solution was mixed with a 0.1 M hexamminecobalt(III) chloride solution and stirred, an orange, needle-shaped precipitate [hexamminecobalt(III) chloride thiosulfate] was formed; the coprecipitation of this salt with a metal complex salt caused a large error in the determination of the metal ions, but the formation of this complex salt was repressed by adding a certain amount of acetate salt. When 10 ml. of each

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precipitant was added to 15 ml. of a 1 M ammonium acetate solution, this complex salt was not formed at least for 20 min. It was evident from this fact that the ammonium acetate solution acted not only as a buffer but as a masking agent. It was then decided to use 10 ml. of each 0.1 M precipitant and 15 ml. of the 1 M ammonium acetate solutions in the following study.

Possibility of the Formation of Various Metal Complexes.—By adding 1 ml. of a 0.1 M solution of various metal ions to the mixed solution of the three reagents mentioned above, the possibility of the formation of various metal complex salts was examined. The elements used in this examination were lithium, sodium, potassium, silver, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury, boron, aluminum, gallium, indium, thallium, scandium, germanium, tin, arsenic, antimony, bismuth, vanadium, chromium, molybdenum, tungsten, uranium, manganese, iron, cobalt and nickel. It was also found that, in addition to copper and lead, silver, mercury and cadmium were precipitated, forming an insoluble complex salt in solutions with 5.0∼10.5 pH values and that bismuth precipitated as its hydroxide in the neutral solution, but formed an insoluble complex in the solution with a pH value of 3.

Determination of the Compositions of Various Complexes.—

1) Hexamminecobalt(III) chloride thiosulfate.

Found: $[Co(NH_3)_6]^{3+}$, 49.4; $S_2O_3^{2-}$, 34.3; Cl^-, 11.6; H_2O, 5.0. Calcd. for $[Co(NH_3)_6]$-$(S_2O_3)Cl \cdot H_2O$: $[Co(NH_3)_6]^{3+}$, 49.3; $S_2O_3^{2-}$, 34.3; Cl^-, 10.9; H_2O, 5.5%.

2) Silver complex.

Found: $[Co(NH_3)_6]^{3+}$, 31.3; Ag^+, 21.9; $S_2O_3^{2-}$, 45.1. Calcd. for $[Co(NH_3)_6][Ag(S_2O_3)_2]$: $[Co(NH_3)_6]^{3+}$, 32.6; Ag^+, 21.8; $S_2O_3^{2-}$, 45.4%.

3) Mercury complex.

Found: $[Co(NH_3)_6]^{3+}$, 26.9; Hg^{2+}, 24.0; $S_2O_3^{2-}$, 42.0; H_2O, 7.4. Calcd. for $[Co(NH_3)_6]_4$-$[Hg(S_2O_3)_3]_3 \cdot 10H_2O$: $[Co(NH_3)_6]^{3+}$, 26.5; Hg^{2+}, 24.7; $S_2O_3^{2-}$, 41.4; H_2O, 7.4%.

4) Cadmium complex.

Found: $[Co(NH_3)_6]^{3+}$, 31.2; Cd^{2+}, 15.8; $S_2O_3^{2-}$, 48.8; H_2O, 5.2. Calcd. for $[Co(NH_3)_6]_4$-$[Cd(S_2O_3)_3]_3 \cdot 6H_2O$: $[Co(NH_3)_6]^{3+}$, 30.7; Cd^{2+}, 16.1; $S_2O_3^{2-}$, 48.1; H_2O, 5.2%.

5) Bismuth complex.

As has been previously mentioned, this complex was formed in the solution with a pH value of 3, but the composition of this complex was not determined, for this complex could not be separated from the sulfur formed as a result of the decomposition of the sodium thiosulfate reagent.

Relation between the Amount of the Precipitate and the pH Value of the Solution.—As the compositions of the silver, cadmium and mercury complexes were determined in addition to those of copper and lead, we studied on the determination methods for these metal ions based on the formation of a complex salt. At first, the relation between the amount of the precipitate and the pH value of the solution was studied under the same conditions as for the preparation of a metal complex. The results are shown in Figs. 1a and 1b. From these results, the cadmium complex was shown not to precipitate quantitatively; when the pH value of the solution became larger than 8, lead did not precipitate as its complex salt, but as its hydroxide, and the gravimetric determination of lead by making use of its complex became useless.

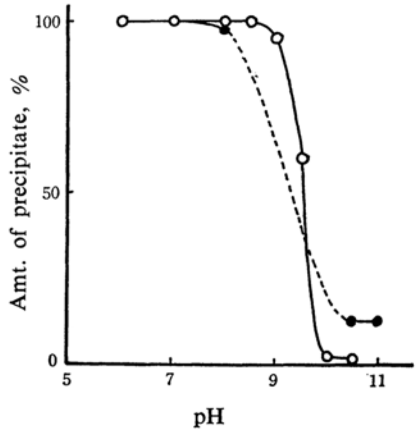

Fig. 1a

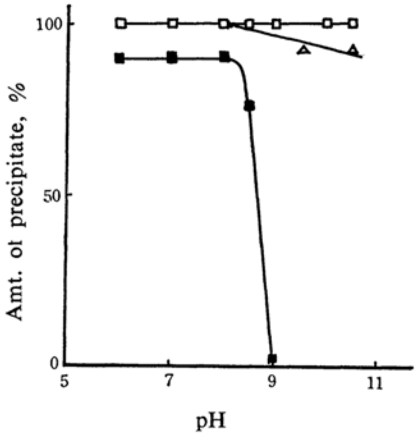

Fig. 1b

Figs. 1a and 1b. Relation between the amount of the precipitate and the pH value of the solution.

—○—	Copper	—△—	Silver
—●—	Lead	—■—	Cadmium
—□—	Mercury		

The Effect of Ammonium Acetate on the Precipitation of the Metal Complex. — We studied the effect of ammonium acetate on the precipitation of a silver complex by measuring the concentration of excess sodium thiosulfate by iodometry, for we were afraid that the acetate repressed not only the formation of hexamminecobalt(III) chloride thiosulfate but also that of the metal complex. The results are shown in Table I. It is evident from this table that the addition of 2∼30 ml. of a 1 M ammonium acetate solution does not repress the formation of the silver complex.

TABLE I. EFFECT OF AMMONIUM ACETATE IN THE PRECIPITATION OF SILVER COMPLEX

Ag taken mg.	1 M ammonium acetate added ml.	Ag found mg.
10.8	0	10.8
10.8	3	10.7
10.8	5	10.7
10.8	10	10.8
10.8	15	10.8
10.8	30	10.7

Relation between the Amount of the Precipitate and the Time Allowed for the Precipitate to Form.—The effect of the time on the amount of the precipitate was studied under general conditions. The results are shown in Fig. 2. From these results, the time which the solution should be allowed to stand after the precipitants had been added to the sample solution was concluded to be 5 min. for the volumetric method for silver and 20 min. for the other metals.

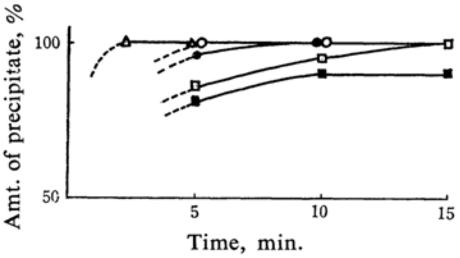

Fig. 2. Relation between the amount of the precipitate and the time allowed for the precipitate to form.
—○— Copper —△— Silver
—●— Lead —■— Cadmium
—□— Mercury

Washing and Drying of Metal Complexes.—Metal complexes were almost insoluble in water, acid, alcohol, ether, acetone, etc., while hexamminecobalt(III) chloride thiosulfate was fairly soluble in water. These salts were decomposed by heating above 60°C but were stable below 50°C, so in the gravimetric determination the precipitate was washed with water, alcohol and ether and then dried in an air bath at 50°C.

Volumetric Determination of Silver.—Silver was precipitated, forming the insoluble complex salt in the neutral solution by adding hexamminecobalt(III) chloride and sodium thiosulfate solutions to a silver nitrate solution. We studied the determination method of silver by measuring volumetrically the excess of sodium thiosulfate, and various concentrations of silver were determined by the general procedure; the results are shown in Table II. It was also concluded that the indirect titration of silver was satisfactorily carried out. As has been previously mentioned, copper, cadmium, mercury and lead were precipitated together with

TABLE II. DETERMINATION OF VARIOUS CONCENTRATIONS OF SILVER BY GENERAL PROCEDURE

Ag taken mg.	Ag found mg.	Ag found/ Ag taken %
5.4	5.4	99.8
10.8	10.7	100.5
21.6	21.7	99.0
53.9	53.8	99.4

TABLE III. DETERMINATION OF SILVER IN THE PRESENCE OF FOREIGN IONS

0.1 M sodium thiosulfate added, ml.	2.5	5.0	10.0
Foreign ion	Ag found, mg.		
Mg(II)	4.6	5.4	—
Ca(II)	5.4	5.5	—
Al(III)	4.6	5.5	—
Cr(III)	4.8	5.4	—
Mn(II)	4.4	4.7	5.3
Fe(III)	4.4	4.6	5.4
Co(III)	5.5	5.4	—
Ni(III)	4.9	5.4	—

Silver added : 5.4 mg.
Each foreign ion added : 2.5 mg.

TABLE IV. GRAVIMETRIC DETERMINATIONS OF VARIOUS CONCENTRATIONS OF COPPER, MERCURY AND LEAD

Metal	Metal taken mg.	pH of solution	Metal found mg.	Error mg.
Cu	3.4	7.4	3.5	+0.1
	6.9	7.4	7.2	+0.3
	14.5	7.4	14.8	+0.3
Hg	5.4	7.4	5.4	0.0
	10.8	7.4	10.8	0.0
	21.6	7.4	21.9	+0.4
	10.8	11.0	11.0	+0.2
Pb	3.0	7.4	3.0	0.0
	6.0	7.4	6.2	+0.2
	12.1	7.4	12.5	+0.4

TABLE V. DETERMINATIONS OF MERCURY AND LEAD BY EDTA TITRATION

Metal	Metal taken mg.	pH of solution	Foreign ion taken mg.	Metal found mg.	Error mg.
Hg	5.4	7.4		5.5	+0.1
	10.8	7.4		10.8	0.0
	21.6	7.4		21.5	−0.1
	10.8	11.0		10.7	−0.1
	10.8	11.0	Cu: 2.9	10.6	−0.2
	10.8	11.0	Cd: 11.5	10.8	0.0
	10.8	11.0	Cu: 6.9 Cd: 11.5	10.7	−0.1
Pb	3.0	7.4		3.1	+0.1
	6.0	7.4		5.8	−0.2
	12.1	7.4		12.1	0.0

silver, forming insoluble complex salts, and this causes serious interference on the determination of the silver. When the sample solution contained calcium, magnesium, aluminum, chromium, manganese, iron, cobalt and nickel together with silver, the precipitate of the silver complex was not formed quantitatively, for the foreign ions existing in the solution formed thiosulfate complexes and, consequently, the free thiosulfate ion in the solution decreased and was not enough to produce the insoluble silver complex perfectly. In this case, good results in the determination were obtained by adding a large excess of sodium thiosulfate. The results are shown in Table III.

Gravimetric Method.—We studied the gravimetric determination of copper, mercury and lead, for these metals are precipitated quantitatively, producing insoluble complex salts. The results obtained by the general procedure are shown in Table IV. The positive error of the observed value in every run seems to be caused by the water adhering to the precipitate.

Determination by EDTA Titration. — As mercury and lead existing in the solution together with cobalt can be determined by EDTA titration without being separated from cobalt[26,27], these metal ions were determined by this method after their complexes had been decomposed by alkali and acid treatments. The results obtained by the general procedure are shown in Table V.

Studies of the Isolation of these Complex-forming Metals.—In order to mask the formation of bismuth hydroxide in the neutral solution and of lead hydroxide in a solution with a pH value above 8, the masking actions of ammonium oxalate, ammonium citrate, ammonium succinate and ammonium tartrate solutions were examined; among them only the ammonium citrate solution was effective in preventing the hydroxides from forming, but at the same time this reagent repressed the formation of the metal complex to be measured and so was found to be useless. It is evident from the results described above that silver and mercury could be separated from copper and cadmium, but that the ultimate isolation of each element could not be effected.

Summary

1) When hexamminecobalt(III) chloride and sodium thiosulfate solutions were mixed, a precipitate was formed; the composition of this salt was found to be

$$[Co(NH_3)_6](S_2O_3)Cl\cdot H_2O$$

2) In addition to copper and lead, silver, cadmium, mercury and bismuth were precipitated, forming insoluble metal complexes, by adding hexamminecobalt(III) chloride and sodium thiosulfate solutions as precipitants to the solutions of these metal ions. The compositions of these salts, except for bismuth salt, were found to be

$[Co(NH_3)_6][Ag(S_2O_3)_2]$,
$[Co(NH_3)_6]_4[Cd(S_2O_3)_3]_3\cdot 6H_2O$ and
$[Co(NH_3)_6]_4[Hg(S_2O_3)_3]_3\cdot 10H_2O$

3) Various determination methods based on the formation of metal complexes were studied; that is, silver was studied by volumetrically measuring the excess of sodium thiosulfate with an iodine solution, copper and mercury, by gravimetrically weighing their complex salts, and mercury and lead, by EDTA titration after their complex salts had been decomposed.

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