

〔原報〕

Study on the Stability of Ammonium Cobalt Thiocyanate Solution And the Formation of Perthiocyanuric Acid

By

Chong-Ihn Choi*

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崔宗仁 : Ammonium Cobalt Thiocyanate 溶液의 安定度 및 Perthiocyanuric acid 의 生成反應에 關한 研究

Cobalt thiocyanate ion 에 미치는 影響을 研究하였다. Cobalt ion 이 NH_4CNS 溶液에 依해서 生成되는 ion 의 色의 Transmittance 는 鑛酸에 依하여 적어지며, 黃酸存在下에서는 黃酸의 量과 Transmittance 사이에 比例的 關係가 있다. 鹽酸 및 窒酸도 亦是 Transmittance 의 값에 影響을 미치기는 하나 鹽酸의 境遇에는 이 錯 ion 이 黃酸存在下보다 多少 不安定하며 窒酸에 依해서는 安定도가 極히 적어서 短時間內에 Perthiocyanuric acid 로 認定되는 物質로 分解한다. 또한 그 Transmittance 가 過量의 鑛酸存在下에서 적어지는 現象으로 부터 $\text{Co}(\text{SCN})_n^{2-n}$ 의 n 의 값이 커지는 것은 ether 에 移行하는 SCN^- 을 Volhard 氏法으로 定量함으로써 確證하였다.

Spectrometric studies indicate that the Co ion react with SCN^- ion stepwise, forming a series of complexes of the formula $\text{Co}(\text{NCS})_n^{2-n}$ where n is an integer between one and four inclusively.¹⁾

This complex ion has a blue colour and show the maximum absorption at 610—615 μ (Fig. 1) and this colour has been used in Cobalt analysis.²⁾

Fomula was the first to propose the photometric determination of cobalt by mean of its intensely blue thiocyanate complex.

According to this method, small amounts of Cobalt are determined in an aqueous acetone solution containing ammonium thiocyanate, by comparing the extinction of this solution with that of a standard solution of similar Cobalt concentration containing the same quantities of ammonium thiocyanate and acetone. A satisfactory result is obtained when the concentration of cobalt is above 8×10^{-3} mole per liter.³⁾

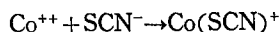
On making further experiments, it was found that the making color intensity of the Co thiocyanate ion is effected by the concentration of thiocyanate ion.⁴⁾

A high concentration of thiocyanate ion is essential in the aqueous solution to preventionization of

*College of Pharmacy, Sung Kyun Kwan University, Seoul, Korea

the complex which causes some change from blue to the pink color of the cobalt ion. The minimum concentration of ammonium thiocyanate necessary for the complete formation of this complex is 25% and it is usual to use a concentration of over 30% of ammonium thiocyanate. This also intensifies the color.

In the presence of a small excess of thiocyanate ion, the formation of a weakly colored complex proceeds according to:



In the presence of large excess of SCN ion, the formation of an intensively colored blue complex proceeds according to:



This ionization constant of the latter in 50% acetone solution is 1.5×10^{-4} .⁸⁾ This color may be extracted with amyl alcohol⁵⁾ or ether⁶⁾ and intensified by addition of acetone.⁷⁾

The present experiment had objective of determining the optimum pH for the formation of cobaltous thiocyanate complex and investigating the effect of mineral acids on absorbance of the cobaltous thiocyanate solution. And the stability of cobaltous thiocyanate in the presence of excess amount of sulfuric acid is also investigated in this experiment.

In the determination of absorbance, the Beckman model DU spectrophotometer equipped with tungsten-light source and photomultiplier attachment was used. Slit setting was 0.15 mm. for 610 m μ wavelength, using the blue sensitive phototube, and the sensitivity switch and phototube load register switch were set at load 2 respectively. In the determination of pH, Beckman Zeromatic pH meter was used.

In the determination of the amount of thiocyanate ion formed, special buretts equipped with stopper are used in order to prevent the ether layer from evaporating.

EXPERIMENTAL

The absorbance of cobaltous thiocyanate solutions are measured at various concentrations of mineral acids. The absorbances measured at constant cobalt ion concentration are different depending on the concentration of acid and the kind of mineral acid.

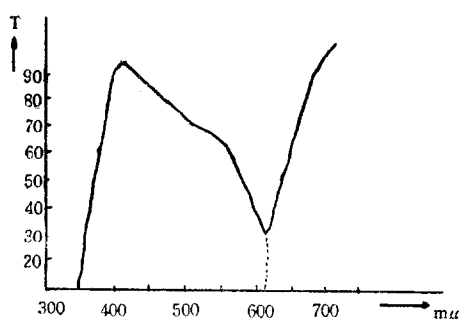


Fig. 1

The value of absorbance for 1 mm. layer of a solution containing 0.1 mg. of cobalt per ml. under the condition of 100% cobaltous thiocyanate complex formation was found to be 1291 in the spectral region of 610–615 m μ , corresponding to a molar extinction of 75. Once the proportionality of the extinction with the concentration of cobaltous thiocyanate was established, it was easy to calculate, from the extinction data, the amount of cobaltous thiocyanate complex in an unknown sample.

For the purpose of the investigation, cobaltous nitrate solution which has pH value 0.9–1.0 was used.

Pipette 5 mls of the aqueous cobalt standard solution into a test tube, and add various amounts of acid and 5 mls of 60% Ammonium thiocyanate solution, this amount of ammonium thiocyanate is considered to form the cobaltous thiocyanate complex completely. Determine the extinction of this

solution preferably in the spectral region of $610\text{ m}\mu$ - $615\text{ m}\mu$.

The experiment to study the effect of varying the amounts of sulfuric acid are outlined in table 1 and Fig. 2. This transmittance, T' is the transmittance, of the solution to which the same amount of distilled water (in ml.) is added instead of sulfuric acid.

A solution which contains 0.1 mg. of cobalt ion per ml. is used. The pH of the solution is 1.0. To this solution, the same mls. of 60% ammonium thiocyanate solution as that of cobalt ion solution was added to cause the complex.

TABLE 1.—The effect of sulfuric acid on the T of cobaltous thiocyanate

Gms. of H_2SO_4 per 100 ml.	T	T'	$T-T'$
0	71.1	71.1	0
3.68	70.1	70.08	0.7
11.04	66.7	74.2	6.0
18.40	64.4	76.5	11.8
25.76	61.2	76.5	15.3
33.12	54.3	76.5	22.2

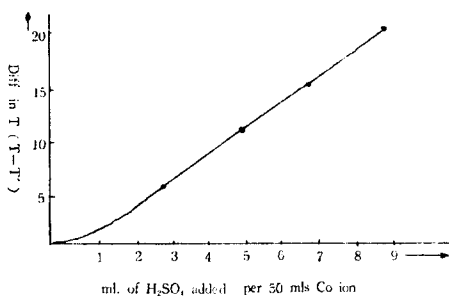


Fig. 2.—The relationship between T and mls. of sulfuric acid added.

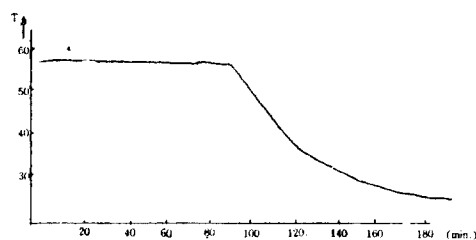
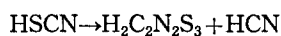


Fig. 3.—The change of T as the time passed

It is found that the cobaltous thiocyanate ion is very stable in the presence of relatively large amounts of sulfuric acid and the value of absorbance become large as the concentration of sulfuric acid is increased.

No noticeable decomposition of the complex ion by sulfuric acid is found in 90 minutes even in the solution containing 33 gm. of sulfuric acid per 100 mls. of cobalt ion solution (0.5 mg cobalt ion per 5 mls), but on further standing the thiocyanate ion is decomposed rapidly. (Fig. 3)

Therefore it can be said that a large amount of sulfuric acid (33 Gm. H_2SO_4 per 100 mls of cobalt ion solution) does not only effect the transmittance determination, but also the color of the complex ion is intensified by the sulfuric acid and in the presence of sulfuric acid below 33 Gm. per 100 mls of cobalt ion solution, perthiocyanuric acid is not formed. It is thought that rapid lowering of transmittance is due to the decrease in the concentration of thiocyanate ion by the formation of perthiocyanuric acid according to



In the presence of hydrochloric acid, the complex ion is also stable (Table II), but the stability of the complex ion is not so great (Fig. 3) in comparison with the case of sulfuric acid.

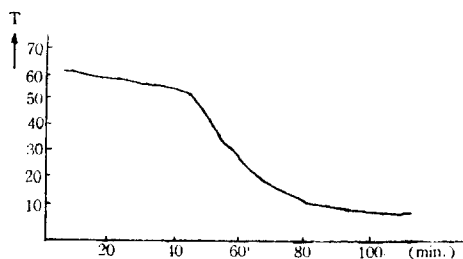
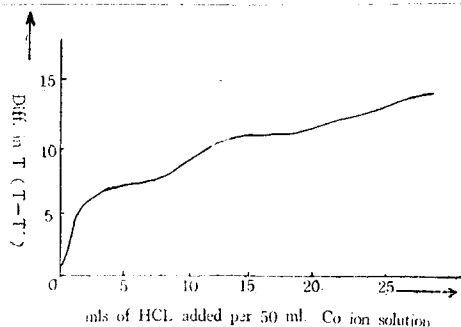


Fig. 4.

Fig. 5.—mls of HCl added per 50 ml. Co^{++} Soln.

The complex ion begins to decompose in a few minutes in the presence of 6.2 mole of hydrogen chloride per one liter of cobalt ion solution, therefore, it is practically impossible to determine the amount of the complex ion in the presence of such a large amounts of hydrochloric acid. It was apparent that in the presence of less than 3.7 moles of hydrogen chloride per one litre of cobalt ion solution, the complex is so stable that no decomposition is recognised as the time passes, but the value of $T-T'$ is not strictly proportional to the amounts of HCl present although it was found that the value of $T-T'$ is increased as the amounts of HCl is increased. (Fig. 5)

This proves that the complex ion is less stable in the presence of HCl than in the presence of sulfuric acid and it can be said that the reaction of formation of $\text{H}_2\text{C}_2\text{N}_2\text{S}_3$ is more accelerated by HCl than H_2SO_4 .

In the presence of nitric acid, the complex ion is so unstable that it is decomposed even in the presence of 0.31 moles of HNO_3 per one liter of cobalt ion solution and after one hour the transmittance is lowered from 68 to 52-54.

TABLE II.—The effect of HCl on Transmittance of cobaltous thiocyanate complex ion

Gms. 38% HCl g/100 ml. of Co-Soln.	Mol/1000 ml. of Co-Soln.	T	T-T'
2.4	0.25	73.2	1.0
12.0	1.25	70.2	4.2
24.0	2.5	66.9	10.6
36.0	3.75	67.0	13.6
48.0	5.0	66.2	14.3
60.0	6.25	63.2	19.9

In the presence of 0.62 moles of HNO_3 per one litre of cobalt ion solution, it is rapidly decomposed, but no noticeable decomposition was found in the presence of HNO_3 less than 0.031 moles per one litre of cobalt ion solution. (Fig. 6)

It is thought that the complex ion is unstable in the presence of oxidizing agent such as nitric acid. If we assume that this phenomenon is due to the formation of perthiocyanuric acid, the formation reaction is accelerated more by HNO_3 than H_2SO_4 or HCl.

In the above experiment, the pH of cobalt ion solution which was used was 1.0. No noticeable affect of pH on the stability of cobaltous thiocyanate in the region between pH 1.0 and pH 7.0 was found although the transmittance was slightly smaller at pH 3-4 than that at other pH regions.

The effect of acetone on the extinction was also studied. For this purpose, pipette 5 mls of the aqueous cobalt ion solution (0.1 mg. per ml. pH 1.0) into a test tube and add 5 mls of 60% ammo-

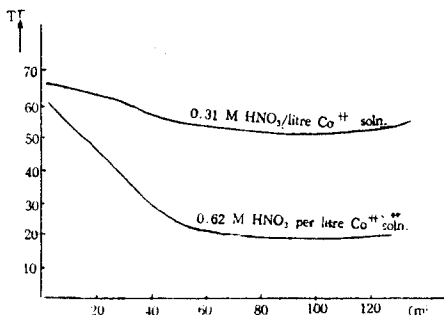


Fig. 6. —

Pipette 5 mls of the aqueous cobalt standard solution into a buret with stopper and add various amounts of sulfuric acid and 5 mls of 60% ammonium thiocyanate solution. 20 ml. of ether are added to this solution. The cobaltous thiocyanate ion is converted into the ether layer and the amounts of the cobaltous thiocyanate ion in the ether layer are determined by means of Volhard process. Namely 2 ml of the above ether layer are taken and 20 ml. of 0.1 N-AgNO₃ solution and 2 ml. of iron alum test solution are added. The silver nitrate remained are titrated with 0.1 N-ammonium thiocyanate solution.

Blank tests are done by means of the Volhard process. In the above experiment the very valuable results are obtained. The amounts of cobaltous thiocyanate formed is almost proportional to the amounts of sulfuric acid present. (Table. 3) and (Fig. 7)

It is apparent that the value n in $\text{Co}(\text{SCN})_n^{2-n}$ which is the general formula become large in the presence of excess amount of acids.

mium thiocyanate solution and various amounts of acetone are added, and the extinctions of these solutions are measured. It was found that 5 mls of acetone per 5 mls of cobalt ion solution produce the most intense color which is considered to be the color of the cobaltous thiocyanate complex ion.

The amount of cobaltous thiocyanate formed in the presence of various amount of sulfuric acid is determined as follows.

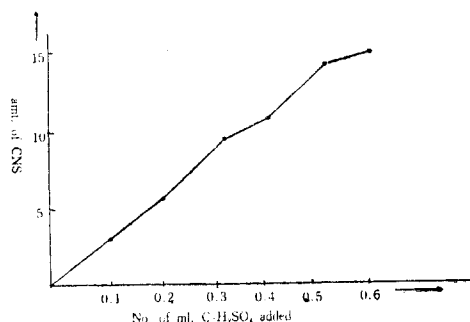


Fig. 7.

TABLE III.—Determination of the amount of SCN⁻

C H ₂ SO ₄ ml.	0	0.1	0.2	0.3	0.4	0.5	0.6
ml. of n-NH ₄ CNS consumed(a)	19.6	16.6	13.3	10.4	8.2	5.6	5.2
Amount of CNS ⁻ (b) i. e. 20 ml-a	0.1	3.4	6.7	9.6	11.8	14.4	14.8

b. indicate the amount of SCN in the ether layer:

5 ml. cobaltous nitrate solution (0.1 mg. Cobalt per ml) was used in this experiment.

SUMMARY

The stability of cobaltous thiocyanate complex has been determined at various concentrations of mineral acid, and the rate of decomposition of this complex ion in the presence of acid as the time passes has also been studied.

In this experiment, enough amount of ammonium thiocyanate solution was used so that dissociation of the complex by the shortage of thiocyanate ion can be neglected.

The stability of complex was calculated on the basis of spectrophotometric extinction measurements. It was found that the complex was very stable in the presence of sulfuric acid, fairly stable in

hydrochloric acid and unstable in nitric acid. Therefore it can be said that in the case of cobalt analysis by means of thiocyanate, excess amount of sulfuric acid does not causes any interference and trouble and the color of the cobaltous thiocyanate ion is intensified. It is possible to determine the absorbance directly without removing the excess amount of sulfuric acid. The effect of the excess amount of sulfuric acid on the absorbance is shown by figure 2.

An excess amount of nitric acid interferes very much with the formation of the cobaltous thiocyanate complex ion, but an excess amount of hydrochloric acid interferes only a little.

In a conclusion, attention should be paid to the fact that the color of cobaltous thiocyanate ion is not only intensified by the excess amount of sulfuric acid but also the color intensity is almost proportional to the amounts of sulfuric acid but also the color intensity is almost proportional to the amounts of sulfuric acid present. It is considered that the stability of cobaltous thiocyanate ion is increased in the presence of the excess amounts of sulfuric acid.

The experimental result about the effect of the excess amount of sulfuric acid on the absorbance which is obtained by the above experiment prove that the value in $\text{Co}(\text{SCN})_2^{2-}$ which is the general formula of cobaltous thiocyanate ion is increased with the amount of sulfuric acid present.

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