

Preparation of Potassium Hexathiocyanatochromate

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崔宗仁 : Potassium hexathiocyanatochromate(Ⅵ)의 製造에 關한 實驗

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Chloropentammine chromium(Ⅲ) chloride를 出發物質로 하여 여러가지의 thiocyanatoammine系 錯化合物을 合成하는 實驗에 있어서 그 收得量이 豫想보다 매우 적고 그 鹽의 母液이 濃赤紫色이라는 點으로 보아 그 母液中에 어떠한 다른 錯化合物이 多量 形成되어 있으리라고 推測하여 그 分離를 試圖하였던바 美麗한 赤紫色의 結晶을 얻었다. 그리고 分析에 依하여 이 物質이 Potassium hexathiocyanatochromate(Ⅵ)임을 證明하였다. Cr⁺⁺⁺의 thiocyanate 錯化合物形成에 關하여는 Niel Bjerrm⁽¹⁾에 依한 報告文이 있고 또 이들의 製法으로서는 Roesler⁽²⁾들에 依하여 Potassium chromium alum에서부터 이 物質을 만드는 方法만이 報告되어 있을 뿐이다. 따라서 Chloropentammine chromium(Ⅲ) chloride에서부터 이 物質을 만드는 이 새로운 方法이 이러한 化合物들의 製法으로서 앞으로 利用될 수 있는 것으로 思料한다.

製造方法

Chloropentammine chromium(Ⅲ) chloride 3g을 KSCN 24g, 水醋酸 24ml 및 물 48ml의 混合水溶液에 懸濁시킨 混合物을 처음에는 잘 攪拌하면서 加溫하고 다음 完全히 溶解될 때까지 끓인다. 冷却시킨 다음 生成된 橙黃色의 沈澱 Thiocyanatopentammine chromium(Ⅲ) thiocyanate를 濾過하고 濾液 65ml에 KSCN 50g을 追加하여 完全溶解시킨다. 이 溶液을 放冷시키면 赤紫色의 美麗한 結晶이 析出되므로 이 結晶을 濾過하여 ethanol로 洗滌하고 眞空 desiccator 中에서 乾燥시켰다. 收得量 1.2~1.3g.

The fact that chromium ion forms various thiocyanato-complex compounds with NCS ion in aqueous solution, was reported in detail by Niel Byerrm. (1)

According to the report, mono and dirhodan complex compounds exist only in an aqueous solution, i.e., it is impossible to obtain them as solid states. These complex compounds are insoluble in ether. Trirhodan complex compound is obtained as a crystalline state but pure crystal cannot be obtained. This compound is nonelectrolyte and soluble in ether.

The tetra-rhodan complex compound (the free acid) is found in an aqueous solution and soluble in ether. Oily precipitate is obtained by adding quinoline to the aqueous solution of the free

acid. Pentarhodan complex compound is also soluble in ether and very beautiful crystal is precipitated by adding quinoline to the aqueous solution. From the quinoline salt (water insoluble), the free acid and sodium salt can be obtained. Hexarhodan complex compound was prepared early by Roesler (2). This compound is soluble in water. Red-violet crystal is precipitated by pyridine and quinoline quantitatively. All of the above complex compounds have red-violet color in their solution, and the hexa one is so stable, among them, that it is obtained as a solid state from the aqueous solution.

Author conducted some experiments for the purpose of obtaining various thiocyanato-ammine chromium complex salts from chloropentammine chromium chloride as a starting material (3).

During these experiments, it was found that the yield was very poor and the mother solution of the thiocyanato complex salt was very deep red-violet in color. From the above experimental results, author concluded that there should be a large amount of some other chromium complex salts in that solution and set about isolating the complex compounds from this solution, and succeeded in the separation of a very beautiful red-violet crystal. It was proved that the compound was potassium hexathiocyanatochromate. Consequently author succeeded in developing a new preparatory method of potassium hexathiocyanatochromate using chloropentammine chromium chloride as a starting material.

Experimental.

Although several preparatory processes of this compound have been reported, in these processes (2) KCNS and potassium chromium alum are used as the starting materials.

In this new process, this compound is made from chloropentammine chromium chloride and the following procedures are used.

The chloride (30 g) is suspended in a solution of KSCN (240g), glacial acetic acid (240ml.) and water (480 ml.). The mixture is heated with stirring until it almost boils and boiled until it is completely dissolved. After cooling, the deposited orange-yellow thiocyanatopentammine chromium thiocyanate is filtered off. To the filtrate (about 650 ml.), 500 g of KSCN is added and the mixture is warmed until a clear solution is obtained. After cooling, potassium hexathiocyanatochromate is crystallized as a very beautiful red-violet crystal.

The yield was 13—15g from 30g of the chloride which is the starting material.

For the purpose of separation of the complex compound from the mother liquid of thiocyanatopentammine chromium thiocyanate, ethanol, ether, benzene, acetone, toluene and glacial acetic acid are added excessively to the solution.

No precipitation was obtained by ethanol, acetone and glacial acetic acid, and no complex ion is transferred toward the layer of the solvents.

But, when an excess amount of KSCN was added, some precipitation was obtained, therefore this process was used in the separation of this complex compound.

The optimum amount of KSCN used was determined as follows.

The KSCN is added to 10 mls of the mother liquid, and the resulting crystal is weighed. It was found the fact that the more amount of KSCN is added, the more amount of crystals was obtained. But when KSCN is used more than 7.7g/10 mls, SCN content of the crystal obtained is larger than theoretical amounts. It is thought that in this case KSCN is contained in the complex compound. The result of this experiment is shown in the following table.

Determination of the amount of KSCN used.

No. of Gm. of KSCN used	3.0	4.0	5.0	6.0	7.0	7.3	7.5	7.7	7.8	7.9	8.1
No. of Gm. of the salts obtained	0.15	0.2	0.28	1.0	1.7	1.8	1.9	2.0	2.1	2.3	2.5
SCN %	58.8	58.7	59.1	59.2	58.8	58.9	59.0	59.0	61.0	62.0	67.5

The composition of this compound is proved by using following usual method of analysis for Cr, K, and SCN.

1) % of thiocyanate (3)

Weigh 0.1g of the dry salt into a beaker, and add 20ml. of water and 5ml of 0.1N NaOH solution. Boil for a while until the mixture becomes clear.

Transfer the beaker and contents to the boiling water bath, add bromine water until the liquid is brown with excess of bromine, and then heat on the bath for 30 min. (or longer), the beaker being covered by a glass. Finally expel excess of bromine by boiling for a short time, increase the volume to 20 ml, acidify with 2 ml. of hydrochloric acid, boil, and add a solution of 0.4 g of BaCl₂ crystal in a small volume of hot water.

The precipitated BaSO₄ is treated for weighing as usual. The sulfur of thiocyanate is quantitatively oxidized to sulfate by the above process.

A sample weighing 0.1028 g gave 0.2378 g of BaSO₄. % of SCN; 58.50%.

The formula requires SCN: 59.02%

2) % of chromium (4)

Weigh 0.2g of the dry salt into a beaker, add 25 ml of N-alkali, and boil the mixture until the green precipitate of Cr(OH)₃ is quantitative (10—15 min.) Filter the liquid while hot through a fast-running paper, and wash the Cr(OH)₃ on the filter twice with hot water.

Carefully extract the paper with the precipitate from the funnel, and place it in a beaker containing 25 ml of water to which 3 ml of c-H₂SO₄ have been added. Boil until the hydroxide is completely dissolved, and the paper disintegrated. Filter into a conical flask, and wash the residue of paper on the filter with further 25—30 ml of hot water, used in portions.

To the filtrate add 1.5 g of KBrO₃, and then boil for 10 min. Dissolve 5 g of ammonium sulfate in a small volume of hot water, filter if necessary, and then add to the hot solution, in which chromium is now present entirely as chromic acid.

Boil the whole until nearly all the excess of bromine has been volatilized (30-40 min.) and then add 10 ml of N-HCl, and again boil until starch-iodine paper is not stained when held in the steam. Cool the liquid, add 10 ml of c-HCl, and 1 g of KI. Titrate the liberated iodine with approximately 0.05N sodium thiosulfate, standardized with potassium dichromate
% of Cr found (by using 0.2070 of salt); 8.88. The formula requires Cr; 8.83%

3) % of potassium (5)

0.1 g of the sample is decomposed with aqua regia, evaporated to dryness, and then taken up with water, and $\text{Cr}(\text{OH})_3$ is precipitated by addition of ammonium hydroxide.

The filtrate is evaporated with H_2SO_4 and potassium determined as the sulfate.

% of K found (by using 0.9902 of salt) : 19.72. The formula requires K; 19.86%

Summary of Analytical results;

	$\text{K}_3\text{Cr}(\text{NCS})_6 \cdot 4\text{H}_2\text{O}$ requires
% of K; 19.72	K; 19.86%
% of Cl; 8.88	Cr; 8.83%
% of SCN; 58.50	H_2O ; 12.25%

The following reactions are involved in the conversion of potassium chromate to chloropentammine chromium (III) chloride which are previously known (6).

Alcohol(95%) 40 ml and c-HCl 80 ml are added to potassium dichromate 30 g, and zinc 60 g is added to the green solution and heat for 40-60 min. at 80-90° C (covered with ligron layer).

After cooling, the solution is added to a solution of NH_4Cl 50g, $(\text{NH}_4)_2\text{SO}_4$ 50 g and c- NH_4OH 200 ml (zinc is remained), and iron alum 10g is added cooling with ice.

Set it aside in refrigerator for 24 hrs, filter and wash with alcohol.

The hexammine chromium chloride which is obtained in the above process is dissolved in 400ml water at 30-35° C.

2 ml NH_4OH and 2 ml 30% hydrogen peroxide are added and filtered. The residue is $\text{Fe}(\text{OH})_3$. 400 ml of c- HNO_3 is added to the filtrate. After cooling, hexammine chromium nitrate(III) is crystallized.

The crystals are dissolved in 1/1 volumes of hot water and equal volume of c-HCl is added. Boil for 30-60 min. and cool. The chloropentammine chromium chloride thus obtained is recrystallized.

Discussion and Summary

This new process has following advantages;

- 1) The product is so pure that it does not need to purify.
- 2) Alcohol is not used in this preparatory method.
- 3) Thiocyanato pentammine chromium thiocyanate is obtained besides this compound.
- 4) No high temperature and no heating process for a long time are needed.
- 5) The operation is comparably simple.

Whereas, in old process.

A large amount of alcohol is used in order to separate potassium sulfate and it is necessary to heat for about 2 hrs., at high temperature above 170-180°C for a fairly long time.

In this new process, it is considered that chloropentammine chromium ion is so reactive that it is destroyed by the presence of excess amount of SCN ion and so chromium ion is produced easily.

The ammonium ion and chlorine ion which are produced in these processes can be easily separated from potassium hexathiocyanato chromate, since ammonium chloride is more soluble than this complex compound in water containing KSCN.

Therefore after cooling this compound is deposited and ammonium chloride is remained in the solution.

It can also be said that the ability of forming complex ion of SNC ion for chromium is greater than NH₃ radical and Cl ion.

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