CADMIUM COBALTINITRITE--ITS PREPARATION AND PROPERTIES.

By

L.A.Dunlap

WASHINGTON AND LEE UNIVERSITY

Submitted to the Chemistry Department of Washington and Lee University as partial requirement for the degree of Bachelor of Arts, with a certificate in Chemistry.

OUTLINE OF CONTENTS

CADMIUM COBALTINITRITE--ITS PREPARATION AND PROPERTIES.

Cadmium Cobaltinitrite is a heretofore practically unknown compound. It was partially isolated in 1920 by S.C.Ogburn and J.T.Dobbins in the course of some original investigation of inorganic cobaltinitrites. Little is known of any of the cobaltinitrites save sodium cobaltinitrite, although several of them have been prepared and described. Sodium cobaltinitrite has been used for some time as a reagent in determining the amount of potash in fertilizer, in testing for small amounts of potassium and silver in solution, and in distinguishing between primary, secondary, and tertiary amines. Besides this, little has been definitely determined concerning any of the cobaltinitrites.

Sodium cobaltinitrite was the reagent used in the preparation of cadmium cobaltinitrite.

PREPARATION OF REAGENT.

Sodium cobaltinitrite, the reagent used in the preparation of cadmium cobaltinitrite, was prepared according to the method of Cunningham and Perkin, journal of the Chemical Society, Volume 95, page 1562.

This was done by dissolving 150 grams of sodium nitrite in 150 c.c. of hot water. This solution was then cooled to 50 degrees; then 50 grams of cobaltinitrite were added. After solution takes place, 25 c.c. of glacial acetic acid were added. This was then shaken well and kept at 60 degrees for 20 minutes. Passing a rapid stream of air thru the solution for one-half an hour removed any excess of the oxides of nitrogen that might be pres-

ent. Now 650c.c. of 95% alcohol were added and the mixture shaken well, and sodium cobaltinitrite came down in orange colored flakes. This was then filtered by suction, washed once with 60% alcohol and 95% alcohol until the washings were clear, and then dried on a porous plate. The yield of sodium cobaltrinite according to this method was about 60%.

PREPARATION OF CADMIUM COBALTINITRITE.

A saturated solution of sodium cobaltinitrite was prepared and a saturated solution solution of cadmium sulfate added to it in equivalent amount. This was allowed to stand overnight. A slight precipitate appeared but it was insufficient for isolation in an appreciable quantity. Several ways were tried to increase this precipitation. The best one found was by fractional crystallization of the solution either over H_2SO_4 or in an oven at 60 degrees C. In this way a mixture of cadmium cobaltinitrite and sodium sulfate was obtained.

The oven was found to be the better of the two ways because the H_2SO_4 method was extremely slow, while the crystallization took place with fair rapidity in the oven. The separation of the cadmium cobaltinitrite from sodium sulfate is accomplished by washing with cold water, allowing it to stand for a minute, rewashing and so on for several times. The sodium sulfate is soluble in cold water and the cadmium cobaltinitrite is not, so by washing thoroughly all of the sodium sulfate was washed out and the pure cadmium cobaltinitrite is left in the form of a bright yellow ~~crystals~~ powder.

Two other methods of preparation were tried but neither gave satisfactory results. The first was to prepare solutions of equivalent amounts of $CdSO_4$, $Ca(NO_3)_2$ and $NaNO_2$ respectively. Glacial acetic acid was added to this and a rapid stream of NO_2 run in at a constant temperature of 60 degrees for one hour. Several of the other cobaltinitrites were successfully prepared in this way. However, the method would not work in the case of cadmium cobaltinitrite.

The second was to prepare the saturated solution of sodium cobaltinitrite and cadmium sulfate respectively and mix the two in the presence of bromine water.

ANALYSES.

To get the cadmium content, the cadmium cobaltinitrite was dissolved in the least possible amount of concentrated HCl. This was then diluted with water and ~~the~~ concentrated ammonium hydroxide added in excess. This forms a complex cadmium ammonium salt $Cd(NH_3)_4Cl_2$ which is transformed into a double cyanide of potassium, $K_2Cd(CN)_4$ by adding a small amount of KCN solution. The equation is as follows:

$$Cd(NH_3)_4Cl_2 + 4KCN = K_2Cd(CN)_4 + 2KCl + 4NH_3$$

$$K_2Cd(CN)_4 + H_2S = \downarrow CdS + 2KCN + 2HCN$$

A rapid stream of H_2S was then run in. This precipitates the cadmium sulfide which was filtered out, washed with cold water, dried and weighed. The per cent of Cd in CdS was then calculated.

To get this cobalt content the filtrate from which the cadmium

had been removed was was boiled in a porcelain casserole with enough sodium hydroxide to insure complete precipitation of the $Co(OH)_2$ and until the blue color present was completely gone. It was necessary to add to this small amount of bromine and boil to complete precipitation. This mixture was allowed to stand over night after which it was filtered. The residue was washed until the washings were neutral. This residue was then completely ignited ~~in an electric oven~~. The product was weighed as Co_3O_4 and the per cent of Co in Co_3O_4 was calculated.

The NO_2 was obtained by simply adding together the per cents of cobalt and of cadmium, and subtracting the sum from 100%.

To determine the water of crystallization a small amount of cadmium cobaltinitrite was weighed when cooled. It was then heated in an electric oven to 110 degrees, again weighed, and then heated to 120 degrees and weighed for the third time. The weights were all the same, proving that there was no water of crystallization present. Most of the other cobaltinitrite has from 6 to 12 parts of water of crystallization. My work, however, proves that this is not the case in cadmium cobaltinitrite.

In the determination of the formula the theoretical calculations were just made by dividing the molecular weight of the whole compound by the weight of the desired element as it occurs in the compound. These theoretical calculations were made from the formula. They are:

Cadmium = 33.48%, Cobalt = 11.72%, NO_2 = 54.8%.

The observed values were:

Cadmium = 33.32%, Cobalt = 11.64%, NO_2 = 55.04%.

These figures prove that the formula of the cadmium cobaltinitrite is $Cd_3[Co(NO_2)_6]_2$. This conclusion was arrived at by simply comparing the observed values with the theoretical values. This compound ionizes, the 3Cd carrying six positive ions and the $[Co(NO_2)_6]_2$ radical carrying six negative ions, as was proved by the following reaction:

$$6NaNO_2 + Cd_3[Co(NO_2)_6]_2 = 3Cd(NO_2)_2 + 2Na_3[Co(NO_2)_6]$$

solution + solution = solution + deep orange precipitate

PROPERTIES OF CADMIUM COBALTINITRITE.

Cadmium cobaltinitrite is a hygroscopic flaky compound, bright canary yellow in color.

The fact that it is a hygroscopic compound was determined by allowing a carefully weighed sample to stand in air for a day or two. When the compound was again weighed it was found that it had gained weight.

Cadmium cobaltinitrite is only slightly soluble in cold water, but is soluble in ~~hot~~ boiling water ~~at the boiling point~~. It is partially soluble in ether, carbon tetrachloride and chloroform, but in every case decomposition takes place. It is decomposed by acids and concentrated alkalies. In the latter case the respective hydroxides of cobalt and cadmium were found. Its melting point could not be determined as it decomposes to the oxides at 175 to 180 degrees. In solution cadmium cobaltinitrite is very stable, differing in this respect from the majority of the other cobaltinitrites.

SUMMARY.

Cadmium cobaltinitrite was obtained by simple decomposition from sodium cobaltinitrite and cadmium sulfate. It is a bright canary yellow powder, very stable, slightly hygroscopic, and practically insoluble in everything except boiling water. It is obtained from the mother liquor by fractional crystallization and has the formula $Cd_3[Co(NO_2)_6]_2$. Its uses are yet to be determined.

BRIEF BIBLIOGRAPHY OF REFERENCES.

(1) Adie, R.H., and Wood, T.B., -"A New Method of Estimating Potassium", for Chem. Soc. (Trans)-1900-77-1076.

A short elementary paper on the preparation and uses of sodium cobaltinitrite as a reagent for the estimation of potassium, with an outline of the results obtained. The results obtained by both Volumetric and Gravimetric analyses were given. The authors also suggested the used of cobaltinitrite as a reagent to be used for the determination of potash in manure and soil, giving the results that they had obtained along these lines.

(2) Rosenheim, A., and Koppel, I., -"Uber Kobaltoxydnitrite und einige Kobaltnitrocyan verbindungen." Zeitsch anorg Chemie--1898-XVII-42.

This paper described the preparation of cobaltinitrites. Rosenheim and Koppel condidered the cobaltinitrites as double salts of oxides with the general formulae: $3R_2O.Co_2O_3.6H_2O_3$ Some water of crystallization was found by them to be present in all of the compounds. They divided the different cobaltinitrites that they prepared and analyzed into the three classes according to the occurrence of the NO_2 radical.

These classes have formulas as follows:

(1) $3R_2O.Co_2O_3.6N_2O_3 + x H_2O$ In this class they put sodium ammonium, yellow barium and lead cobaltinitrite.

(2) $2R_2O_3.Co_2O_3.4N_2O_3 + xH_2O$. In this class they put the cobaltinitrites of Red Sodium, Red Barium, and Red Strontium.

(3) $2R_2O_3.Co_2O_3.3N_2O_3 + xH_2O$. In this class were put zinc and cobalt cobaltinitrites. The work on the cobalt cyanides consisted in a preparation of a few of the simpler cyanides with the determination of their formulas. They also prepared and analyzed some of the organic cobaltinitrites which were discussed in the same paper.

(3) Cunningham, Mary, and Perkin, F.M., "Studies on the Cobaltinitrites." J.Chem.Soc.-1909-95-1562.

This is a complete paper on the cobaltinitrites, both organic and inorganic. The chief discussion is upon their preparation and analysis. However, a short discussion is given on the advisability of using potassium cobaltinitrite as a reagent to be used in the analysis of compounds containing potassium and cobalt. The authors advise against their use.

Eleven different cobaltinitrites are discussed with reference to their preparation and use.

(4) Drushel, W.A., "On the Volumetric Estimation of Potassium as the Cobaltinitrite". Amer. J. Sci.-1907-24-433. This is one of a series of papers on potassium cobaltinitrites. This paper discusses the various different ways in which the cobaltinitrite solution may be prepared and the results obtained in the different cases. Some space is given to the various short cuts and simplifications of the process.

(5) Drushel, W.A., " The Application of Cobaltinitrite Method to the Estimation of Potassium in Soils". Amer.J.Sci.-1908-26-329-332.

A paper on the cobaltinitrite method as it may be practically applied to the estimation of potassium in soil. This paper gives in detail the procedure to be followed in the estimation of potassium in soil. Description with results, of several experiments carried out by the author was fully discussed.

(6) Drushel, W.A., "The Volumetric Estimation of Potassium in Animal Fluids".Amer.J.Sci.-1908-26-555-562.

This paper discusses fully the method to be followed in the Volumetric estimation of potassium in such animal fluids as, urine, circulatory fluids, and milk, by the precipitation of potassium cobaltinitrite. The causes for the chief errors in this work were discussed and methods by which they may be avoided are given. Reference was made to the work of seven men, chief among whom were Macallum and Kretschy.

(7) Burgess, L.L., and Kamm, O., "A Study of Cobaltinitrites and Their Application to Analytical Chemistry." J.Amer.Chem.Soc. 1912-34-652-659.

This paper describes the silver potassium cobaltinitrites and reccomends them as a delicate qualitative test for potassium, giving full directions for the application of the test, its delicacy and all interference are discussed in detail.

Other corresponding silver salts with ammonium, rubidium, cerium, thallium, and lead are mentioned and their possible uses indicated.

Also, the preparation of a corresponding series of double salts

with alkali metals were described.

(8) Bowser,L.T.,"On the Determination of Potassium by the Cobaltinitrite Method". J.of Ind.and Eng. Chemistry-1909-I-792.

A detailed discussion of the uses of the cobaltinitrites reagent with some mention of the men originating them. The method of Adie and Wood was discussed as most successful. A short discussion was made of some of the chief difficulties arising, and the most successful ways of combatting them. The advantage of the use of this method was discussed and a complete description of a modification of the procedure used in the Adie and Wood process given. References were made to the work of five men,among whom was Drushel.

(9) Dobbins,J.T.,and Ogburn,S.C.Jr.,"Recent Studies of the Inorganic Cobaltinitrites". Unpublished work at laboratories of the University of North Carolina,1920.

This paper takes up fully the discussion,preparation,and analysis,of Bismuthyl cobaltinitrite by the simple double decomposition of sodium cobaltinitrite plus a saturated solution of Bismuth nitrite. The paper also discusses a partial investigation of cadmium cobaltinitrite .

Methods to be followed in the preparation of the reagents used are given as well as properties of the obtained cobaltinitrites.

The Bismuthyl compound isolated varied in composition depending upon the time allowed. The precipitate to remain in the mother liquor and the amount of the reagents present.Their formulae ran:

(1) $(BiO)_3Co(NO_2)_6$ (2) $(BiO)_2Co(NO_2)_5(BiO)$
(3) $(BiO)Co(NO_2)_4(BiO)_2$ (4) $Co(NO_2)_3^2(BiO)_3$