[CONTRIBUTION FROM THE LABORATORY OF INORGANIC CHEMISTRY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

AMMONATES OF COPPER SELENATE[1]

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Certain of the metallic salts which form complex addition products with ammonia have been subjected to numerous investigations on the part of several workers of the past. Outstanding is the work of Alfred Werner and his students on the preparation and study of the members of the cobalt and platinum systems. In contrast to the cobalt ammines, which are for the most part relatively stable, there exists another class of compounds, the ammonates, which are relatively unstable and which may be represented by the general formula $MA \cdot xNH_3$. As a part of the study of selenium and its compounds carried out at this Laboratory, it was thought that an investigation of the compounds formed by the action of ammonia on the metallic selenates and selenites might yield results of interest. The present report deals with the compounds formed by the addition of ammonia to copper selenate.

Dennis and Koller[2] prepared three ammonates of copper selenate, two of which were products resulting from the partial decomposition of their primary salt, $CuSeO_4 \cdot 4NH_3 \cdot H_2O$. The method utilized by these workers was to pass ammonia gas into a solution of copper selenate to which had been added an excess of ammonium hydroxide. After the ammonia had been passed into the solution for about two hours, clusters of dark blue crystals separated. The product was washed twice with ammonia solution and dried over lime for two hours. Analysis of the material yielded results in accord with the formula ascribed to the tetrammonate monohydrate. Finely ground crystals of the salt were dried in the air for two hours. Ammonia was lost and the resulting pale blue compound was found to be $CuSeO_4 \cdot 3NH_3 \cdot H_2O$. Crystals of the tetrammonate monohydrate were desiccated over lime at a pressure of 25 mm. of mercury for one week. Analysis of the resulting compound showed that one molecule of water had been lost with the formation of the tetrammonate, $CuSeO_4 \cdot 4NH_3$. Willy Lange[3] has recently reported the formation of an ammonate of copper selenate corresponding to the formula $CuSeO_4 \cdot 4NH_3 \cdot 2H_2O$. The method of preparation was not stated. The product was described as a very solu-

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[1] Abstracted from a portion of a thesis submitted to the faculty of the Graduate School, University of Wisconsin, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1929. The thesis was started under the direction of the late Victor Lenher, continued under the supervision of the late George Kemmerer and completed under the guidance of Professor V. W. Meloche.

[2] Dennis and Koller, THIS JOURNAL, **41**, 949 (1919).

[3] Willy Lange, *Ber.*, **59**, 2113 (1926).

ble, sky-blue crystalline material. The author states that the compound lost water to give the tetrammonate—a blue-violet product. The tetraammonate upon heating decomposed without melting to give the green diammonate. Identification of the tetrammonate is based on one copper determination. No analysis is reported for the diammonate.

Materials

Selenic acid was prepared from purified selenium dioxide by direct chlorination of a 10% solution of selenious acid, according to the method of Metzner.[4] The resulting selenic and hydrochloric acid mixture was neutralized with basic copper carbonate, the solution filtered, and the bulk of the copper selenate isolated from the copper chloride by means of precipitation with ethyl alcohol according to the method of Lenher and Kao.[5] Following four or five precipitations of the selenate by means of alcohol the material was twice recrystallized from water. Chlorides were shown to be absent by testing a 1% nitric acid solution of one gram of the copper selenate with a few cc. of saturated silver selenate solution. Failure of a turbidity or opalescence to appear was taken as evidence of the absence of appreciable amounts of chloride.[6]

The ammonia used throughout this work was obtained for the most part from the National Ammonia Company. The commercial material was transferred into a small iron tank containing sodium. Gas used for the preparation of the ammonates described was obtained by distillation from the dry liquid.

Analytical Methods

Selenium.—Selenium was determined according to the method of Lenher and Kao[7] as described by Hoffman and Lenher.[8]

Copper.—Copper selenate when ignited in a porcelain crucible over a Bunsen burner leaves a residue of copper oxide. The selenium is volatilized as the dioxide. In the case of the ammonates of copper selenate the direct immediate ignition must be avoided because of the reducing action of the ammonia on the copper residue at high temperatures. Consequently it is necessary first to drive off most of the ammonia at a low heat, and then to follow the preliminary heating by a gentle ignition. The temperature of the crucible is then raised to the full heat of the burner. If the preliminary heating is not sufficiently slow, the results obtained will be erratic and the crucible will become stained with a rose-colored deposit produced by the action of metallic copper or cuprous oxide on the glaze of the crucible.

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[4] Metzner, *Ann. chim. phys.*, **15**, 203 (1898).

[5] Lenher and Kao, THIS JOURNAL, **47**, 1521 (1925).

[6] Chung Hsi Kao, B.S. thesis, University of Wisconsin, 1924. Dr. Kao states that the sensitivity of this test is limited only by the solubility of silver chloride in water.

[7] Lenher and Kao, THIS JOURNAL, **47**, 769 (1925).

[8] Hoffman and Lenher, *ibid.*, **51**, 3178 (1929).

That the method of ignition is satisfactory for the determination of copper oxide in compounds of the type to be described was demonstrated by numerous analyses, the following two of which may be considered representative.

Compound	CuO, Calcd., %	CuO found %	Detns.	Max. dev., %
$CuSeO_4 \cdot 5H_2O$	26.79	26.73	3	0.14
$CuSeO_4 \cdot 3NH_3 \cdot H_2O$	28.85	28.92	3	0.07

In cases where because of small amounts of sample or difficulty in weighing, it was desirable to estimate the copper content of the filtrate from the selenium determination, the determination was made according to the sulfocyanate method of Rivot[9] as modified by Treadwell.[10]

Ammonia.—Ammonia was determined by distillation of the gas from an alkaline solution which had been freed from copper. In the course of an investigation of the copper sulfate complexes, Horn and Taylor[11] experienced considerable difficulty in the direct distillation of ammonia from alkaline solutions of the ammonates. These workers found that when sodium hydroxide is added to a solution containing appreciable amounts of copper sulfate, the ammonia is expelled with difficulty and prolonged boiling is necessary to drive over the last traces of ammonia. In all cases they found that it was necessary to distil until the residue in the Kjeldahl flask had evaporated almost to dryness in order to arrive at quantitative results.

It was found that copper selenate behaves in a like manner. Because of this difficulty it was considered necessary to remove the copper from the solution before distillation. This was accomplished by warming the sulfuric acid solution of the ammonate with a piece of metallic aluminum. The copper was quantitatively deposited along with a portion of the selenium. Evaluation of the amount of ammonia remaining in the solution was then made by distillation into an excess of acid of known strength and back-titration with sodium hydroxide.

Water.—Horn and Taylor[11] collected the water evolved from the combustion of the ammonates of copper sulfate by absorption in a U-tube containing solid potassium hydroxide. The evolved ammonia passed through the alkali tube and was absorbed in sulfuric acid. An attempt was made to apply this method of determining water and ammonia to the ammonates of copper selenate. It was found that when the temperature was raised to a point required for the complete decomposition of the ammonate, a partial combustion of the ammonia took place. As a result the water results were high and the ammonia low. The explanation for this behavior probably lies in the fact that ammonates of copper selenate de-

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[9] Rivot, *Compt. rend.*, **38**, 868 (1854).

[10] Treadwell and Hall, "Analytical Chemistry," Vol. II, **1924**, 5th ed., p. 186.

[11] Horn and Taylor, *Am. Chem. J.*, **32**, 253 (1904).

compose principally into copper oxide, selenium dioxide, ammonia and oxygen at 190°. Inasmuch as it is necessary to heat the compounds to at least 180° in order to drive off the last two molecules of ammonia, it is probable that the oxidation takes place when the selenate group decomposes to yield the selenite. Heating in a current of oxygen-free dry nitrogen likewise yielded high water results and low ammonia results.

The method adopted for the determination of water in the ammonates was that of complete combustion in a tube containing copper oxide and metallic copper. Selenium was retained in the boat by covering the sample with a layer of sodium chromate of known water content. The percentage of ammonia having been determined in a separate sample, the water existing as such in the compound was calculated.

Hydrated Ammonates of Copper Selenate

Copper Selenate Tetrammonate Monohydrate.—The method of Dennis and Koller[2] was followed in the preparation of this salt: 100 g. of copper selenate pentahydrate was dissolved in 125 cc. of concentrated ammonia solution and ammonia gas passed into the dark blue solution for two hours. The crystals were filtered on a sintered glass plate, washed with a cold concentrated ammonia solution and desiccated over soda lime for three days. Analysis of the material was in accord with the formula assigned by the above workers.

Anal. Calcd. for $CuSeO_4{\cdot}4NH_3{\cdot}H_2O$: CuO, 27.16; Se, 27.04; NH_3, 23.22; H_2O, 6.15. Found: CuO, 27.04 (av. 3 detns.); Se, 26.91 (av. 4 detns.); NH_3, 22.94 (av. 4 detns.); H_2O, 6.31 (av. 3 detns.).

Ammonia results were usually found to be slightly lower than the calculated values. This was probably brought about as a result of loss of ammonia during the drying process. The color is close to that of Mulliken's standard BV—Shade 2.[12]

Attempts were made to prepare the compound by adding alcohol to ammoniacal solutions of copper selenate. The blue precipitate produced was found to be a basic salt the composition and color of which varied with the preparation. The precipitate corresponded most nearly with the tetrammonate monohydrate when small amounts of alcohol were used in strongly ammoniacal solutions of the selenate.

Copper Selenate Triammonate Monohydrate.—Copper selenate tetrammonate monohydrate when treated with a current of dry air loses one molecule of ammonia to form the triammonate monohydrate. Samples of the tetrammonate were treated in the manner described by Dennis and Koller.[2] Analysis of the product yielded results in harmony with the findings of these workers.

Anal. Calcd. for $CuSeO_4{\cdot}3NH_3{\cdot}H_2O$: CuO, 28.85; Se, 28.72; NH_3, 18.52; H_2O, 6.98. Found: CuO, 28.91; Se, 28.78; NH_3, 18.51; H_2O, 6.90 (all av. of 3 detns.).

The color of this salt is almost identical with that of standard B—Tint I.[12]

The monohydrate of copper selenate under ordinary conditions is the most stable ammonate of the series. The composition of the salt is not altered by prolonged exposure to the air and desiccation over phosphorus pentoxide for several weeks fails to remove the molecule of water. When heated to a temperature of 110° under a pressure of 2 mm. of mercury, water and ammonia are lost. Samples treated in this manner

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[12] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, **1904**, Color Charts, Vol. I.

were found to come to constant weight after a loss of approximately 14%. The calculated loss in weight for the conversion of the triammonate monohydrate to the dihydrate is 12.72%. Analysis of the residue showed that in all cases the amount of ammonia in the material was lower than the calculated amount for the diammonate, the average ammonia content of three typical preparations being 13.65% against a calculated value of 14.14%. Copper and selenium results were correspondingly high.

Copper Selenate Tetrammonate Dihydrate.—Willy Lange[3] has reported the isolation of an ammonate of the composition $CuSeO_4 \cdot 4NH_3 \cdot 2H_2O$. The only analysis reported upon the compound is one water determination which is about 1% lower than the calculated value. The compound is described as a very easily soluble, sky-blue crystalline substance which by the loss of water yields the blue-violet anhydrous tetrammonate.

Various methods were used in an effort to isolate this compound. Ammonia gas when passed into either dilute or concentrated solutions of copper selenate always yielded the monohydrate. It had been previously noticed that by cooling the reaction tube during the precipitation of the tetrammonate monohydrate, an increased yield of the product was obtained. It was thought that the greatly lessened solubility might indicate that the dihydrate was the stable phase at temperatures in the neighborhood of 0° and that during subsequent operations decomposition took place with the formation of the monohydrate. Accordingly an effort was made to isolate and dry the product at a temperature but slightly above 0°. Precipitation of the salt was brought about by passing ammonia gas into a solution of copper selenate contained in a pyrex test-tube. The tube was immersed in an ice-salt mixture at a temperature of about $-2°$ at the time of precipitation. It is interesting to note that the deposition of the ammonate from solution is nearly complete at this temperature, the supernatant liquid having but a faint blue color after crystallization. The precipitate was quickly transferred to a sintered glass filter provided with a jacket through which cold brine was circulated. The blue material was washed several times with a solution prepared by saturating water with ammonia gas at 0°, transferred to a soda lime desiccator and placed in the lower compartment of an electric refrigerator. At no time did the temperature of the product greatly exceed 4°.

Analysis of several products so prepared did not yield results in agreement with the calculated values for the dihydrate. In order to safeguard against possible loss of appreciable amounts of ammonia or water during the weighing process, large samples were taken from previously weighed glass-stoppered bottles, quickly transferred to dilute acid solutions and diluted to known volumes. Analysis of aliquot portions enabled us to determine the percentages of the various constituents in the original sample. Water thus determined by difference was usually high by one or two per cent. In no case did the complete analysis agree with the calculated values for the dihydrate.

Because of our inability to isolate the dihydrate with the aid of ordinary precautions. it was thought advisable to investigate the warming curve of the compound formed by the action of ammonia gas on a solution of copper selenate at 0°. Accordingly a large quantity of the ammonate was precipitated at $-1°$ and isolated in the usual manner. When the deposition of the product was complete the supernatant liquid was removed and the ammonia inlet tube replaced by a thermometer. The ammonia gas was swept from the tube by means of a blast of air and the sample quickly mixed with about one-third its volume of cold copper selenate tetrammonate monohydrate of established purity. The reaction tube, which throughout this manipulation was cooled in brine, was wrapped in several thicknesses of cold cloth and allowed to warm slowly. Examination of one of the characteristic curves obtained in this manner (Fig. 1) shows the absence of the break which usually accompanies a change of the solid phase. Temperature readings were taken every thirty seconds and the total time of the experiments was about forty-five minutes. It is to be concluded as a result of the physical and chemical investigation either that the compound described by Lange does not exist or that it is not formed under the conditions described in the above experiments. The product obtained by Lange was in all probability the tetrammonate monohydrate which contained water mechanically retained in the crystals. It has been noted that the monohydrate is dried with difficulty.

Anhydrous Ammonates of Copper Selenate

Copper Selenate Pentammonate.—Copper selenate pentahydrate when exposed to ammonia gas behaves in much the same manner as the corresponding hydrate of copper sulfate.[13] Copper selenate pentahydrate when exposed to a stream of ammonia gas very quickly evolves heat, turns dark blue and assumes a pasty consistency. The tetrammonate monohydrate behaves in a similar manner. Prolonged exposure of either of the two salts to anhydrous ammonia under a pressure of 10 cm. of mercury and at a temperature of 0° results in a quantitative absorption of ammonia to produce the pentammonate of copper selenate, a dark blue product which upon warming evolves ammonia and which very quickly decomposes in moist air. The pentammonate may be prepared most conveniently by the action of liquid ammonia on copper selenate tetrammonate. The monohydrate is first treated with a slow stream of anhydrous ammonia gas at slightly elevated temperatures in order to remove the water. The resulting product is transferred to a pyrex test-tube and immersed in a Dewar flask containing liquid ammonia. Liquid ammonia is then condensed in the reaction chamber. The low temperature and the pressure are sufficient completely to transform the tetrammonate to the pentammonate. Samples of the product after removal of the excess liquid ammonia were sealed in small tubes, weighed and broken under dilute hydrochloric acid. Analysis for various constituents was then made on the filtrate in the usual manner.

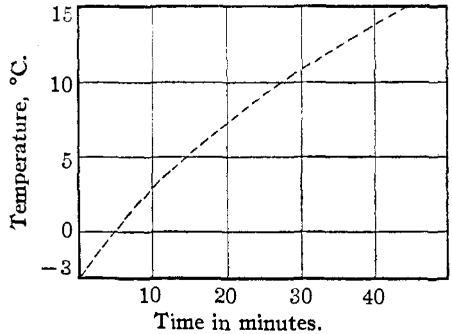

Fig. 1.

Anal. Calcd. for $CuSeO_4 \cdot 5NH_3$: CuO, 27.22; Se, 27.13; NH_3, 29.25. Found: CuO, 27.01; Se, 27.05; NH_3, 29.12 (all av. of 4 detns.).

The transition point for the system copper selenate pentammonate–copper selenate tetrammonate was determined dilatometrically to be at 19 ± 0.3°. The color of the pentammonate is between that of the standards B and BV of the normal tones.[12]

Kao[6] found from a study of the copper selenate–water system evidence which led him to suspect strongly the existence of a heptahydrate of copper selenate at low temperatures. Attempts to isolate the heptammonate of copper selenate have failed. Chemical analysis of the product formed by the action of liquid ammonia on copper selenate, copper selenate pentammonate and copper selenate tetrammonate yielded results which were not concordant with different preparations and which did not correspond to those calculated for any one simple compound. Inasmuch as Ephraim[14] has shown that in some cases of this type a continuous series of solid solutions exists between different ammonates and ammonia, it is doubtful if analytical results would have great

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[13] Horn, *Am. Chem. J.*, 39, 195 (1908).

[14] Ephraim, *Ber.*, 52, 940 (1919).

significance anyhow. Investigation of the warming curve of the copper selenate-ammonia system between the temperature of boiling liquid ammonia and 15° yielded no irregularity which might be attributed to compound decomposition. It is to be concluded that if the pentammonate of copper selenate does exist it is not stable at atmospheric pressure above the boiling point of liquid ammonia.

Copper Selenate Tetrammonate.—This compound has been previously reported by Dennis and Koller[2] and more recently by Willy Lange.[8] The former investigators obtained the product as a result of the decomposition of copper selenate tetrammonate monohydrate at room temperature under a pressure of 27 mm. of mercury and in the presence of freshly ignited quicklime. Lange gives none of the details of preparation but states that the compound is formed as a result of the decomposition of the tetrammonate dihydrate with the production of the anhydrous product.

The directions of Dennis and Koller were followed in the preparation of this compound. After seven days in a desiccator containing lime and at a pressure of about 17 mm. of mercury it was found that the tetrammonate monohydrate had lost water and that there was formed the anhydrous tetrammonate. Analysis of representative samples yielded results substantially in agreement with those calculated from the assigned formula.

Anal. Calcd. for $CuSeO_4 \cdot 4NH_3$: CuO, 28.94; Se, 28.84; NH_3, 24.76. Found: CuO, 28.41; Se, 28.81; NH_3, 24.94 (av. of 4 detns.).

The tetrammonate is stable above 100° provided the sample is maintained in an atmosphere of ammonia gas. Because preparations made according to the method of Dennis and Koller usually appeared to have undergone a secondary decomposition with the production of a small amount of the triammonate monohydrate and basic salts, the following method of preparation was devised to yield a product free from the triammonate monohydrate.

Copper selenate pentahydrate of established purity was dissolved in water and 50 cc. of the saturated solution transferred to a large pyrex test-tube fitted with a delivery and outlet tubes. Ammonia gas was passed into the hot solution and after most of the water had been removed the tube was transferred to an oil thermostat regulated to about 120°. Passage of the ammonia was continued through the blue mass until the last traces of water had been removed. The preparation was removed, crushed and again treated with ammonia gas at 120°. Analysis of several products prepared in this manner yielded results in strict agreement with the calculated values. In two typical preparations the ammonia content was found to be 24.70 and 24.76% against the calculated value of 24.76%. The color of the tetrammonate is between that of standards VB and BV of the normal tones.[12]

Copper Selenate Diammonate.—Horn and Taylor[11] prepared a series of apple-green decomposition products of copper sulfate tetrammonate and concluded that the products were basic salts and not definite chemical individuals. Lange[8] has reported that if heated the tetrammonate of copper selenate will pass directly without melting to the diammonate.

It was found that if the anhydrous tetrammonate of copper selenate was heated with access to air there were formed various decomposition products, the ammonia content of which was usually lower than that calculated from the diammonate and which varied depending upon the length and rapidity of heating as well as with the maximum temperature. Samples of the tetrammonate placed in an oven regulated at 80° lost approximately 12.5% in weight. Although this loss corresponds rather closely to the calculated loss in the conversion of tetrammonate to the diammonate, the analytical results were not in close agreement for the calculated values for the diammonate. If. however, the sample is maintained in an atmosphere of ammonia gas at atmospheric pressure, the loss in weight will not be appreciable until the temperature of 178° is reached. At this point ±2° the compound breaks down to form the diammonate. Analyses of the products obtained by heating copper selenate tetrammonate to a temperature of 185° in an atmosphere of ammonia gas at atmospheric pressure are in close agreement with the calculated values.

Anal. Calcd. for $CuSeO_4 \cdot 2NH_3$: CuO, 33.04; Se, 32.88; NH_3, 14.14. Found: CuO, 33.03; Se, 32.56; NH_3, 14.14 (all av. of 3 detns.).

The diammonate is a light blue powder. It corresponds somewhat to the BG normal tone of Mulliken's standards[12] and is insoluble in water but soluble in dilute mineral acids and ammonia solution. The compound is stable if preserved in a closed container. Below 178° the material absorbs ammonia to form either the tetrammonate or the pentammonate depending upon the temperature and pressure. Heated above 192° the diammonate is decomposed with the production of ammonia and a black residue which consists of a mixture of copper oxide and copper selenide. Selenium dioxide has been noticed in the cooler parts of the reaction tube when the temperature exceeds 200°.

Summary

1. Copper selenate pentammonate and copper selenate diammonate have been prepared and identified.

2. A new and satisfactory method for the preparation of copper selenate tetrammonate has been described.

3. No evidence was found for the existence of the tetrammonate dihydrate of copper selenate reported by Lange.

4. Copper selenate tetrammonate monohydrate, copper selenate tetraammonate and copper selenate triammonate monohydrate have been prepared according to the methods of Dennis and Koller. Analysis of the products indicates composition in accord with ascribed formulas.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

MOLECULAR RAY EXPERIMENTS. THE CHEMICAL ACTIVITY OF MOLECULAR AND ATOMIC OXYGEN[1]

BY WORTH H. RODEBUSH AND W. A. NICHOLS, JR.

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The initial purpose of this investigation was to find some chemical reaction by which the image of a beam of oxygen molecules could be formed on a target for a Stern-Gerlach experiment. The first attempts in this direction in this Laboratory were made at the time that the magnetic moment of atomic hydrogen was measured. It became evident[1c,d] at that

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[1] Previous publications on molecular rays from this Laboratory are as follows: (a) Kunz, Taylor and Rodebush, *Science*, **63**, 550 (1926); (b) Taylor, *Phys. Rev.*, **28**, 576 (1926); (c) Phipps and Taylor, *Science*. **64**, 480 (1926); (d) Phipps and Taylor, *Phys. Rev.*, **29**, 309 (1927); (e) Rodebush, *Proc. Nat. Acad. Sci.*, **13**, 50 (1927); (f) Rodebush and Copley, *Phys. Rev.*, **33**, 1083 (1929); (g) Kurt and Phipps, *ibid.*, **34**, 1357 (1929); (h) Rodebush and Nichols, *ibid.*, **35**, 649 (1930); (i) Shaw, Phipps and Rodebush, *ibid.*, **35**, 1126 (1930).