[CONTRIBUTION FROM NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Studies in the Chromammines. III. Preparation of Di-acido Diethylenediamine Salts by Thermal Decomposition of Triethylenediamine Luteo Salts[1,2]

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It has been observed that $[\mathrm{Cr\ en_3}]\mathrm{Cl_3}\cdot 3^1/_2\mathrm{H_2O}$[5] and $[\mathrm{Cr\ en_3}](\mathrm{SCN})_3\cdot\mathrm{H_2O}$ lose one-third of their ethylenediamine (and all their water of crystallization) when heated for several days, the former at 160°,[6] and the latter at 130°.[7,8,9,10] The products of thermal decomposition of the luteo chloride and luteo thiocyanate are, respectively, *cis*-$[\mathrm{Cr\ en_2Cl_2}]\mathrm{Cl}$[6] and *trans*-$[\mathrm{Cr\ en_2(SCN)_2}]\mathrm{SCN}$.[8]

These reactions are of practical importance as means for preparing salts of the *cis*- and *trans*-di-acido series and as essential steps in *cis–trans* isomerization cycles.[11] The influence of the anion on the configuration of the product is theoretically significant. It is noteworthy that *trans*-$[\mathrm{Cr\ en_2Cl_2}]\mathrm{Cl}$ is not converted to the *cis* isomer when heated at 160°[12] nor is *cis*-$[\mathrm{Cr\ en_2(SCN)_2}]\mathrm{SCN}$ converted to the *trans* isomer at 130°.[8]

The order of temperatures at which the two luteo salts decompose, namely, $\mathrm{Cl^-} > \mathrm{SCN^-}$, is in accord with results reported for other metal ammines. The vapor pressure curves for a series such as $[\mathrm{Ni(NH_3)_6}]\mathrm{X_2}$ parallel the curves for the corresponding ammonium salts, $\mathrm{NH_4X}$; *i. e.*, the order of temperatures at which a given pressure is reached is $\mathrm{I^-} > \mathrm{Br^-} > \mathrm{Cl^-} > \mathrm{SCN^-}$ for both the hexammine salts and the ammonium salts.[13]

The apparent simplicity of these reactions is misleading, however. Preliminary attempts to prepare the *cis*-dichloro salt by thermal decomposition of the luteo chloride were completely unsuccessful. Weighed samples of the latter were heated by various means under a variety of conditions, including temperatures ranging from 160 to 220°, times up to one month, application of vacuum and use of surface extenders such as ground Pyrex or green glass, ground porous plate and glass beads. Although the samples lost weight slowly, the yellow color of the luteo salt never changed to the characteristic red-violet of the *cis*-dichloro salt. None of the desired compound could be obtained by recrystallization of the brown products.

It was then found that the reaction is catalyzed by traces of ammonium chloride. In a series of experiments carried out to determine the effect of impurities, a quantity of triethylenediamine chromic chloride prepared by the chromic sulfate method (1) was repeatedly recrystallized and a sample of each fraction heated in a small oven whose temperature was automatically controlled at 208 ± 3°. The results were disappointing until a fraction unintentionally contaminated with ammonium chloride was tested. This turned red-violet in a short time. Other samples to which ammonium chloride was deliberately added were then heated for several hours and *cis*-$[\mathrm{Cr\ en_2Cl_2}]\mathrm{Cl}$ was obtained from the products by recrystallization.

Previously it had been found that the luteo thiocyanate could be thermally decomposed to the *trans*-dithiocyanato salt without difficulty at 130°. It was determined that ammonium thiocyanate rather than ammonium chloride is the catalyst in this case.

The preparative methods used account for our success with the thiocyanate and failure with the chloride in the preliminary experiments. Our samples of luteo thiocyanate had been prepared by reaction of the chloride with ammonium thiocyanate as described by Pfeiffer[10] and we found that such samples contain catalytic quantities of ammonium thiocyanate. On the other hand, our original luteo chloride was never in contact with ammonium salts since it was prepared directly from chromous chloride.[14] The luteo chloride which Pfeiffer decomposed was prepared by a method involving reaction of the luteo sulfate with ammonium chloride,[6] a fact whose significance was at first overlooked. Such samples still contain catalytic amounts of ammonium chloride after recrystallization.

To demonstrate conclusively the catalytic nature of these reactions, pure samples of luteo chloride and thiocyanate, to which ammonium chloride and ammonium thiocyanate, respectively, were added in various ways, were heated at controlled temperatures until decomposition was nearly complete as shown by weight loss. To insure freedom from ammonium salts except those intentionally added, the luteo chloride was prepared by the reaction of the sulfate with hydrochloric acid[1] and the luteo thiocyanate from the chloride by means of sodium thiocyanate[1]; the products were recrystallized. Pure samples of the

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[1] For the second paper in this series, see Rollinson and Bailar, THIS JOURNAL, **65**, 250 (1943).

[2] Presented at the 99th meeting of the American Chemical Society, Cincinnati, Ohio, April 9, 1940.

[3] Abstracted from a portion of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry at the University of Illinois, 1939.

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[5] The symbol "en" represents one molecule of ethylenediamine.

[6] Pfeiffer, Koch, Lando and Trieschmann, *Ber.*, **37**, 4277 (1904).

[7] Pfeiffer, *et al.*, *ibid.*, **37**, 4256 (1904).

[8] Pfeiffer, *et al.*, *ibid.*, **37**, 4269 (1904).

[9] Pfeiffer, *ibid.*, **33**, 2690 (1900); **34**, 4303 (1901).

[10] Pfeiffer, *Z. anorg. Chem.*, **24**, 294 (1900); **29**, 107 (1901).

[11] Ref. 6, p. 4265.

[12] Ref. 6, p. 4264.

[13] Weinland, "Komplex-Verbindungen," Ferdinand Enke, Stuttgart, 1924, p. 485.

[14] Balthis and Bailar, THIS JOURNAL, **58**, 1474 (1936).

two salts as controls were heated along with those contaminated with ammonium salts. The effect of recrystallization of luteo chloride and thiocyanate contaminated with ammonium salts was also determined.

In all cases the contaminated samples decomposed faster than the controls. The pure luteo chloride turned brown while that to which ammonium chloride had been added turned red-violet. While Pfeiffer reported a temperature of 160° and a time of several days,[6] we found that thermal decomposition of the chloride is nearly complete in a few hours at 210°; this reaction is too slow to be practical even at 180°. Decomposition of the thiocyanate is also complete in a few hours, at 130°, instead of several days as was indicated by Pfeiffer[9]; the discrepancy may be due to difference in ammonium thiocyanate content of Pfeiffer's luteo thiocyanate and that used in the present investigation.

Recrystallization of the luteo thiocyanate containing ammonium thiocyanate greatly decreases the rate of thermal ~~decom~~position. Recrystallization of the luteo chloride containing ammonium chloride, on the other hand, causes no change in the rate of thermal decomposition. This may be due to the fact that the luteo thiocyanate is much less soluble than the chloride while ammonium thiocyanate is much more soluble than ammonium chloride. Consequently, recrystallization is more efficient in the case of the thiocyanate.

The specificity of catalyst action seems to indicate that negative ions from the catalyst molecules actually enter the complex nucleus. While ammonium thiocyanate catalyzes the thermal decomposition of the luteo thiocyanate, ammonium chloride does not, even though the luteo thiocyanate crystals obviously contain thiocyanate ions in tremendous excess over the amount required (in the form of ammonium thiocyanate) for catalysis. No attempt was made to test the effect of ammonium thiocyanate on the decomposition of the luteo chloride, since this reaction proceeds at practical rates only at temperatures above that at which ammonium thiocyanate is converted to thiourea.

The water of crystallization of both the luteo chloride and thiocyanate (accounting for 51.2 and 23.1%, respectively, of the total theoretical weight loss) is readily driven off whether or not a catalyst is present. Pure samples decompose rapidly to an extent corresponding approximately to the loss of water of crystallization and thereafter lose weight at a greatly decreased rate. On the other hand, samples contaminated with ammonium salts continue to decompose rapidly even after the weight loss corresponds to the water of crystallization, marked decrease in rate occurring only after considerable ethylenediamine has been driven off.

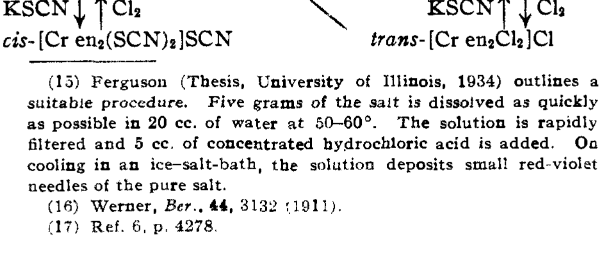
Determination of the conditions on which these reactions depend makes them available as synthetic procedures superior to the usual methods for preparing *cis*-[Cr en_2Cl_2]$Cl \cdot H_2O$ and *trans*-[Cr $en_2(SCN)_2$]$SCN \cdot H_2O$. The *cis*-dichloro salt is prepared from pure luteo chloride recrystallized from 1% ammonium chloride solution. The salt, spread in a thin layer, is heated for several hours at 208–212°. The course of the reaction is followed by weighing at intervals. The product may be recrystallized[15] but for most purposes it suffices to wash it with cold concentrated hydrochloric acid. A yield of 50% is easily obtained.

trans-[Cr $en_2(SCN)_2$]$SCN \cdot H_2O$ is prepared in a similar way from the luteo thiocyanate recrystallized from 25% ammonium thiocyanate solution. The salt is heated at about 130°, but not above 134°. The product is recrystallized from warm water. The yield is 60% or better.

These methods are definitely superior in convenience and efficiency to the usual procedures. The *cis*-dichloro salt is ordinarily prepared from potassium chromioxalate by a series of reactions involving synthesis of [Cr $en_2C_2O_4$][Cr en$(C_2O_4)_2$] and [Cr $en_2(C_2O_4)$]Cl as intermediates. Werner[16] reported a yield of only five grams of the *cis*-dichloro salt from one hundred grams of chromioxalate. The *cis*-dichloro salt may also be prepared by repeated evaporation of a solution of the luteo chloride with hydrochloric acid, but the yield is poor.[17]

Pfeiffer prepared *trans*-[Cr $en_2(SCN)_2$]$SCN \cdot H_2O$ by the action of ethylenediamine on $K_3[Cr(SCN)_6]$[8,9] as well as by thermal decomposition of the luteo salt. The yield by the former method is only 22% since separation of the *cis* and *trans* isomers is necessary. Pfeiffer's objection that the method of thermal decomposition is too slow is invalidated by the results of the present investigation.

The importance of these thermal decompositions is indicated by the following cycle based on reactions reported by Pfeiffer and co-workers[11] and those reported here and in a previous communication[1]:



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[15] Ferguson (Thesis, University of Illinois, 1934) outlines a suitable procedure. Five grams of the salt is dissolved as quickly as possible in 20 cc. of water at 50–60°. The solution is rapidly filtered and 5 cc. of concentrated hydrochloric acid is added. On cooling in an ice–salt-bath, the solution deposits small red-violet needles of the pure salt.

[16] Werner, *Ber.*, **44**, 3132 (1911).

[17] Ref. 6, p. 4278.

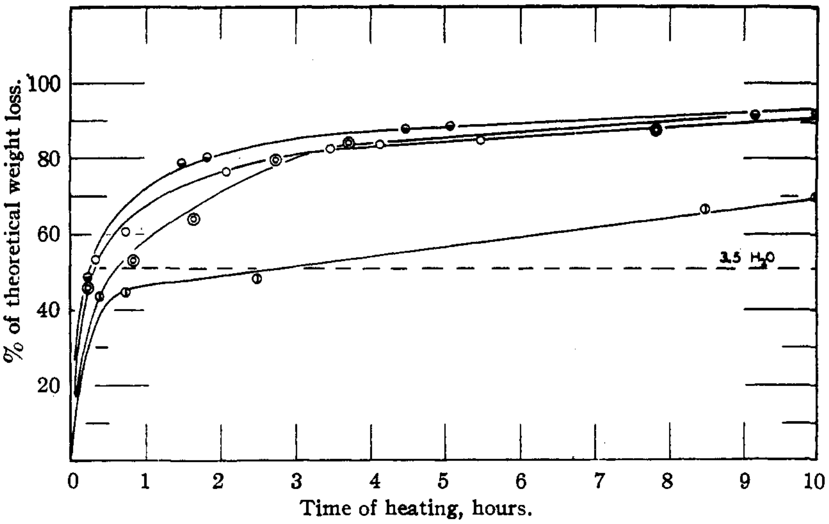

Fig. 1.—Effect of NH_4Cl on the thermal decomposition of [Cr en_3]$Cl_3\cdot 3.5H_2O$ at 210°: ⦶, pure [Cr en_3]$Cl_3\cdot 3.5H_2O$; ◎, pure [Cr en_3]$Cl_3\cdot 3.5H_2O$ ground with 2% solid NH_4Cl; ○, pure [Cr en_3]$Cl_3\cdot 3.5H_2O$ recrystallized from 1% NH_4Cl solution; ◒, pure [Cr en_3]$Cl_3\cdot 3.5H_2O$ recrystallized from 1% NH_4Cl solution, then from H_2O.

Repeated evaporation of the *cis*-dichloro salt with hydrochloric acid and mercuric chloride results in the formation of a mercury *trans*-dichloro double salt, but the yield is poor.[18] This *cis*-*trans* isomerization may be readily accomplished by use of the above reactions.

Preliminary rate studies indicate that these thermal decompositions are first order reactions, but lack of consistency of results of successive runs precludes a final conclusion. The method used, which evidently requires certain refinements, comprised heating the luteo chloride and thiocyanate (contaminated with ammonium salts) in an apparatus arranged to permit absorption and titration of the ethylenediamine evolved.

Experimental

Apparatus.—In determining the catalytic effect of ammonium salts, a small electric oven whose temperature could be closely controlled was used. This was made from a thin-walled refractory tube, closed at one end, 20 cm. long by 9 cm. inside diameter, wound with chromel wire and covered with alundum cement. The cylinder was enclosed in a transite box and fitted with a door made of transite. A thermometer and mercury thermoregulator were inserted through holes in the closed end of the cylinder. Temperature was controlled by auxiliary resistances which were short-circuited out of the system by a relay except when it was actuated by the thermoregulator.

Thermal decomposition of larger quantities of the luteo chloride and thiocyanate, in preparation of the di-acido salts, was carried out in a large electric oven heated by a set of coils at the bottom. A baffle was placed over the coils to minimize the temperature gradient from the bottom to the top of the oven.

Catalytic Effect of NH_4Cl on the Thermal Decomposition of [Cr en_3Cl_3]$\cdot 3^1/_2H_2O$.—Pure luteo chloride, prepared by the method previously described,[1] was treated with ammonium chloride in various ways. One-gram samples of the products were heated in the small oven at 208–210° and weighed at intervals. Samples of the following were included for comparison: pure luteo chloride as a control; luteo chloride prepared from the sulfate by reaction with ammonium chloride; a sample prepared by recrystallization of luteo chloride contaminated with ammonium chloride.

The results are shown in Graph 1. It is evident that traces of ammonium chloride profoundly affect the course of the reaction and that the catalytic effect is not nullified by recrystallization of the luteo chloride containing ammonium chloride. It is also apparent that the luteo chloride prepared by action of ammonium chloride on the luteo sulfate contains catalytic amounts of ammonium chloride.

The effect of temperature on the course of the reaction was also determined. A 3-g. sample of pure luteo chloride recrystallized from 1% ammonium chloride solution was heated at 180° and weighed at intervals. The experiment was repeated at 170°. The data are plotted on Graph 2 with a plot of data for 210° for comparison. It is evident that the reaction would be inconveniently slow at 160° as specified by Pfeiffer.

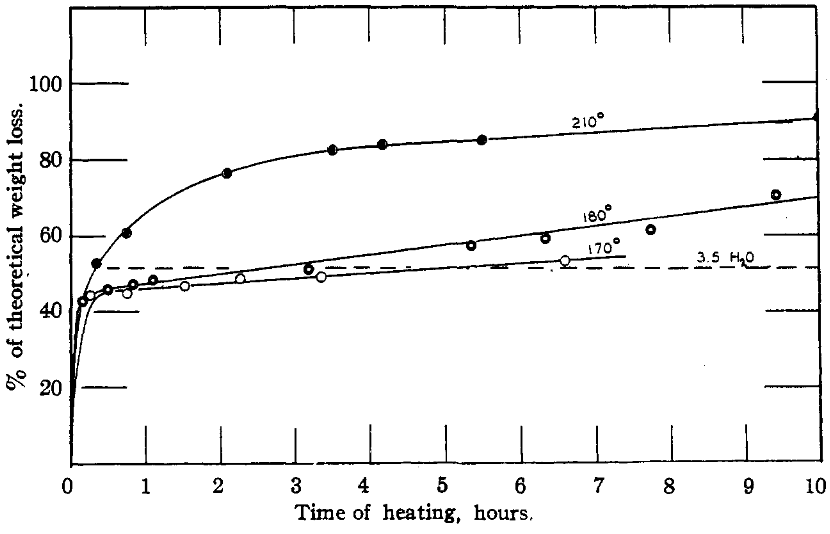

Fig. 2.—Effect of temperature on the thermal decomposition of [Cr en_3]$Cl_3\cdot 3.5H_2O$ recrystallized from 1% NH_4Cl solution.

Catalytic Effect of NH_4SCN on the Thermal Decomposition of [Cr en_3]$(SCN)_3\cdot H_2O$.—Similar experiments were carried out with 3-g. samples of luteo thiocyanate containing small amounts of ammonium thiocyanate. To insure

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(18) Ref. 6, p. 4279.

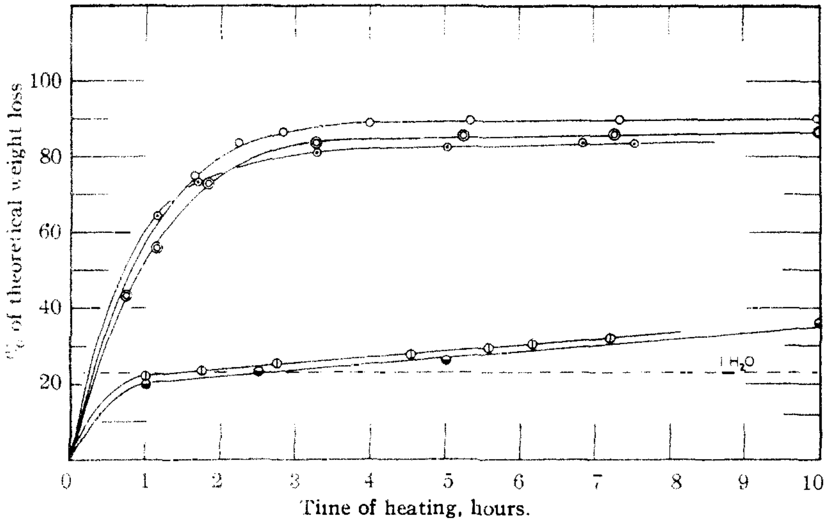

Fig. 3.—Effect of NH_4SCN on the thermal decomposition of $[Cr\ en_3](SCN)_3\cdot H_2O$ at 130°: ⦶, pure $[Cr\ en_3](SCN)_3\cdot H_2O$; ◎, pure $[Cr\ en_3](SCN)_3\cdot H_2O$ ground with 2% solid NH_4SCN; ○, pure $[Cr\ en_3](SCN)_3\cdot H_2O$ recrystallized from 25% NH_4SCN solution; ◉, pure $[Cr\ en_3](SCN)_3\cdot H_2O$ washed with saturated NH_4SCN solution; ◒, NH_4SCN-contaminated $[Cr\ en_3](SCN)_3\cdot H_2O$ recrystallized from water.

freedom from ammonium salt except that intentionally added, the luteo thiocyanate was prepared from the pure chloride by means of sodium thiocyanate. Samples for thermal decomposition were prepared by adding ammonium thiocyanate to the triethylenediamine compound in various ways. A sample of the pure luteo thiocyanate, as a control, and a sample of the pure salt ground with 2% of ammonium chloride were included in the heating experiments. The oven was controlled at 128–130°.

Triethylenediamine chromic thiocyanate was also prepared by the reaction of ammonium thiocyanate with the luteo chloride. Samples of the product as obtained and after one and two recrystallizations were included in the heating experiments.

The results are plotted in Graph 3. The catalytic effect of the ammonium thiocyanate is apparent. Recrystallization of the thiocyanate containing ammonium thiocyanate decreases the rate of reaction to that of the pure salt, in contrast to the behavior of the luteo chloride noted above. Ammonium chloride does not catalyze the reaction; the curve for the sample containing ammonium chloride (not shown on graph) was practically identical with the curve for the pure luteo salt.

Preparation of *cis*-$[Cr\ en_2Cl_2]Cl\cdot H_2O$.—Thermal decomposition of triethylenediamine chromic chloride contaminated with ammonium chloride provides a convenient method for preparing the *cis*-dichloro salt. The chloride $[Cr\ en_3]Cl_3\cdot 3^1/_2H_2O$ recrystallized from 1% ammonium chloride solution (or prepared from the luteo sulfate by metathesis with ammonium chloride) is spread in a thin layer on a large watch glass and heated at about 210° but not above 215°. If the temperature is too low, the reaction is inconveniently slow; if it is too high, deep-seated decomposition occurs with formation of brown reaction products. Some care must be taken to obtain the right temperature, especially with ovens in which there is a shelf above a set of heating elements, as was used in these experiments; it is convenient to use two thermometers, one above and the other below the shelf, and adjust the oven so that the temperature gradient is not more than a few degrees.

Shortly after heating is started, the yellow luteo salt darkens and ethylenediamine evolution begins. After an hour or two the color has changed to red-violet. The reaction is followed by weighing at intervals, complete decomposition corresponding to a loss of 30.6%. In a few hours the reaction is 85% complete and subsequent decomposition is very slow.

The red-violet product may be recrystallized as described by Ferguson[16]; the yield is increased if the filtrate from the first crop of crystals is treated with one-fourth its volume of concentrated hydrochloric acid and evaporated in a stream of air. However, the salt may be obtained pure enough for resolution and most other purposes by washing the product of thermal decomposition with ice-cold concentrated hydrochloric acid. The yield in either case is 50% or more. Analysis of a typical product by ignition of a sample to Cr_2O_3 gave the following results:

Anal. Calcd. for $[Cr\ en_2Cl_2]Cl\cdot H_2O$: Cr, 17.51. Found: Cr, 17.6.

Preparation of *trans*-$[Cr\ en_2(SCN)_2]SCN\cdot H_2O$.—Excellent yields of the *trans*-dithiocyanato salt may be obtained by a similar procedure. The starting material is pure luteo thiocyanate washed with saturated ammonium thiocyanate solution or unrecrystallized luteo thiocyanate prepared by reaction of the chloride with ammonium thiocyanate. The decomposition is carried out as described for the chloride; the temperature is not allowed to rise above 134°. The theoretical loss in weight for complete decomposition to the di-acido salt is 18.4%. Orange yellow needles are obtained by recrystallizing the product from water as described by Pfeiffer.[10] The yield is 60–65%. Analysis of a typical product gave the following results:

Anal. Calcd. for $[Cr\ en_2(SCN)_2]SCN\cdot H_2O$: Cr, 14.29. Found: Cr, 14.4.

Summary

It has been shown that ammonium chloride and ammonium thiocyanate catalyze the thermal decomposition of triethylenediamine chromic chloride and thiocyanate, respectively.

Methods for the preparation of *cis*-$[Cr\ en_2Cl_2]Cl\cdot H_2O$ and *trans*-$[Cr\ en_2(SCN)_2]SCN\cdot H_2O$ have been described. These procedures, based on the thermal decomposition of the luteo chloride and thiocyanate, are superior to the usual methods in convenience and efficiency.

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