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

Some Chromous and Chromic Ammines

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In the course of some work on the stereochemistry of chromium, it has been necessary to know something of the stability of chromous ammines toward water and air. Very few chromous ammines have been studied in this respect; apparently no investigation has been made of the ones in which we are particularly interested—those containing ethylenediamine and its homologs.

Traube and Passarge[2] prepared chromous ammines by the action of hydrazine and of hydrazine sulfate upon chromous salts. These compounds were so stable that they showed no change on standing in the air for several days. Traube, Burmeister and Stahn[3] by treating chromous chloride and chromous formate with pyridine obtained complexes which absorb oxygen from the air, but which are stable, even when wet, if protected from the air. Barbieri and Tettamanzi[4] found that [Cr dip$_3$] Br$_2$·6H$_2$O (dip = dipyridyl) oxidizes slowly in the air. The same investigators prepared chromous complexes containing hexamethylenetetramine, and found them to be readily oxidized when wet. Chromous ammonia complexes are stable when dry[5] but when a solution of a chromous salt is treated with ammonium hydroxide and an ammonium salt, hydrogen is evolved and the chromic complex is formed.[6] We have found that ethylenediamine and its homologs behave in this same way, liberating hydrogen very rapidly.

When a solution of chromous chloride in an atmosphere of nitrogen was treated with a solution of ethylenediamine with or without the addition of ethylenediamine hydrochloride a transient blue precipitate formed. This was perhaps a chromous complex. Rapid oxidation to the chromic state prevented its isolation, however. As soon as the solutions were mixed, evolution of hydrogen began, and within an hour and a half the oxidation was practically complete.

The use of chromous acetate instead of the chloride gave essentially the same results. In this case an 80% yield of triethylenediamine chromic bromide [Cr en$_3$] Br$_3$·3H$_2$O was obtained by concentrating the solution and adding sodium bromide. A small amount of hexaethylenediamine-hexol-tetrachromic bromide [Cr$_4$(OH)$_6$en$_6$]Br$_6$·4H$_2$O[7] was formed, also.

An unstable chromous ammine must have been formed before the oxidation took place, for the chromic ion will not react with ethylenediamine under these conditions. Although the conditions of the experiment were varied in many ways, no chromous compound could be isolated. In the hope of obtaining more stable compounds 1,2-propylenediamine and 2,3-butylenediamine (for which an improved method of preparation was developed) were substituted for the ethylenediamine. Again, only chromic compounds were obtained. Chromous ammines containing bases of this series are apparently too readily oxidized by water to be isolated from aqueous solution. This furnishes a much easier method of preparing the triethylenediamine chromic salts than any which has previously been described. A simplified procedure for this preparation is outlined in the Experimental Part.

We were led by these observations to study briefly the stability of chromous ammines containing bases with nitrogen in the ring. In agreement with the results of Barbieri and Tettamanzi, we found the dipyridyl complex to be quite stable. In the case of the pyridine complex the nitrogen to chromium bond is evidently less stable for the compound which we prepared, [Cr py$_2$]Cl$_2$, lost pyridine gradually on standing. Quinoline complexes are still less stable. Chromous chloride and acetate dissolved readily in quinoline to give deeply colored solutions, but the addition of alcohol precipitated the original chromous salt. None of the complex ions containing ring bases were oxidized by water.

Experimental

Most of the experiments were carried out in the apparatus shown in Fig. 1. A novel feature of this device is the combined stirrer-filter B. The shaft of this stirrer is a heavy-walled 8-mm. tube. The lower end is expanded to an

(1) Abstracted from part of a thesis submitted for the degree of Doctor of Philosophy at the University of Illinois.

(2) Traube and Passarge, Ber., 46, 1505 (1913).

(3) Traube, Burmeister and Stahn, Z. anorg. allgem. Chem., 147, 50 (1925).

(4) Barbieri and Tettamanzi, Atti Accad. Lincei, 15, 877 (1932).

(5) These compounds are discussed by Schlesinger and Hammond, THIS JOURNAL, 55, 3971 (1933).

(6) Asmanow, Z. anorg. allgem. Chem., 160, 209 (1927).

(7) Pfeiffer, ibid., 58, 272 (1908).

internal diameter of 10 mm. and is packed with glass wool. A short piece of glass rod is sealed to the shaft just above the expanded portion. During filtration the upper end of the shaft is connected (at C) to the vacuum line by a piece of light rubber tubing; when the device is used for stirring the rubber is disconnected from the vacuum line and closed by a piece of glass rod. By placing B very close to the bottom of the flask, practically all of the liquid can be drawn off. Liquids for washing precipitates are introduced through K and withdrawn through B. The apparatus is convenient and has proved to be very efficient.

Preparation of Chromous Acetate.—Chromic chloride is reduced by zinc and hydrochloric acid in F, the excess hydrogen escaping through the small Erlenmeyer, which is partially filled with water. When the reduction is complete, stopcock D is opened and rubber tube H is closed by a clamp. This forces the liquid in F through the glass wool filter A into the reaction flask G, through which a slow stream of oxygen-free nitrogen is passing. A concentrated solution of sodium acetate (excess) is added through K, and the precipitated chromous acetate is washed by stirring it with small portions of freshly boiled water. If it is to be removed from the apparatus it must be washed with alcohol and ether and dried by the stream of nitrogen. The yield is over 90%.

Chromous Chloride.—Eighteen grams of chromous acetate in the reaction chamber G is dissolved in 60 cc. of ice cold concentrated hydrochloric acid. With the flask immersed in an ice-bath, a steady stream of hydrogen chloride gas is passed into the flask with the nitrogen. (With undiluted hydrogen chloride, there is a tendency for water to be sucked in from flask L.) After about an hour, blue crystals of $CrCl_2 \cdot 4H_2O$ precipitate. The liquid is filtered off and the crystals washed with cold, concentrated hydrochloric acid. The yield is 90%, based on weight of chromous acetate, or 81% based on the weight of chromic chloride used.

Action of Ethylenediamine and its Homologs upon Chromous Chloride.—Solid chromous chloride tetrahydrate (from 15 g. of $CrCl_3 \cdot 6H_2O$) was dissolved in 30 cc. of freshly boiled ice-cold water in an atmosphere of nitrogen, and 30 cc. of an ice-cold saturated solution of ethylenediamine hydrochloride was added. Thirty cubic centimeters of a 65% solution of ethylenediamine was then added gradually with stirring. During the addition a pale blue precipitate formed, but soon redissolved. Even though the solution was kept at 0°, oxidation began at once and was complete in a few hours. Addition of alcohol to the cherry red solution precipitated $[Cr(NH_2CH_2-CH_2NH_2)_3]Cl_3 \cdot 3.5H_2O$ as orange crystals. A second crop was obtained by evaporation. The total yield was 16 g. Dehydration over phosphorus pentoxide showed the compound to contain 15.65% water; (calcd., 15.69%). Analysis of the anhydrous material by ignition to Cr_2O_3 showed 15.7% chromium; calcd., 15.4%.

The substitution of 1,2-propylenediamine for ethylenediamine led to similar results, $[Cr(NH_2CH(CH_3)CH_2-NH_2)_3]Cl_3 \cdot H_2O$ being obtained. Analysis for chromium: Found, 13.12%. Calcd., 13.05%.

In another experiment, a slight excess of butylenediamine was added to the solid chromous chloride, which had been freed from hydrochloric acid by washing with acetone. The results were the same as with the other bases. After oxidation was complete, the solution was poured into 50 cc. of concentrated hydriodic acid. The iodide precipitated in beautiful orange needles, which are soluble in water, alcohol and acetone, and were recrystallized from water. The loss in weight upon drying at 50° in a vacuum over phosphorus pentoxide was negligible. Analysis for iodide: Found, 54.85%. Calcd. for $[Cr-(CH_3CH(NH_2)CH(NH_2)CH_3)_3]I_3$, 54.63%. This is the first member of the butylenediamine series to be described.
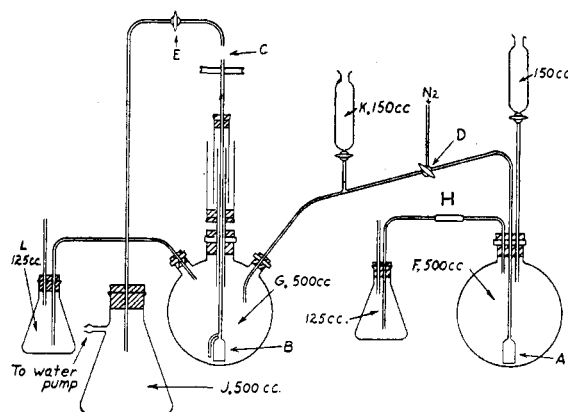

Fig. 1.

Action of Ethylenediamine upon Chromous Acetate.—When chromous acetate was dissolved in 65% ethylenediamine oxidation took place as with the chloride. Addition of sodium bromide followed by evaporation gave triethylenediamine chromic bromide and a small amount of hexaethylenediamine-hexol-tetrachromic bromide, $[Cr_4-(OH)_6en_6]Br_6 \cdot 4H_2O$. These were separated through the difference in solubility in water and the tetrachromic salt was identified by analysis. Calcd.: Cr, 16.20; N, 13.8. Found: Cr, 16.13, 16.14; N, 13.7.

Action of Nitrogen Ring Bases upon Chromous Salts.—The directions of Barbieri and Tettamanzi[4] were followed in the preparation of the dipyridyl complex $[Cr dip_3]Br_2 \cdot 6H_2O$. In agreement with their report, we find the compound to be fairly stable toward water, and only slowly oxidized by exposure to the atmosphere.

An excess of pyridine was added to chromous chloride dissolved in water. The pale green precipitate which formed was filtered, washed successively with water, alcohol and ether, and dried by heating to 80° in a current of nitrogen. Analysis showed it to be $[Cr py_2]Cl_2$. Calcd.: Cr, 18.5; Cl, 25.1. Found: Cr, 18.0; Cl, 25.3. The compound undergoes slow oxidation when exposed to air. It has a faint odor of pyridine and evidently loses pyridine continuously. Since the completion of this work Chatelet[8] has reported the preparation of this compound from anhydrous chromous chloride and pyridine. Traube, Burmeister and Stahn[3] isolated this compound as the dihydrate.

Chromous acetate and chloride were dissolved in wet quinoline in an atmosphere of nitrogen to give deep red solutions. No oxidation was apparent after the solutions had stood for several days. Addition of alcohol to the solution reprecipitated the original chromous salt.

(8) Chatelet, *Compt. rend.*, **199**, 290 (1934).

Simplified Procedure for the Preparation of [Cr(NH₂·CH₂·CH₂·NH₂)₃]Br₃·3H₂O.—A one-liter flask is equipped with a mercury sealed stirrer, a dropping funnel, an inlet for nitrogen and an outlet for escaping gases. Twenty grams of chromium in small pieces and 400 cc. of water are placed in the flask and the water is boiled to expel dissolved oxygen. Air is swept from the flask by a current of nitrogen. One hundred cubic centimeters of concentrated hydrobromic acid is added over a period of five minutes, followed immediately by 70 cc. of ethylenediamine monohydrate. The solution is allowed to stand with occasional stirring until oxidation is complete (eight to ten hours), is filtered and evaporated. The bromide crystallizes as orange needles. The yield in a typical run was 47 g. or 81% based upon the fact that 5.8 g. of chromium dissolved.

Preparation of 2,3-Butylenediamine.—Angeli[9] has described the preparation of 2,3-butylenediamine by reduction of an alcoholic solution of dimethylglyoxime. This method gives very poor yields, apparently because the sodium salt of dimethylglyoxime is insoluble in alcohol. The substance has been prepared also by the action of ammonia on 2,3-dibromobutane[10] and by the catalytic reduction of dimethylglyoxime dissolved in alcohol.[11] The catalytic reduction gives excellent yields of the base when very dilute solutions are used. Under these conditions it is difficult to obtain the material in large amounts. We have found that it is possible to obtain 2,3-butylenediamine readily by the following modification of Angeli's directions: dimethylglyoxime is acetylated by the method of Biltz.[12] Seventy grams of the diacetate is dissolved in two liters of anhydrous alcohol in a flask fitted with a stirrer and an efficient reflux condenser. One hundred and sixty grams of sodium in lumps the size of marbles is introduced

rapidly. When the sodium has dissolved 200 cc. of water is added and the mixture is steam distilled. Most of the amine is obtained in the first three liters of distillate. Addition of a saturated solution of oxalic acid precipitates the oxalate. More of the oxalate can be obtained by concentrating the solution and adding alcohol and ether. The total yield is 27 g. or 40% of the theoretical. This material is pure enough for preparation of the free base. A sample, after recrystallization from water and drying over phosphorus pentoxide, melted at 235°. Angeli[9] reported 238°.

The base is liberated by mixing the oxalate with its own weight of sodium hydroxide in a small amount of water. Distillation gives a nearly quantitative yield of a fuming, somewhat viscous liquid with an odor similar to that of ethylenediamine. The hydrated base boils at 130°.

The major portion of the dimethylglyoxime not accounted for in the yield of diamine may be recovered from the original reaction mixture.

Summary

The stability of chromous ammines has been studied. Ammines containing ethylenediamine, 1,2-propylenediamine and 2,3-butylenediamine could not be isolated from water solution because of rapid oxidation to the chromic state by the water. On the other hand, when the chromous ion is coördinated with dipyridyl, pyridine or quinoline it is stable toward water, and in the case of the dipyridyl at least is somewhat stabilized to atmospheric oxidation.

A new and simple method for the preparation of triethylenediamino chromic salts and similar compounds has been presented.

An improved synthesis of 2,3-butylenediamine is described.

(9) Angeli, *Ber.*, **23**, 1357 (1890).

(10) Morgan and Hickinbottom, *J. Soc. Chem. Ind.*, **43**, 307T (1924).

(11) Frejka and Zahlova, *Spisy vydávané Přírodovedeckou Fakultou Masarykovy Univ.*, No. **73**, 3 (1926); Strach and Schwaneberg, *Ber.*, **67**, 1006 (1934).

(12) Biltz, *Ber.*, **41**, 1883 (1908).

The Transference Number of Lanthanum Chloride as a Function of the Concentration

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Introduction

The purpose of this paper is to test the general validity of several equations which have been proposed for the variation of the transference numbers of electrolytes with the concentration by the use of new data on lanthanum chloride covering a wide range of concentration. Although the old classical theory predicts that transference numbers should be independent of the concentration, it has long been known that variations do occur, especially among salts of polyvalent ions.

In 1924 Drucker and Riethof[1] found that the data for the transference numbers for the chloride ion in hydrochloric acid between 0.01 and 0.1 normal, inclusive, could be expressed by the two parameter equation: $t_- = 0.172(1 - 1/N^{0.51})$; where t_- is the transference number of the anion and N is the moles of water per mole of salt. The figures 0.172 and 0.51 were selected to fit the data, but the figure 0.172 obviously must be the limiting value of t as the concentration approaches

(1) C. Drucker and G. Riethof, *Z. physik. Chem.*, **111**, 20 (1924).