quency has a range for its position from 6.8 $\mu$ (N-triphenylborazine) to 7.3 $\mu$ (B-trichloro-N-triphenylborazine) and is always the strongest band. However, the B-aminoborazines prepared always showed the strongest band at 6.7 $\mu$. That there is practically no range for the position of this absorption may be explained by the basic structure of the B-aminoborazines, *i.e.*, regardless of other substituents, the boron atoms are always bonded to three nitrogen atoms. Thus the influence of the substituent seems to be greatly reduced and the B–N ring frequency is restricted to a very small range.

It is remarkable that all the B-aminoborazines showed a band in the 7.4 $\mu$ region. This might be attributed to the absorption of the bond between the boron atoms and the nitrogen of the side chains.

An infrared band at 2.92 $\mu$ is shown by all the B-aminoborazines where the ring nitrogen is not substituted by an organic group. It is typical for a relatively unassociated NH bond, as it is appreciably greater than the value of *ca*. 3 $\mu$ for amines. The nuclear magnetic resonance spectrum of the B-tris-(diethylamino)-borazine shows the typical ethyl group structure, $CH_2$ at 172 cycles and $CH_3$ at 245 cycles when measured against benzene; diethylamine was run for comparison. The NH of diethylamine is sharp and its position is temperature dependent; sharp because exchange is fast and temperature dependent because of varying degrees of association with temperature. It is hard to find the N–H peak in the n.m.r. spectrum of the B-tris-(diethylamino)-borazine, but it is probably the broad shallow band just to the right of the spikes due to methyl resonance. This suggests that the rate of exchange is relatively slow. The sharpness and high frequency of the infrared N–H band indicated very little association; it is probably too sterically hindered. The long residence time of a given proton on nitrogen allows quadrupole relaxation and thus gives a broad band.

The B-aminoborazines are representatives of a new class of compounds where one boron atom is bonded to three different nitrogen atoms. They may be considered as the first polymerization products of boron triamides, $B(NR_2)_3$. The existence and the preparation of boron triamides has been described elsewhere.[16]

**Acknowledgment.**—The authors gratefully acknowledge the determination of the infrared and nuclear magnetic resonance spectra by Dr. Keith S. McCallum, Redstone Arsenal Research Division, Rohm and Haas Company, Huntsville, Alabama.

[16] E. Wiberg and K. Schuster, *Z. anorg. allgem. Chem.*, **213**, 77 (1933); A. Dornow and K. H. Gehrt, *ibid.*, **294**, 81 (1958).

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# Hydrolytic Polymerization in Boiled Chromic Solutions[1]

BY JOHN A. LASWICK AND ROBERT A. PLANE

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Cationic species present in boiled solutions of chromic perchlorate have been resolved using ion-exchange chromatography. In addition to $Cr(H_2O)_6^{+3}$, which is retained least strongly by Dowex-50 cation-exchange resin, two new species can be isolated. The first is identical in visible absorption spectrum and ion-exchange behavior to the product obtained by oxidation of chromous solutions by $O_2$ and $Tl^{+3}$ and believed to be dinuclear. The second is apparently more highly polymerized. A small residual fraction of the original chromium seems to be irreversibly sorbed to the resin. Attempts to further characterize the dissolved fractions by reaction with molybdate fail, apparently due to fragmentation of chromic species and depolymerization of molybdate species. The rates of formation of the separable olated ions in boiling 0.05 to 0.10 *M* chromic solutions are followed. The dinuclear species reaches a maximum concentration (11% of the total Cr) within minutes; the next fraction attains a steady value of 12% only after some hours. Approximately 74% remains in the unreacted form. However, very prolonged refluxing causes deposition of nearly all of the chromium as a crystalline solid giving an X-ray pattern identical with that of $HCrO_2$. Addition of base, prior to refluxing, leads to formation of a colloid, which was not detected in any experiment without added base.

The presence of polynuclear complexes in solutions of many relatively highly charged ions has been demonstrated.[2] The chromium(III) system has been studied more intensively than perhaps any other,[3] because of the technical importance of basic chromium solutions in tanning leather. This system is a particularly interesting one for investigation since the changes which chromic species undergo are generally quite slow, thus allowing a variety of techniques for study which are not applicable to labile systems. Indeed, this slow response of chromic species to a change of environment also makes difficult the interpretation of many of the experiments conducted in the past. Nearly all such investigations involved the addition of base, either gradually, or in large increments. Kohlschütter and co-workers have demonstrated that the subsequent behavior of such systems is dependent upon the method of addition of the base,[4] and thus cannot represent an equilibrium situation.

A technique for studying these "olated" chromic solutions which does not involve addition of base was devised by Hall and Eyring.[5] This method, based on conductometric titration of the chromic

(1) From the thesis submitted by John A. Laswick to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Presented in part at the 133rd National Meeting of the American Chemical Society, San Francisco, California, April, 1958.

(2) See, *e.g.*, S. Hietanen and L. G. Sillen, *Acta Chem. Scand.*, **8**, 1607 (1954).

(3) E. Stiasny, "Gerbereichemie," Verlag Theodor Steinkopff, Dresden, 1933, pp. 344–399.

(4) H. W. Kohlschütter and O. Melchior, *Angew. Chem.*, **49**, 865 (1936).

(5) H. T. Hall and H. Eyring, THIS JOURNAL, **72**, 782 (1950).

species with paramolybdate, seems to indicate that the degree of olation becomes constant after about 60 hours. In interpreting the results, the authors favored the view that the molybdenum attaches to all of the coördination sites of chromium which are not involved in bridging adjacent Cr atoms. However, detailed interpretation of their results is made difficult by their lack of evidence that these solutions are monodisperse.

Earlier work by Bjerrum and Faurholt provides evidence that heated chromic solutions are not monodisperse.[6] They found that such solutions apparently contain most of the chromium as a mononuclear species (precipitable as the cesium-chrome alum) plus at least one other soluble species. In apparent disagreement with the results of Hall and Eyring, Bjerrum and Faurholt found that equilibrium was not attained in less than 107 days at reflux temperature. After this period of time, approximately 90% of the chromium in a sample originally 0.1 *M* in $Cr(NO_3)_3$, with no added base, was present in a solid of the approximate composition $Cr_2O_3 \cdot 2H_2O$.

In view of apparent discrepancies and unanswered questions arising from the previous work on this system, it seemed appropriate to investigate several aspects of the nature of the hydrolytic polymerization in boiled chromic solutions. The present research is concerned with a separation by ion-exchange chromatography of the species formed in such solutions, attempts to characterize these separated species, identification of the hydrated oxide reported by Bjerrum and Faurholt and determination of the equilibrium composition of dilute chromic solutions at reflux temperature.

## Experimental

Chromic perchlorate was prepared from $CrO_3$, $H_2O_2$ and $HClO_4$.[7] Lanthanum perchlorate was crystallized from a solution made by addition of excess Lindsay Chemical Co. 99.9+% $La_2O_3$, to diluted AR $HClO_4$, filtration to remove excess $La_2O_3$, and evaporation of solvent. Reagent grade ammonium paramolybdate solutions were used after filtering. The cation exchanger Dowex-50-X 12 was used after wet screening (140–200 mesh fraction utilized), thorough washing with saturated sodium monohydrogen citrate followed by 6 *M* HCl and finally partial decolorization by gentle heating with a solution of 5% $H_2O_2$ and 5% NaOH.

Chromium analyses were performed by two methods, depending upon total Cr content of the given sample. Small amounts were oxidized by basic peroxide or, in the case of solids, by repeated fusions in sodium carbonate with free access to air. After dilution to known volume, the absorbancy at 372 m$\mu$ of the resulting chromate solution was measured with a Beckman DU spectrophotometer. Larger amounts were titrated with standard ferrous solution after $S_2O_8^=$ oxidation in acid solution. Molybdenum was precipitated with lead acetate, ignited and weighed as $PbMoO_4$.[8]

Conductometric titrations were performed with an a.c. bridge (1000 cycles/second) which included a Campbell-Shackelton ratio box.

## Results and Discussion

**Separation of the Chromic Species.**—Solutions of chromic perchlorate were refluxed for various periods of time, cooled and added to columns containing the strong acid cation exchanger Dowex-50, in the hydrogen form. If no base had been added to the chromic solution prior to reflux, it was quantitatively sorbed by the resin. The sorbed chromium could be resolved into various fractions by elution with solutions containing various cations. A large fraction of the chromium was relatively easily eluted by *ca.* 1 *M* $HClO_4$. For the remaining species the order of increasing effectiveness of eluting cation was: $Mg^{++} < Ba^{++} < Al^{+3} << La^{+3}$.

In the experiments described below, the following separation procedure was employed: A column 12 mm. in diameter and *ca.* 40 mm. high of Dowex-50 in the hydrogen form was charged with sufficient chromic solution to consume about half its capacity. Fraction 1 was eluted with $HClO_4$ (0.7 to 1.5 *M*); fraction 2 with $La(ClO_4)_3$ (0.01 to 0.03 *M*, *p*H 2), which incidentally pushed ahead of it a sharply defined band identical with fraction 1, designated below as 1a. (It was not possible to determine whether all of fraction 1a was originally present in this form, or whether it formed *in situ* from other species upon displacement of $H^+$ by $La^{+3}$.) The $La(ClO_4)_3$ concentration was increased to *ca.* 0.2 *M* to elute fraction 3. In all cases, a distinct green coloration remained at the top of resin column, indicating the presence of uneluted chromium. This material was not displaced even by 2 *M* $La(ClO_4)_3$, but was removed by concentrated $H_2SO_4$. It also was converted to $CrO_4^=$ by treatment with basic peroxide, after removal of lanthanum as the citrate complex.

Table I lists the compositions of chromic perchlorate solutions after various reflux times, as determined by ion-exchange chromatography. The last column is for a solution with NaOH equal in concentration to the $Cr(ClO_4)_3$ added prior to reflux. Extensive investigation of solutions with added base was not carried out since previous work had shown a dependence of properties on method of addition of base.[4] It is worth noting that the solution with added base gave rise to one chromic fraction, labeled 0, which was absent from all solutions not containing added NaOH. This fraction was only very incompletely held by the resin and emerged just slightly behind the effluent acid from the column. At flow rates of *ca.* 1 cm./min., one milliequivalent of resin retained only 0.0012 mmole of chromium in this form. Passing this unsorbed material through a fresh column resulted in the same amount of retention, but repeated passages through the same column caused retention to fall sharply at each successive pass. Nor was sorption of fraction 0 significantly greater on Dowex-50 containing only 1% divinylbenzene. The small amount of fraction 0 which was sorbed could not be eluted by 4 *M* $HClO_4$ nor 0.5 *M* $La(ClO_4)_3$, but was eluted readily (without significant change in visible absorption spectrum) by unbuffered sodium citrate solution.

The ion-exchange behavior of fraction 1 is identical with that of the starting material ($Cr(H_2O)_6^{+3}$) and it is seen from Table I that its concentration drops fairly rapidly during the early stages of reflux and then remains nearly constant. Fraction 2 reaches a maximum concentration after quite short reflux time (less than 1 hr.); fraction 3 requires longer refluxing before reaching its maximum concentration.

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[6] N. Bjerrum and C. Faurholt, *Z. physik. Chem.*, **130**, 584 (1927).

[7] A. L. Phipps and R. A. Plane, This Journal, **79**, 2458 (1957).

[8] U. S. Bureau of Mines, Bulletin 212, p. 108.

**Characterization of the Separated Fractions.**—The visible absorption spectra of fractions 1, 2 and 3 are given in Fig. 1. That for fraction 1 is identical with the spectrum of $Cr(H_2O)_6^{+3}$; this fact and the identity of the ion-exchange behavior of fraction 1 and unrefluxed chromic perchlorate solution are taken to mean that fraction 1 is unreacted $Cr(H_2O)_6^{+3}$. The spectrum of fraction 2 is identical with that of the dimeric species, most simply represented $(CrOH)_2^{+4}$ or $CrOCr^{+4}$, formed when $Cr^{++}$ is oxidized by molecular oxygen.[9] That the species are the same is confirmed by identical ion-exchange behavior in the two cases.

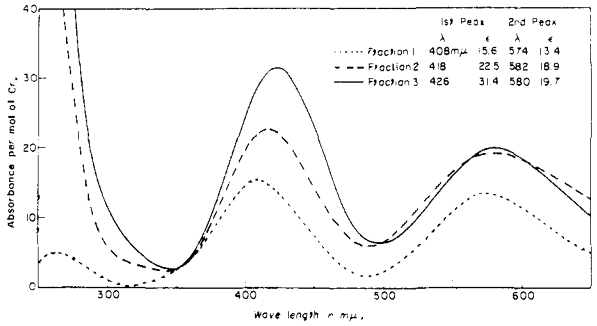

Fig. 1.—Absorption spectra of isolated fractions.

TABLE I

COMPOSITIONS OF REFLUXED CHROMIC PERCHLORATE SOLUTIONS

| Reflux time | 10 min. | 1 hr. | 8 hr. | 24 hr. | 5 da. | 27 da. | 3 hr. (NaOH added) |
|---|---|---|---|---|---|---|---|
| Fraction | | | | | | | |
| 1, % | 84.2 | 75.4 | 72.6 | 70.4 | 74.2 | 72.5 | 38.8 |
| 1a | 1.5 | 0.6 | 1.2 | 3.8 | ... | 3.7 | ... |
| 2 | 10.1 | 11.8 | 10.7 | 10.0 | 11.4 | 9.3 | 15.7 |
| 3 | 2.4 | 10.2 | 12.5 | 12.4 | 11.3 | 10.4 | 23.3 |
| 0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 13.4 |
| Residue | 1.8 | 2.0 | 2.9 | 3.4 | 3.1 | 4.1 | 8.8 |
| $[Cr_T] \times 100$ | 6.13 | 6.92 | 5.94 | 6.10 | 7.85 | 8.20 | 7.64 |

It is seen from Fig. 1 that the spectrum of species 2 differs from that of species 1 in both a shift of the peaks to longer wave lengths and an increased absorbancy. These same features appear in a comparison of the spectrum of species 3 with that of species 2. Such trends might indicate that species 3 is a more highly polymerized form. A similar conclusion can be drawn from ion-exchange results. Species 3 is more tightly held to an ion exchanger than species 2 which in turn is more tightly held than species 1, a trend usually observed for cations of increasing total charge. Furthermore, the change of elution constant (volume through which a band center moves per volume of eluent passed) with change of $La^{+3}$ concentration is indicative of species 3, being a highly charged species. For an eluent of 0.010 $M$ $La(ClO_4)_3$ plus 0.010 $M$ $HClO_4$, the elution constants for species 1, 2 and 3 are 0.041, 0.016 and $7.9 \times 10^{-4}$, respectively; for 0.030 $M$ $La(ClO_4)_3$ plus 0.010 $M$ $HClO_4$, 0.14, 0.094 and 0.010; for 0.10 $M$ $La(ClO_4)_3$ plus 0.010 $M$ $HClO_4$, 0.56, 0.26 and 0.069. While this sort of experiment does not permit precise quantitative interpretation, it should be noted that species 3 is by far the most sensitive to concentration of eluent as would be demanded by the ion-exchange mass action expression for a more highly charged species. Thus, it seems that species 3 is a polynuclear ion differing from species 2 in probably being at least trinuclear, and hence having a higher total charge.

The separated fractions, as well as the unseparated refluxed mixture, were titrated with molybdate solutions by the conductometric method of Hall and Eyring.[5] Results obtained for titration of the unrefluxed chromic solutions and the refluxed, but unseparated, chromic solutions were in agreement with the previously published data.[5]

Data for the molybdate titration of unseparated, refluxed chromic solutions can be examined in the light of the data of Table I. Sixty-hour refluxed solutions, which consumed 4.78 Mo per average Cr, are seen to contain about 74% hexaquochromic ion. Since this species reacts with 6 Mo per Cr, the remaining Cr species apparently reacted with but 1.3 Mo per Cr average.

Molybdate titration of fraction 0 slowly yielded a pale green gelatinous precipitate preceded by a sharp break in the conductivity plot at 0.16 to 0.18 Mo/Cr. The precipitate contained very little molybdenum, which could be extracted by repeated washing. Similar flocculation also was induced by sulfate or ferrocyanide. Such results, together with its previously noted ion-exchange behavior, are taken to mean that fraction 0 is colloidal.

The separated fractions 2 and 3 gave apparent end-points on molybdate titration at Mo/Cr values of approximately 2.8 and 1.3, respectively. However, these numbers are probably not especially meaningful. It was noted that there were appreciable drifts of conductivity with time during the course of the titration and not only did the conductivity continue to change after periods of hours, but the end-point was a function of the time between the incremental additions of molybdate. Furthermore, the direction of drift reversed at definite points during the course of the titrations. These drifts, which are absent in the titration of hexaquochromic seem to be due to the depolymerization of the polynuclear chromic species accompanied by fragmentation of the polymolybdate. Such results seem to rule out the possibility of obtaining the number of bridge O atoms from experiments of this type.

**The Slow Formation of Solid Hydrolysis Product.**—The data in Table I indicate little change in the concentrations of dissolved species after relatively few hours at 100°. It was found, however, that the optical density of the mixture, particularly at shorter wave lengths, continued to increase for several weeks. After about two months of refluxing, a very fine turbidity developed; it could not be removed by ordinary filtration or centrifugation. After about four months of refluxing, a crystalline precipitate settled spontaneously; this is in agreement with previous findings.[6] The remaining dissolved chromium was almost entirely hexaquochromic; the amount remaining dissolved depended upon the area of solid surface in contact with the solution during refluxing.

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(9) M. Ardon and R. A. Plane, THIS JOURNAL, **81**, 3197 (1959).

Solutions initially containing added NaOH required about the same time for the initial precipitation which was, however, more nearly complete. The product exhibited poorer crystallinity, as judged by powder X-ray diffraction patterns.

The solid forms irregular platelets of various colors and possessing metallic luster. It is extremely inert to cold acids, bases and complexing agents, but is oxidized slowly by boiling 4 $M$ $HClO_4$ and by air when in fused $Na_2CO_3$. Boiling concentrated sulfuric acid slowly converts it to an inert solid which gives an X-ray pattern different from that of the original solid.

The solid from the refluxed solutions was dried at 100° and analyzed for chromium. The result led to the composition $Cr_2O_3 \cdot 1.7H_2O$. Further dehydration to approximately $Cr_2O_3 \cdot 1.2H_2O$ was effected by heating to 300° in a nitrogen atmosphere. Powder X-ray photographs of both the freshly filtered product and the material dried at 300° gave the same pattern, by which it was possible to establish that the bulk (crystalline portion) of the product is identical to the compound designated by Laubengayer and McCune as CrOOH,[10] and by Thamer, Douglass and Staritzky as $HCrO_2$.[11] The previous preparations employed hydrothermal methods at temperatures above 300°. Douglass recently has reported the structure to consist of distorted $CrO_6$ octohedra, each sharing six edges with six surrounding coplanar octahedra to form continuous sheets. The sheets are stacked so that oxygens of adjacent sheets are exactly superposed; hydrogens presumably lie midway between.[12]

In an attempt to determine the composition of refluxed solutions at equilibrium, a solution initially 0.05 $M$ in $Cr(ClO_4)_3$ was refluxed for 30 months. After this time, the chromium remaining in solution was found to be $2 \times 10^{-3}$ $M$. Refluxing of the solid product with 1.0 $M$ $HClO_4$ for one year produced a solution that was but $4 \times 10^{-3}$ $M$ in chromium, as $Cr(H_2O)_6^{+3}$.[13] Thus, it seems that in acid solution at 100°, neither hexaquochromic ion nor its soluble polynuclear derivatives are stable with respect to formation of $HCrO_2$.

**Acknowledgment.**—The authors are indebted to the National Science Foundation for Fellowships to J. A. L. during the course of the research.

[10] A. W. Laubengayer and H. W. McCune, THIS JOURNAL, **74**, 2362 (1952).

[11] B. J. Thamer, R. M. Douglass and E. Staritzky, *ibid.*, **79**, 547 (1957).

[12] R. M. Douglass, *Acta Cryst.*, **10**, 423 (1957).

[13] This portion of the work was conducted with the aid of Michael Collums.

ITHACA, N. Y.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

# Hexacoördinate Copper(II) in Trisethylenediaminecopper(II) Sulfate

BY GILBERT GORDON AND RALPH K. BIRDWHISTELL

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Evidence is offered for the existence of hexacoördinate copper(II) in its trisethylenediaminecopper(II) sulfate complexes. Studies of the infrared spectra of these and related compounds indicate that no free amine is present. Analytical data and visible absorption spectra are given. These data and optical rotation studies can be used in support of an octahedral structure. Clarification in procedures for the preparation of diaquomonoethylenediaminecopper(II) sulfate, bisethylenediaminecopper(II) sulfate and trisethylenediaminecopper(II) sulfate is given.

## Introduction

Several recent papers[1-3] demonstrate that copper (II) can have coördination greater than four. The present paper offers evidence for the existence and the preparation of hexacoördinate copper (II) in the form of the trisethylenediaminecopper (II) sulfate.

Due to some inconsistences in the literature,[4-6] we attempted to clarify the preparation of bisaquoethylenediaminecopper(II) sulfate and bisethylenediaminecopper(II) sulfate (anhydrous).

## Experimental

**Reagents.**—Eastman White Label ethylenediamine was purified using standard techniques (b.p. 117°, lit. b.p. ethylenediamine monohydrate 118°). Baker Analyzed Reagent copper sulfate pentahydrate was used without further purification.

The copper(II) content was determined by the method of Vogel.[7] The sulfate concentrations were determined using standard procedure.[8] Carbon, hydrogen and nitrogen were determined on all samples by Spang Microanalytical Lab., Ann Arbor, Michigan. The nitrogen was also checked by Kjeldahl determinations.

Infrared spectra were recorded on a Perkin-Elmer recording spectrophotometer, Model 21.

Visible spectra were run on a Beckman recording spectrophotometer, Model DK-2, with one cm. silica cells.

Optical rotation studies were carried out using a Schmidt polarimeter with a mercury lamp and Farrand interference filter (which removed all wave lengths except the mercury 435.835 m$\mu$ line). The light path was one dm.

**Preparation of Bisaquoethylenediaminecopper(II) Sulfate (I).**—$CuSO_4 \cdot 5H_2O$ and ethylenediamine were mixed in a mole ratio of 1:1 with enough water to make an approximately 1 $M$ solution. A blue solution was formed. Addition of 5 volumes of 95% EtOH resulted in a light blue precipitate. This precipitate was washed with EtOH and $Et_2O$. The precipitate was placed in a desiccator and dried *in vacuo* for 24 hr.

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[1] S. Kirschner, THIS JOURNAL, **78**, 2372 (1956).

[2] H. B. Jonassen, R. E. Reeves and L. Segal, *ibid.*, **77**, 2668 (1955).

[3] F. Basolo, Y. T. Chen and R. K. Murmann, *ibid.*, **76**, 956 (1954).

[4] W. Wahl, *Soc. Sci. Fennica Commentations Phys. Math.*, **4**, (14), 1 (1927); *C. A.*, **22**, 3596 (1928).

[5] C. H. Johnson and S. A. Bryant, *J. Chem. Soc.*, **6**, 1338 (1945).

[6] J. J. Fritz, R. Rao and S. Seki, *J. Phys. Chem.*, **62**, 703 (1958).

[7] A. I. Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., New York, N. Y., 1953, p. 433.

[8] A. I. Vogel, ref. 7, pp. 400, 404, 499.