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[CONTRIBUTION FROM THE UNIVERSITY OF UTAH]

## **The Constitution of Chromic Salts in Aqueous Solution<sup>1</sup>**

By H. TRACY HALL<sup>2</sup> AND HENRY EYRING

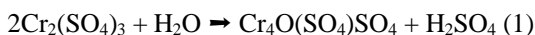
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<sup>1</sup> Presented before the Physical and Inorganic Division of the American Chemical Society at the 112th National meeting in New York City (Sept. 1947). The work reported in this paper is taken in part from the doctoral thesis submitted by H. Tracy Hall to the faculty of the University of Utah in partial fulfillment of requirements for the degree of Doctor of Philosophy.

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It has been known for a long time that aqueous solutions of chromic sulfate exist in both a violet and a green form<sup>3</sup> but the isolation of any definite compounds from the green solution has not been successful. The green solutions of chromic sulfate are obtained either by heating or aging violet solutions. The violet solutions are obtained directly by dissolving violet crystals of chromic sulfate or chrom alum.

It was early recognized that the acidity of the boiled or aged solution of chromic sulfate was greater than that of a violet solution of corresponding concentration. Recoura<sup>4</sup> determined the heat exchanges accompanying the addition of different amounts of sodium hydroxide to given amounts of green chromic sulfate solution (prepared by boiling a violet solution). When the heat liberated was exactly the same as that liberated during the addition of the same amount of sodium hydroxide to an amount of sulfuric acid equivalent to it, he assumed the amount of "free" sulfuric acid present in the green chromium solution to be the same. In this way, he found  $2\text{H}^+/4\text{Cr}$  present in the boiled and cooled solution. Favre and Valson<sup>5</sup> had previously shown that only one-third of the sulfate present in a solution of the boiled salt could be precipitated by barium chloride. This caused Recoura to assume that the reaction taking place on boiling a solution of chromic sulfate is



Godefroy,<sup>6</sup> Recoura,<sup>7</sup> Werner<sup>8</sup> and Gubser's<sup>9</sup> work with chromic chloride established the existence of the varieties  $\text{Cr}(\text{H}_2\text{O})_6\text{Cl}_3$  and  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ . The latter variety is green in solution and two of the chlorine atoms cannot be precipitated with silver nitrate. The dichlorotetraaquo is predominant in concentrated solutions of chromic chloride and is

readily crystallized from them. Bjerrum<sup>10</sup> studied the transformation of the dichlorotetraaquo into the hexaaquo, prepared the monochloropentaquo and was the first to observe the existence of a "hidden basic" compound (or compounds) in boiled solutions of chromic chloride. These compounds would be analogous to the oxygen-containing chromic sulfate of Recoura.

The most recent work concerning boiled solutions of chromic sulfate and chloride is summarized in "Gerberchemie."<sup>11</sup>

With respect to aged or boiled solutions of chromic nitrate, little work has been done. Probably, workers in the past, having observed that a boiled and cooled or aged solution of chromic nitrate had almost the same color as a freshly prepared solution, presumed that no change took place on aging or boiling. Indeed, some present day evidence would indicate that there is no change accompanying the aging of a solution of chromic nitrate.<sup>12</sup>

The primary purpose of this work is to introduce a new reagent that has proved to be useful in the study of chromic complexes in solution. This reagent is the so-called ammonium paramolybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ . Conductometric titration with solutions of this reagent enables one to determine (by difference) the average number of oxygen bridges between chromium atoms in boiled or aged solutions of chromic salts and has made it possible to show definitely that a structural change accompanies the heating or aging of a solution of chromic nitrate.

In this work, the authors have chosen to work mainly with the nitrate rather than the chloride or sulfate because this system seems to be free from the additional complication of the anion becoming coordinated to chromium.

Some evidence against the existence of complexes containing coordinated nitrate is the fact that complexes such as  $[\text{Cr}(\text{H}_2\text{O})_4(\text{NO}_3)_2]\text{NO}_3$  have never been prepared. Contrast this with the fact that  $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{++}$  and  $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$  are well-known ions and the fact that Colson<sup>13</sup> has prepared an analogous series of mono-, bi- and tri- "disguised" sulfates.

<sup>3</sup> See, for example, the chronological bibliography of the change from violet to green in chromic sulfate from 1841 to 1912 given by Graham, *Am. Chem. J.*, 48, 187-190 (1912).

<sup>4</sup> Recoura, *Ann. chim. phys.*, [7] 4, 494 (1895).

<sup>5</sup> Favre and Valson, *Compt. rend.*, 74, 1023 (1872).

<sup>6</sup> Godefroy, *ibid.*, 100, 105 (1885).

<sup>7</sup> Recoura, *Ann. chim. phys.*, 10, 39 (1887).

<sup>8</sup> Werner and Gubser, *Ber.*, 34, 1579 (1901).

<sup>9</sup> Gubser, *Inaugural Dissertation*, Zurich (1900).

<sup>10</sup> Bjerrum, *Z. physik. Chem.*, 59, 336 (1907);

73, 724 (1910); 110, 656 (1924).

<sup>11</sup> E. Stiasny, "Gerberchemie," Verlag Theodor Steinkopff, Dresden, 1931.

<sup>12</sup> N. O. Smith, *THIS JOURNAL*, 69, 92 (1947).

<sup>13</sup> Colson, *Ann. chim. phys.*, (8) 12, 433 (1907).

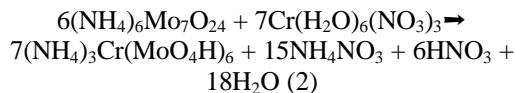
("Disguised" sulfate refers to coordinated sulfate that is not subject to precipitation with barium chloride.)

Further evidence against the existence of such nitrate-containing complexes is the fact that the same number of  $\text{MoO}_4\text{H}$  groups react with a sixty-hour refluxed solution of chromic nitrate, to which an excess of nitrate has been added, as react when additional nitrate has not been added. This fact will become significant later.

The first logical attack on the problem of elucidating the structure of the chromium complexes in the boiled solutions would be to try to crystallize the substance from the solution. No one has yet succeeded in doing this. In the case of the nitrate and sulfate, any crystals obtained by slow evaporation of the solution are violet in color and always yield hexaquo chromic ion on redissolving the crystals. Slow evaporation of boiled chloride solutions gives a crystal which when dissolved yields the ion  $\text{CrCl}_2(\text{H}_2\text{O})_4^+$ . It is apparent that the substances must somehow be studied "in solution" or else must be removed rapidly from the solution by some precipitating reagent for further study since the days of standing required for crystallization allow the complexes to revert to configurations which crystallize nicely.

It was in an attempt to find a reagent that could be used to study chromic complexes "in solution" or that would precipitate them from solution that the usefulness of the ammonium paramolybdate reagent was discovered.

A curve for the conductometric titration of a solution of hexaquo chromic nitrate with ammonium paramolybdate solution is shown in Fig. 1. The conductance increases until the ratio Mo/Cr in the solution is 6/1 at which point the conductance begins to decrease. The over-all reaction is that given.



The increase in conductance is caused by the increase in hydrogen ion concentration produced in the above reaction. When the end-point has been reached (6 Mo/Cr), the excess ammonium paramolybdate solution reacts with hydrogen ion causing the conductance of the solution to decrease. The average value of 4 such conductometric titrations is  $6.000 \pm 0.005$  Mo/Cr expressed as average plus or minus average deviation from the mean. An analysis of the sources of error involved in the titration shows

that the experimentally obtained value should lie within the outside range  $6.00 \pm 0.02$ .

At the beginning of the above titration the solution has a violet color (due to the presence of  $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ ). At the end of the titration, the solution is pink. On mixing more concentrated

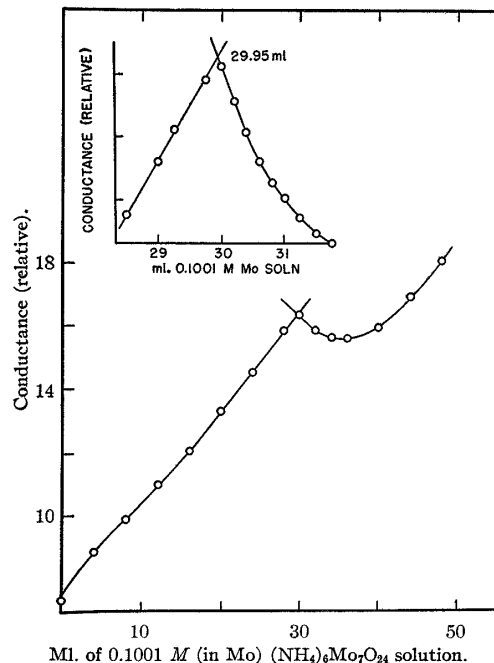


Fig. 1.—Conductometric titration of 25 ml. of 0.0200 *M* chromic nitrate (diluted to approx. 300 ml.) with 0.1001 *M* ammonium paramolybdate solution. Inset gives data near end-point.

solutions of ammonium paramolybdate and violet chromic sulfate, nitrate or chloride (all contain  $\text{Cr}(\text{H}_2\text{O})_6^{+++}$ ) the solution becomes pink and a sparingly soluble salt separates. Microscopic examination shows the crystals are small rhombohedral plates 0.02 to 0.05 mm. on edge; approximately 0.001 mm. thick with a refractive index of 1.72. This substance was prepared by R. D. Hall<sup>14</sup> by boiling a solution containing chrom alum and ammonium paramolybdate and has the composition  $(\text{NH}_4)_3\text{Cr}(\text{MoO}_4\text{H})_6 \cdot 7\text{H}_2\text{O}$ .

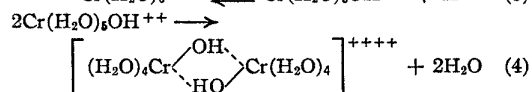
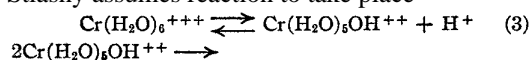
One of the readily observable changes that occurs on heating a solution of chromic sulfate, nitrate, or chloride is the substantial increase in the hydrogen ion concentration of the solution. The *pH* of the freshly prepared violet solutions which contain 0.02 *M* of Cr/liter is approximately 4.0. Upon refluxing 50-ml. portions of 0.10 *M* solutions for fifteen minutes, cooling, transferring to a 250-ml. volumetric flask, and diluting to the mark, the *pH* is found to be for the nitrate, chloride and sulfate,

<sup>14</sup> R. D. Hall, THIS JOURNAL, 29, 692 (1907).

respectively, 2.5, 2.6 and 2.2. (*pH* in this work was measured with a Beckman laboratory model *pH* meter checked against a standard buffer.)

An explanation for the increase of hydrogen ion concentration in boiled solutions of chromic chloride and chromic sulfate has been advanced by Stiasny and his co-workers.

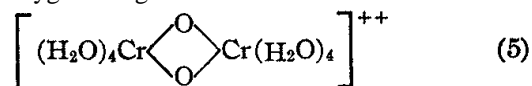
In considering hexaaquo chromic chloride, Stiasny assumes reaction to take place



The second reaction is termed "olation." Because the hydrogen ion concentration decreases by a factor of 10 when a sixty-hour refluxed solution of chromic chloride containing 10 g. of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ /liter is diluted ten times, Stiasny assumes that "olation" is complete and that the hexaaquo configuration has been completely transformed into the "ol" structure above.

While the assumption of some oxygen-bridge type structure seems necessary to explain the increase in acidity accompanying the heating or aging of a chromic salt, the structure assumed by Stiasny is not necessarily correct.

On refluxing for sixty hours solutions of chromic chloride to which sodium hydroxide has been added and subsequently, after cooling, adding hydrochloric acid equivalent to the sodium hydroxide originally added, Stiasny finds the hydrogen ion concentration to be greater than in the case of sixty-hour refluxed chromic chloride to which nothing has been added. On standing at room temperature Stiasny finds that the solution to which sodium hydroxide was added before refluxing "de-olates" (as indicated by a decrease in hydrogen ion concentration) more slowly than a solution to which sodium hydroxide has not been added before refluxing. To explain this behavior, Stiasny assumes that the "ol" structure above has changed into the oxygen bridge structure below.



In his dilution experiment Stiasny assumes the olated structure does not ionize appreciably to give protons. If this were the case, a conductometric titration of a sixty-hour refluxed solution of chromic chloride with sodium hydroxide should give a typical strong-acid, strong-base titration curve. However, a curve such as that of Fig. 2 is always obtained. The first part of this curve is typical of a strong-acid, weak-acid mixture. It seems, then, that the

oxygen bridge type structures present in the sixty-hour solutions ionize appreciably to give protons or else some hexaaquo chromic ion is

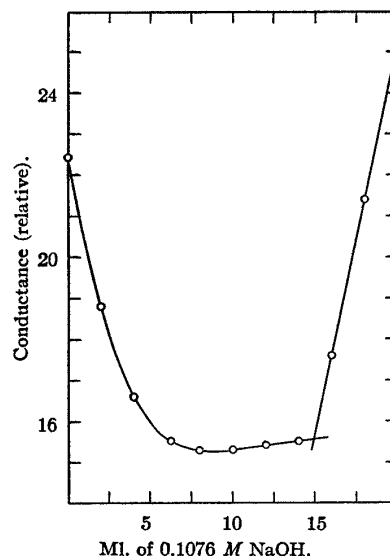


Fig. 2.—Titration of a sixty-five-hour refluxed solution of chromic chloride with sodium hydroxide (50 ml. of 0.1075 *M* chromic chloride refluxed sixty-five hours, transferred to vol. flask and diluted to 250 ml., 25 ml. of resultant solution diluted to approx. 300 ml. and titrated conductometrically with 0.1075 *M* sodium hydroxide).

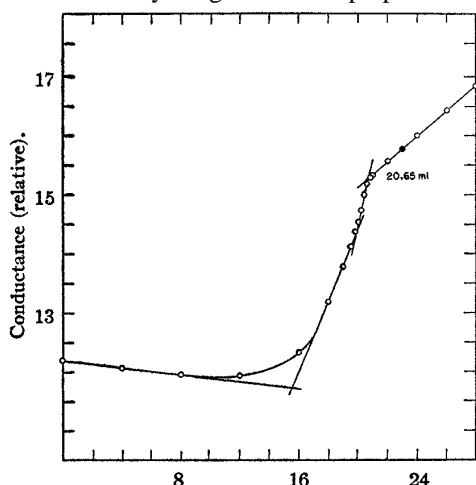
still present in these solutions. (Hexaaquo chromic ion is a weak acid:  $K = 1.0 \times 10^{-4}$ .) A sixty-hour refluxed solution of chromic nitrate behaves similarly when titrated conductometrically with sodium hydroxide.

If a solution of ammonium paramolybdate is titrated with a solution of a chromic salt (the reverse of the titration already considered) a titration curve such as that shown in Fig. 3 is obtained. The inflection points before the final end-point are undoubtedly due to the preferential reaction of one type of molybdenum-oxygen aggregate present in the solution over other types. The question as to the number and types of molybdenum-oxygen aggregates in molybdate solutions is still unsettled.<sup>15</sup> Undoubtedly, conductometric and *pH* titrations of molybdate solutions with solutions containing hexaaquo chromic ion would yield information that would help determine the structure of these molybdates.

The composition of commercial reagent grade ammonium paramolybdate  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  varies slightly with the lot and also the manufacturer. The behavior of ammonium paramolybdate solutions when titrated conductometrically with a solution of a

<sup>15</sup> Emelius and Anderson "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 182-183.

chromic salt depends on this fact and also on the manner in which the solution is prepared and how long the solution stands before use. The most satisfactory reagent is one prepared from

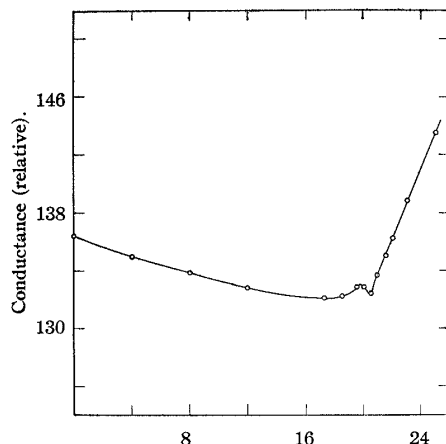


MI. of "fresh" 0.0202 *M* chromic nitrate solution.

Fig. 3.—Titration of 25 ml. of 0.1001 *M* (in molybdenum)  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  (diluted to approx. 300 ml.) with "fresh" 0.0202 *M* chromic nitrate.

the *fine crystal variety* of ammonium paramolybdate by dissolving the calculated quantity in water at room temperature and allowing the solution to stand twenty-four hours to reach an equilibrium condition. The molybdenum content is determined by evaporating a known volume of solution to dryness, firing at  $550^\circ$  and weighing as  $\text{MoO}_3$ .

One molybdate solution prepared from large crystal ammonium paramolybdate (to dissolve these large crystals the solution must be heated) when titrated with freshly prepared



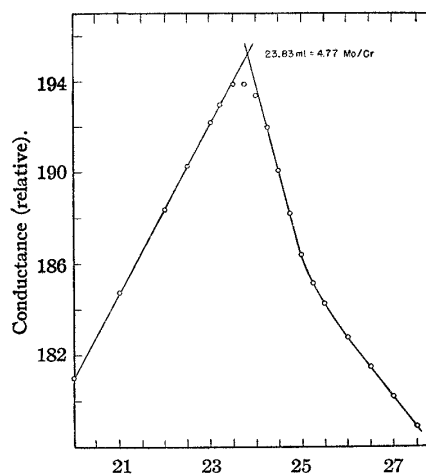
MI. of "fresh" 0.0202 *M* chromic nitrate solution.

Fig. 4.—Conductometric titration of a molybdate solution prepared from "large crystal"  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  with "fresh" chromic nitrate (25 ml. of 0.1000 *M* molybdenum solution diluted to approx. 300 ml.).

chromic nitrate solution gave a conductance curve as shown in Fig. 4. This curve can be

changed into a curve like that of Fig. 3 by adding a few drops of 0.1 *M* nitric acid to the molybdate solution and allowing the solution to stand overnight (to reach an equilibrium condition) before titrating with a freshly prepared solution of chromic nitrate. Similarly, the curve of Fig. 3 can be changed to one like Fig. 4 by adding a little ammonium hydroxide and allowing this solution to come to equilibrium before titrating. Curves of intermediate type can be obtained by adding smaller quantities of acid or base as the case may indicate.

In these titrations it is not absolutely necessary to use solutions of ammonium paramolybdate. Any molybdate solution in which the *pH* has been adjusted to 5.0 will work. If a solution of chromic nitrate which has been refluxed sixty hours or more is titrated with ammonium paramolybdate solution, a curve is obtained similar to that of Fig. 5. The curve before the end-point is essentially a straight line. Apparently if more than one complex is present in the sixty hour chromic nitrate solution, their difference is not sufficiently great for the molybdate solution to react first with one, then with another and so on to give other inflection points in the titration curve. Or, alternatively, there could be a preferential reaction but the differences in conductance of the molecular ions formed are too small to be picked up in the conductometric titration. The end-point for eight



MI. of 0.1001 *M* (in Mo) ammonium paramolybdate soln.

Fig. 5.—Conductometric titration of 411-hours refluxed solution of chromic nitrate with ammonium paramolybdate. (100 ml. of 0.0500 *M* chromic nitrate refluxed 411 hours, transferred to vol. flask and whole diluted to 250 ml. 25 ml. of resultant solution diluted to approx. 300 ml. and then titrated with 0.1001 *M* (in molybdenum) ammonium paramolybdate).

such titrations yields  $4.78 \pm 0.01$  Mo/Cr (expressed as av.  $\pm$  av. deviation from the mean).

All solutions of chromic nitrate or chromic chloride which have been aged or heated give a ratio of Mo/Cr less than 6/1 when titrated conductometrically with ammonium paramolybdate. The Mo/Cr ratio reaches a minimum after sixty hours of refluxing and does not change on refluxing for a longer period. The number of molybdenums reacting per chromium after various reflux times is shown in Table I for chromic nitrate and in Table II for chromic chloride.

TABLE I  
Mo/Cr REACTING AFTER  
VARIOUS REFLUX TIMES FOR  
Cr(NO<sub>3</sub>)<sub>3</sub>

Hours refluxed	Mo/Cr
0	6.00
1/1	5.00
0.25	5.01
2.50	4.92
66.000	4.78
163.0000	4.78
411.0000	4.78

TABLE II  
Mo/Cr REACTING AFTER  
VARIOUS REFLUX TIMES FOR  
CrCl<sub>3</sub>

Hours refluxed	Mo/Cr	Bound Cl/Cr
0	6.00	0.00
1/12	4.84	0.21
0.50	4.78	0.13
1.25	4.55	0.17
64.500	4.50	0.17
310.0000	4.48	

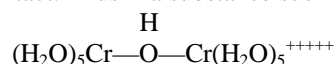
The chloride is more difficult to work with than the nitrate because the bound chloride complexes undergo some change while the titration is being performed. This causes the conductance to change slightly during the titration and makes it more difficult to establish the end-point with certainty. The amount of chloride coordinated to chromium is determined by titrating the solution conductometrically with standard silver nitrate. N. H. Law<sup>16</sup> found that the unbound chloride in solutions of [Cr(H<sub>2</sub>O)<sub>4</sub>Cl<sub>2</sub>]Cl could be determined accurately by conductometric titration with silver nitrate if the pH of the solution being titrated was less than 5. At pH values greater than 5 he found that the "disguised" chloride was also precipitated

with silver ion. In the solutions considered here, the pH is less than 4 and the authors have assumed the bound chloride to remain essentially as such on titration with silver nitrate.

As has been mentioned, it seems necessary to assume that some sort of oxygen-chromium bonds must be formed to explain the increase in acidity of chromic ion solutions on aging or heating. If the presence of these oxygen bridges is assumed, then two possibilities become apparent at this point for the explanation of the fact that less than 6 Mo/Cr react in the case of these boiled salts.

The first explanation would be that the molybdate reagent reacts only with the hexaquo ion and does not react with the complexes containing oxygen bridges. One could then contend that the sixty-hour refluxed solution of chromic nitrate, which must contain complexes containing oxygen bridges because the acidity of the solution has increased, still contains hexaquo chromic ion which reacts with the molybdate reagent but since the "oxygen bridge complexes" do not react, the ratio Mo/Cr is less than 6.

The other explanation would be that the molybdate reagent reacts with the hexaquo chromic ion (if present) but also reacts with the complexes containing oxygen bridges replacing water with MoO<sub>4</sub>H but leaving the oxygen bridges intact. Thus if a substance such as



were present alone, one would expect to find a ratio of 5/1 for Mo/Cr on titrating the solution with ammonium paramolybdate.

The following facts seem to establish that the molybdate reagent does react with the complexes containing oxygen bridges present in boiled solutions of chromic nitrate:

(1) When stoichiometric proportions of sixty-hour refluxed chromic nitrate and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> (4.78 Mo/Cr) are mixed, the solution attains a purple hue whereas stoichiometric proportions of freshly prepared chromic nitrate and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> (6 Mo/Cr) give pink solutions.

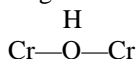
(2) If after mixing stoichiometric proportions of 60-hour refluxed chromic nitrate and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> solutions, silver nitrate solution in excess is added, a grayish-purple precipitate is obtained. If this precipitate is filtered off, it is found that the filtrate does not contain chromium. If silver nitrate solution is added to a sixty-hour refluxed solution of chromic nitrate solution to which no molybdate

<sup>16</sup> Law, Trans, Faraday Soc., 32, 1461-1465 (1936).

reagent has been added, a precipitate is not obtained. It would seem, then that all the chromium present in the sixty-hour refluxed solution of chromic nitrate has reacted with the ammonium paramolybdate and this product forms an insoluble precipitate with silver nitrate.

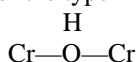
Sixty-hour refluxed solutions of chromic chloride give results that parallel those given above for chromic nitrate.

Having established the fact that all the chromium complexes existing in the above solutions react with the molybdate reagent, the question arises as to whether or not  $\text{MoO}_4\text{H}^-$  replaces all the groups coordinated to chromium. If all the coordinated water were replaced by  $\text{MoO}_4\text{H}^-$  as it is in the case of hexaquo chromic ion, the fact that less than 6 Mo/Cr react must be explained by assuming that the



structure is left intact. Whether or not all the water coordinated to chromium in the complexes containing oxygen bridges is replaced by  $\text{MoO}_4\text{H}^-$  could readily be ascertained if the amount of free  $\text{H}^+$  in the refluxed solutions could be determined.

Let us consider the case of the sixty-hour refluxed solution of chromic nitrate. The value of 4.78 Mo/Cr would indicate an average of 0.61 oxygens per chromium used for bridge forming. If the bridges are of the type



the sixty-hour refluxed solution would contain 0.61 free  $\text{H}^+$ /Cr. Referring to Fig. 2 it is observed that this free  $\text{H}^+$  cannot be determined by direct titration with sodium hydroxide. If, however, the stoichiometric proportion of molybdate reagent is added to a sixty-hour refluxed solution of chromic nitrate and the solution is allowed to stand ten minutes (for reaction to go to completion) before titrating conductometrically with sodium hydroxide solution, a curve such as that shown in Fig. 6 is obtained. One observes that the replacement of water by  $\text{MoO}_4\text{H}^-$  stabilizes the complex to such an extent that the free  $\text{H}^+$  can be titrated without the complex gradually ionizing away protons until precipitation takes place. The titration indicates 0.204  $\text{H}^+$ /Mo. However, this titration has its difficulties. The end-point as determined by the intersection of the two straight lines in Fig. 6 does not give the true free  $\text{H}^+$ . The error is caused by the hydrolysis of the Cr—Mo complex.

From equation 2 one observes that  $1/7 = 0.143 \text{ H}^+/\text{Mo}$  is produced each time  $\text{MoO}_4\text{H}^-$  coordinates to Cr. The conductometric titration with sodium hydroxide, of a solution formed according to equation 2 gives only 0.112  $\text{H}^+/\text{Mo}$

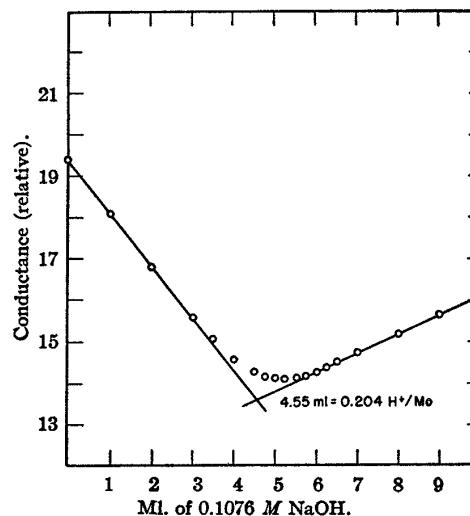
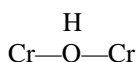


Fig. 6.—Titration (with sodium hydroxide) of a 163-hour refluxed solution of chromic nitrate to which the stoichiometric amount of molybdate solution has been added (4.78 molybdenum/chromium) (50 ml. of 0.0500 *M* chromic nitrate refluxed 163 hours; cooled rapidly; diluted to 250 ml. in vol. flask; 50 ml. of resultant soln. + 23.90 ml. of ammonium paramolybdate soln. (0.1000 *M* in molybdenum) diluted to approx. 300 ml. and then titrated with 0.1076 *M* sodium hydroxide).

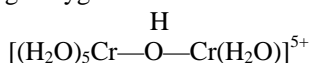
(titration curve is similar to Fig. 6). A synthetic solution (without ammonium nitrate) similar to that formed from equation 2 was prepared by adding a known quantity of hydrochloric acid to a known weight of  $(\text{NH}_4)_3\text{Cr}(\text{MoO}_4\text{H})_6 \cdot 7\text{H}_2\text{O}$ . Conductometric titration of this solution with sodium hydroxide gives a value for free  $\text{H}^+$  lower than the known amount of hydrochloric acid added.

The end-point for the titration of the 60-hour refluxed solution of chromic nitrate, to which the stoichiometric proportion of molybdate reagent has been added, with sodium hydroxide will also indicate a low value for the free  $\text{H}^+$ . There is no way, in this case, to make an end-point correction. As an approximation, however, we may assume that the end-point error here is equal to the end-point error for the case of the hexaquo salt. Subtracting 0.112 from 0.204, 0.092  $\text{H}^+/\text{Mo}$  free acid produced by oxygen bridge formation is obtained. Since the Mo/Cr ratio in this solution is 4.78/1, the free acid produced per Cr is  $4.78 \times 0.092 = 0.44$ . This value is somewhat lower than 0.61 but in view of the approximation involved seems to be in good agreement with the assumption that  $\text{MoO}_4\text{H}^-$

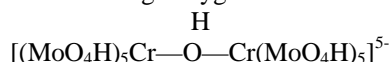
does replace water coördinated to Cr but does not disrupt the



The above experiments also show why the authors have chosen to attach a hydrogen to the oxygen bridging two chromiums. If the bridge were oxygen alone, the free  $\text{H}^+$  in the sixty-hour refluxed solution would be  $1.22 \text{ H}^+/\text{Cr}$  (since the Mo/Cr ratio is 4.78/1). If two hydrogen atoms were bound to the bridge oxygen this would mean that four positive groups would be attached to a single oxygen atom. This is quite improbable. It must be recognized, however, that the ionization constant for the hydrogen attached to the bridge oxygen in



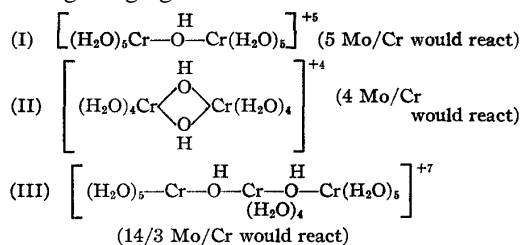
may be greater than that for the hydrogen attached to the bridge oxygen in



The authors have carried out similar experiments with chromic chloride and have found results that parallel those of the nitrate.

The authors have concluded from the above experiments that the average number of oxygens per chromium used in the bridge formation in aged or boiled solutions of chromic nitrate or chloride can be determined by titrating the solution conductometrically with a solution of ammonium paramolybdate.

The value 4.78 Mo/Cr could result from reaction of molybdate solution with a number of oxygen-bridge-containing complexes. However, it is likely that the simpler polymers are present in greater amount. For example, consider the structures I, II and III, of which I is the simplest and might be expected to be the first to form on heating or aging.



If hexaquo chromic ion or I above is present, then to obtain the value 4.78 Mo/Cr, II or III or longer chain polymers must be present.

An interesting reaction is that between dichlorotetraaquo chromic ion  $\text{CrCl}_2(\text{H}_2\text{O})_4^+$  and the molybdate reagent. Dilute solutions of this ion are unstable and change in a few hours to the hexaquo ion. The conductance of a dilute

solution of this ion changes so rapidly that it is quite difficult to titrate with the molybdate solution. The reverse titration (add a solution containing dichlorotetraaquo chromic ion to a solution of ammonium paramolybdate) however is feasible. In this titration the conductance changes slowly and the end-point cannot be determined as accurately as in the case of the hexaquo salt. In this titration the end-point indicates a Mo/Cr ratio of 4 to 1. This means that  $\text{MoO}_4\text{H}^-$  groups have replaced water but not  $\text{Cl}^-$ . (Solutions containing  $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$  are prepared by dissolving the salt obtained by reprecipitating ordinary, commercial, green crystals of chromic chloride hexahydrate with hydrochloric acid.)

Since the bound chloride in tetraaquo dichlorochromic ion is not replaced by  $\text{MoO}_4\text{H}^-$ , it is likely that the small amount of bound chloride in the refluxed solutions (Table II) is also not replaced. This should be taken into account when calculating the average number of oxygens per chromium used in bridge formation.

Chromic solutions to which sodium hydroxide has been added before refluxing give an even smaller ratio of Mo/Cr than the titrations considered above. This indicates a high degree of bridge formation which is also in line with the increased acidity of these solutions. A 1/3 basic<sup>17</sup> two hundred and forty-hour refluxed solution of chromic nitrate is very green in color. On adding the molybdate solution a green precipitate is formed. Undoubtedly the Cr-Mo complex formed here is a large bulky ion (many oxygen bridges) and is insoluble. Not all the chromium is precipitated on adding the molybdate reagent, however. This indicates that at least two types of chromium-oxygen polymers are present in this solution. The total amount of molybdenum reacting per chromium as shown by conductometric titration is in this case 2.98 Mo/Cr. If this stoichiometric amount of ammonium paramolybdate solution is added to the 1/3 basic, two hundred and forty-hour refluxed chromic nitrate solution and the resultant solution is then titrated conductometrically with sodium hydroxide, 0.216  $\text{H}^+/\text{Mo}$  is found. Subtracting from this the

<sup>17</sup> This expression is due to the leather chemists. A 1/3 basic solution of a chromic salt is a solution to which one mole of a base such as sodium hydroxide has been added per mole of chromium. A 2/3 basic solution is one to which 2 moles of base have been added per mole of chromium, etc.



value 0.112 for  $H^+$  produced when  $MoO_4H$  coordinates,  $0.104 H^+/Mo$  or  $2.98 \times 0.104 = 0.31 H^+/Cr$  is obtained. Adding to this the value of  $1.00 H^+/Cr$  to account for the  $H^+$  neutralized by making the solution  $1/3$  basic it is observed that  $1.31 H^+/Cr$  is produced in polymer formation. From the value of  $2.98 Mo/Cr$  and the assumption that one hydrogen is attached to each bridge oxygen the free  $H^+$  should be  $1.46 H^+/Cr$ . The first value is low as might have been expected since the same incalculable errors are involved here as were involved with the sixty-hour refluxed nitrate.

One third basic, sixty-hour refluxed chromic chloride shows  $2.68 Mo/Cr$  and  $0.08$  bound  $Cl^-/Cr$  and forms a precipitate. Always on similar treatment of chromic nitrate and chromic chloride, the ratio  $Mo/Cr$  is smaller for the chloride. Apparently the small amount of coordinated chloride plays a role in oxygen bridge formation. Titration of a  $1/9$  basic ( $1/3 OH^-/Cr$ ), sixty-hour refluxed chromic chloride solution with molybdate solution does not give a precipitate. The  $Mo/Cr$  ratio here is found to be  $3.74$ .

At this point, it would be well to recall Stiasny's structures for the complexes present in sixty-hour refluxed solutions of chromic chloride and  $1/3$  basic chromic chloride (see equations 4 and 5).

For either structure titration with ammonium paramolybdate solution should give  $Mo/Cr = 4/1$ . As shown, however, the ratio is  $4.50/1$  and  $2.68/1$ . It must be concluded that neither solution is adequately represented by Stiasny's structures.

The formation of oxygen bridges is greatly facilitated by adding ethanol to a solution of chromic nitrate before refluxing. Apparently there is competition between chromium ions and alcohol molecules for water molecules and the chromium gives up water to alcohol by forming many oxygen bridges. On refluxing chromic nitrate in 90% ethanol solution, the solution becomes a brilliant green in a very short time and the acidity increases considerably. A typical solution when refluxed for only five minutes gives a green precipitate on conductometric titration with ammonium para molybdate solution and shows only  $1.6 Mo/Cr$ .

It has been mentioned that aged solutions of chromic nitrate also form oxygen bridges. This is shown by the fact that the acidity of a chromic nitrate solution increases on aging and the number of  $Mo/Cr$  found on titration with the molybdate reagent is less than 6. For example:

an approx. 0.1 molar solution of chromic nitrate was prepared and its  $pH$  found to be 2.60. On standing in a glass-stoppered bottle for twenty-six days at room temperature, the  $pH$  was found to be 2.37. The titration of a typical 0.1 M thirty-day-old chromic nitrate solution gives  $5.57 Mo/Cr$ .

In the above work, chromium concentrations were determined by the standard persulfate procedure. Standard solutions of silver nitrate and potassium dichromate (used to standardize ferrous sulfate used in chromium determinations) were prepared by weighing the oven dried salts and diluting to volume in a volumetric flask. Standard carbonate-free sodium hydroxide solutions were prepared according to method 2 on page 1352 of the 30th ed. of "Handbook of Chemistry and Physics." Hydrochloric acid solutions were standardized against this sodium hydroxide. Violet chromic chloride was prepared and stored according to the method of Bjerrum. Violet chromic nitrate was prepared by recrystallizing J. T. Baker analyzed chemical.

The bridge used for measurement of conductance was constructed of conventional components and was of sufficient sensitivity to measure resistance to 0.1 ohm.

The conductance cell consisted of a 400-cc. beaker into which a stirring propeller and two platinum electrodes coated with platinum black could be lowered.

The solution to be titrated was introduced into the titration beaker and the volume of the solution adjusted to approx. 300 cc. before titration was begun.

In all work considered here, the concentrations of the chromic nitrate and chromic chloride solutions that were refluxed were either 0.05 M or 0.10 M in chromium. In either case, the  $Mo/Cr$  ratio was found to be the same for solutions refluxed the same length of time. It is conceivable, however, that much higher or much lower concentrations might give, after refluxing,  $Mo/Cr$  ratios differing from those of the 0.05 M and 0.10 M solutions.

In titrating the chromium solutions with ammonium para molybdate or vice versa a period of approximately 3 minutes must be allowed between the incremental additions in order for the reaction to go to completion and for the conductance to become constant.

#### Summary

1. The conductometric titration of chromic salt solutions with  $(NH_4)_6Mo_7O_{24}$  solution enables one to determine the average number of

oxygen bridges per chromic ion present in aged or heated solutions of chromic nitrate or chloride.

2. The postulated composition of a sixty-hour refluxed solution of chromic chloride and of a 1/3 basic, sixty-hour refluxed solution given by E. Stiasny and co-workers has been shown to require revision.

3. Data are given for the number of  $\text{MoO}_4\text{H}$  groups that will coordinate to chromium in variously treated chromic salt solutions. These data show that the average number of oxygen bridges joining chromic ions increases with time on refluxing solutions of chromic nitrate and chromic chloride until a maximum is reached at sixty hours. Further refluxing does not cause any increase in the number of bridges. The addition of sodium hydroxide before refluxing causes a large increase in the number of oxygen bridges formed as does also the addition of ethyl alcohol.

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