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

A Study of the Equilibria in Acidic Chromium(III) Chloride Solutions[1-3]

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The values of the equilibrium quotients for the reactions, $Cr(OH_2)_6^{+3} + Cl^- = Cr(OH_2)_5Cl^{++} + H_2O$ (reaction 1), and $Cr(OH_2)_5Cl^{++} + Cl^- = Cr(OH_2)_4Cl_2^+ + H_2O$ (reaction 2) have been determined over the temperature range 30–95° in aqueous media in which the sum of the stoichiometric molalities of chloride ion and perchlorate ion is 4.44. The analysis of equilibrated solutions has been performed by spectrophotometric measurements. The values of both Q_1 and Q_2 show dependences upon the concentration of chloride ion which are not inconsistent with the medium effects observed in mixed strong electrolyte solutions of constant molality. It is open to question, therefore, whether the alternate interpretation of the variation in Q_1 in terms of the formation of the outer-sphere complex $Cr(OH_2)_6^{+3}\cdot Cl^-$ is of significance. Values of ΔH and ΔS for reactions 1 and 2 are presented.

The relatively inert inner-sphere complex ions $Cr(OH_2)_5Cl^{++}$ and $Cr(OH_2)_4Cl_2^+$ are present at equilibrium with $Cr(OH_2)_6^{+3}$ in aqueous solutions containing chromium(III) and chloride ion.[4] Because of their inertness, the individual complexes can be prepared by ion-exchange methods and the molar absorbancy indices evaluated. It is then possible to analyze equilibrated solutions for these species and evaluate the equilibrium quotients for the association reactions

$$Cr(OH_2)_6^{+3} + Cl^- \rightleftarrows Cr(OH_2)_5Cl^{++} + H_2O \qquad \text{(Reaction 1)}$$

$$Cr(OH_2)_5Cl^{++} + Cl^- \rightleftarrows Cr(OH_2)_4Cl_2^+ + H_2O \qquad \text{(Reaction 2)}^5$$

To cause the formation of an appreciable amount of $CrCl_2^+$,[6] the chloride ion concentration must be 3-4 molal; thus studies must be made in rather concentrated electrolyte solutions. The media used in this study have the sum of the stoichiometric concentrations of perchlorate ion and chloride ion equal to 4.44 molal. The reason for studying only solutions with such composition was the hope that the activity coefficients of all species would be essentially constant as the chloride ion concentration was varied. The observed approximately 1.8-fold (at 30°) to 2.8-fold (at 95°) change in the value of Q_1, the equilibrium quotient for reaction 1, with the change of the molality of chloride ion from 0.4 to 4.4, indicates either that this hope was ill-founded, which is quite possible, or that the outer-sphere complex $Cr(OH_2)_6^{+3}\cdot Cl^-$ was formed to a significant extent. Interpretations of the data in terms of reactions 1 and 2, both without and with the reaction

$$Cr(OH_2)_6^{+3} + Cl^- \rightleftarrows Cr(OH_2)_6^{+3}\cdot Cl^- \qquad \text{(Reaction 3)}$$

will be presented.

Experimental Methods

Reagents.—All solutions used in this work were prepared using reagent grade chemicals unless otherwise noted. Most solutions were prepared using doubly distilled water, the second distillation being from an alkaline permanganate solution; some solutions were prepared using water distilled only once.

Chromium(III) perchlorate was prepared by the reaction of chromium trioxide and formic acid in perchloric acid solution. The chromium(III) perchlorate was recrystallized

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[1] Taken in part from the Ph.D. thesis of Henry S. Gates, University of Wisconsin, 1956.

[2] Supported in part by grants from the Research Committee of the Graduate School, University of Wisconsin, and the U. S. Atomic Energy Commission (Contract AT(11-1)-64, Project No. 3).

[3] Presented in part at the 129th National Meeting of the American Chemical Society, Dallas, Texas, April, 1956.

[4] N. Bjerrum, *Z. physik. Chem.*, **59**, 581 (1907); J. Olie, *Z. anorg. Chem.*, **51**, 29 (1907).

[5] The dichlorotetraaquochromium(III) ion exists in two forms, the *cis* and *trans* isomers. At each temperature, the two isomers exist in certain relative proportions at equilibrium; it is this equilibrium mixture of the two isomers which is represented by the formula $Cr(OH_2)_4Cl_2^+$. The separation and the characterization of the two isomers is discussed in the accompanying paper, E. L. King, Sr. M. J. M. Woods, O.P., and H. S. Gates, THIS JOURNAL, **80**, 5015 (1958).

[6] Water molecules in the first coördination shell of chromium(III) will not, in general, be shown. Thus, the species $Cr(OH_2)_6^{+3}$, $Cr(OH_2)_5Cl^{++}$, and $Cr(OH_2)_4Cl_2^+$ are represented as Cr^{+3}, $CrCl^{++}$ and $CrCl_2^+$, respectively.

from dilute perchloric acid, and was shown to be free of chromium(VI) by the diphenylcarbazide test.[7]

Silver perchlorate solution, used to precipitate potassium chloride from solution, was prepared by the reaction of freshly precipitated silver oxide with insufficient perchloric acid. The excess silver oxide was removed by filtration.

Dowex-50 resin was used in the hydrogen ion form for all ion exchange studies.

Solutions containing $CrCl^{++}$ as the only chromium(III) species were prepared by the ion-exchange separation of this species from relatively small amounts of $CrCl_2^+$ and Cr^{+3} present in a day old solution of $(Cr(OH_2)_4Cl_2)Cl\cdot 2H_2O$ in 0.1 *M* perchloric acid.[4] The ion-exchange runs were carried out at 3–6°; after first eluting any $CrCl_2^+$ with 0.1 *M* perchloric acid, the cation of charge +2 was eluted with 1.0 *M* perchloric acid.

The preparation of solutions containing $CrCl_2^+$ as the only chromium(III) species with the *cis* and *trans* isomers in their equilibrium proportions proved to be relatively difficult. The total cation concentration in a typical reaction solution was so much greater than the concentration of $CrCl_2^+$ that this chromium complex of charge +1 did not go into the resin phase from the equilibrated reaction solution.[8] Solutions of the composition 0.3 *M* chromium(III) chloride, 3.5 *M* potassium chloride and 0.1 *M* hydrochloric acid were brought to equilibrium at 30, 46, 74 and 96°. Most of the electrolyte was removed from these solutions, which had been quenched by cooling to 0°, by the addition of silver perchlorate in an amount sufficient to precipitate all of the potassium ion. The chromium(III) cation(s) of charge +1 are partially taken up from the resulting solution by the resin; elution with 0.1 *M* perchloric acid completely removes the +1 chromium(III) species. The eluent combined with the solution which came straight through the column was assumed to contain $CrCl_2^+$ as the only chromium(III) species.[9]

The Reaction Medium.—The maintenance of the stoichiometric anion molality constant (at 4.44 *m*) was suggested by the small variation of the activity of water with a change of the concentration of chloride in such media.[10] Since the chromium(III) concentration was not, in every case, very small compared to the concentration of chloride, the ionic strength values of the several reaction solutions were not identical. In 80% of the solutions studied, the true and stoichiometric anion concentrations differed by less than 2% and the maximum difference was 9.5%.

The Molar Absorbancy Indices of Cr^{+3}, $CrCl^{++}$ and $CrCl_2^+$.—The wave lengths 380, 416, 450, 540, 590 and 650 mμ were those at which measurements were made on the equilibrated solutions.[11] A Beckman model DU spectrophotometer was used in most of the spectrophotometric studies. The values of the molar absorbancy indices determined in ~4.4 *m* perchloric acid are[12]

λ(mμ)	380	416	450	540	590	650
a_0(or a_3)	10.0_1	15.0_5	6.64	9.78	12.6_5	3.78
a_1	5.38	19.3_2	17.1_8	5.79	15.0_7	11.6_0
a_2	1.74	13.9_3	26.0_3	3.81	12.3_8	21.1_4

The value of a_2 at 450 mμ, where the *cis* and *trans* isomers of $CrCl_2^+$ have rather different molar absorbancy indices, did not show a significant trend with the temperature of equilibration, thus suggesting that approximately the same relative amounts of *cis*- and *trans*-$CrCl_2^+$ are present at each temperature. This is not unreasonable since the value of ΔS^0 for the isomerization reaction is undoubtedly small; therefore, $\Delta F^0 \cong \Delta H^0$, and the condition which corresponds to the presence of appreciable amounts of both isomers ($\Delta F^0 \cong 0$) also corresponds to a small temperature coefficient for the isomerization equilibrium quotient.

Methods of Analysis of Stock Solutions.—Chromium analyses were performed by measuring the absorbancy at 375 mμ of a solution containing chromate ion, prepared by peroxide oxidation in alkaline media.[13]

The concentration of strong acid in chromium(III) solutions has been determined in either of two ways. The method in which chromium(III) is tied up as the oxalate complex, suggested by the work of Blaedel and Panos,[14] has already been described.[15] A more convenient method is one involving the use of an ion-exchange resin; if a solution containing only the cations Cr^{+3} and H^+ is passed through an ion-exchange column in the hydrogen ion form, a solution of the same total normality containing only hydrogen ion will come out of the column. The concentration of strong acid in the original solution is obtained from the known concentration of chromium(III) and the acidity of this final solution.[16]

Experimental Results

Equilibrium Studies.—Solutions of varying composition (0.009 to 0.45 *m* chromium(III), 0.48 to 4.4 *m* chloride), were brought to equilibrium at the temperatures 30.0, 46.3, 63.5, 73.7_5, 84.8 and 95.4°; in practically all cases, duplicate samples were kept in the thermostat for varying lengths of time to provide proof of the attainment of equilibrium.[17] After the solutions were quenched by cooling to room temperature, the absorbancy values were measured at the six wave lengths. The method of averages was used to calculate the molarities of $CrCl^{++}$, $CrCl_2^+$ and Cr^{+3}.[18] These molarity values were converted to molalities by the use of appropriate density data.

The values of Q_n (n = 1, 2) at each temperature were not constant but showed a dependence upon the molality of chloride ion consistent with the equation

$$\log Q_n = \log Q'_n - \alpha_n(Cl^-) \qquad (1)$$

where (Cl^-) is the molality of chloride ion, α_n is a constant and Q'_n is the value of the equilibrium quotient for reaction n, valid for $(Cl^-) = 0$ (*i.e.*,

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(7) B. E. Saltzman, *Anal. Chem.*, **24**, 1016 (1952).

(8) In a situation such as this, in which a cation under consideration is a minor contributor to the total cation normality, the observation that a species passes through the column with essentially the same velocity as the solvent does not prove that this species is neutral or anionic.

(9) This procedure leads to solutions which may contain some $CrCl_3$; in view of the magnitude of the equilibrium quotients governing the concentration of $CrCl^{++}$ and $CrCl_2^+$, however, it seems unlikely that the equilibrium value of $(CrCl_3)/(CrCl_2^+)$ would exceed 0.1 in ~4 *M* chloride ion at these temperatures. (A formula in parentheses stands for the molal concentration of the species.)

(10) The values of the activity of water in 4 *m* hydrochloric acid and in 4 *m* perchloric acid differ by 1.5% while values of this quantity in 4 *M* hydrochloric acid and 4 *M* perchloric acid differ by 7%.

(11) The terms used in describing the spectrophotometric work are those suggested in Natl. Bur. of Standards Letter Circular LC 857 (1947); the absorbancy $A = \log I_0/I = abc$, where *a*, *b* and *c* are the molar absorbancy index, the cell length and the molar concentration, respectively. The molar absorbancy indices of Cr^{+3}, $CrCl^{++}$, $CrCl_2^+$, and $Cr^{+3}\cdot Cl^-$ are designated as a_0, a_1, a_2 and a_3, respectively.

(12) The values reported for a_2 are not, in all cases, the values determined directly. A trend in the calculated value of a_2 at 380 mμ with the concentration of $CrCl_2^+$ was rationalized by the demonstrated presence of a trace of chromium(VI) in the green chromium(III) chloride used. In each solution used to prepare $CrCl_2^+$, there was the same total amount of chromium(III) and also, therefore, the same amount of chromium(VI). In the solutions heated at different temperatures a different amount of chromium(III) was present as $CrCl_2^+$; thus solutions in which the amount of $CrCl_2^+$ was greater yielded values of a'_2, the apparent molar absorbancy index of $CrCl_2^+$, which were more nearly correct. The linear plot of the values of a'_2 *versus* $1/[CrCl_2^+]$, where $[CrCl_2^+]$ is the molarity of $CrCl_2^+$, yielded as an intercept the true value of a_2. It is only at the shorter wave lengths, where chromium(VI) has a large molar absorbancy index, that this correction is appreciable.

(13) G. W. Haupt, *J. Research Natl. Bur. Standards*, **48**, 414 (1952).

(14) W. J. Blaedel and J. J. Panos, *Anal. Chem.*, **22**, 910 (1950).

(15) E. L. King and J. A. Neptune, THIS JOURNAL, **77**, 3186 (1955).

(16) L. M. Orlova, *Zhur. Anal. Khim.*, **5**, 370 (1950); *C. A.*, **45**, 925 (1951).

(17) The results of the experiments at 0.45 *m* chromium(III) were omitted from most of the calculations because of the rather large medium effects anticipated.

(18) The sum of the calculated molarities of the chromium(III) species should have been equal to the known stoichiometric molarity of chromium(III); in general, the sum of the calculated molarities was slightly higher, being an average of 2.2% too high.

4.4 *m* perchlorate). The values of α_1 which correlated the observed Q_1 values are 0.074, 0.082, 0.094, 0.099, 0.109 and 0.111 at 30, 46.3, 63.5, 73.7$_5$, 84.8 and 95.4°, respectively. If one is to interpret this trend in Q_1 as a non-specific medium effect, the conclusion is drawn that the activity coefficient function $\log\{\gamma_{\text{Cr}^{+3}} \times \gamma_{\text{Cl}^-}/\gamma_{\text{CrCl}^{++}}\}$ decreases linearly with the replacement of perchlorate ion in the medium by chloride ion. Such a relationship is not unreasonable in the light of numerous observations on the activity coefficients of electrolytes in mixed electrolyte solutions of constant ionic strength.[19] The value of ΔZ^2 for reaction 1 is -6; with respect to charge type, therefore, the quotient $\{\gamma_{\text{Cr}^{+3}} \times \gamma_{\text{Cl}^-}/\gamma_{\text{CrCl}^{+2}}\}$ is analogous to the *sixth power* of the mean activity coefficient of a 1–1 electrolyte. Since the activity coefficients of perchlorates are generally higher than the corresponding chlorides,[20] it would be expected that the quotient $\{\gamma_{\text{Cr}^{+3}} \times \gamma_{\text{Cl}^-}/\gamma_{\text{CrCl}^{++}}\}$ would decrease with the replacement of perchlorate by chloride.

The values of Q_2 obtained at only the two highest concentrations of chloride ion ((Cl$^-$) $\cong$ 1.8 and 4.2) are considered reliable since even at ~4.2 *m* chloride ion only 8% (at 30°) to 25% (at 95°) of the chromium(III) is present as dichlorochromium(III) ion. The dependence of Q_2 upon (Cl$^-$) over this range is consistent with values of $\alpha_2 \cong 0.67\ \alpha_1$; the factor 0.67 is introduced because the value of ΔZ^2 for reaction 2 is -4, 0.67 of the value for reaction 1. The values of Q_1' (for (Cl$^-$) = 0) and Q_2 (for (Cl$^-$) $\cong$ 4.2) as a function of the temperature are presented in Table I.

TABLE I

VALUES OF THE EQUILIBRIUM QUOTIENTS[a] AS A FUNCTION OF TEMPERATURE

Medium: total stoichiometric anion molality = 4.44

T, °C.	Q'_1	Q_2	$\bar{Q}_1$	$\bar{Q}_3$
95.4	1.43	0.11$_6$	1.82	0.65
84.8	1.14	.10$_1$	1.34	.52
73.7$_5$	0.83	.084	0.98	.49
63.5	.64	.067	.73	.41
46.3	.38	.049	.42	.34
30.0	.24	.033	.27	.29
25.0				.30$_5$[b]

[a] The subscripts refer to reaction number. The Q'_1 values were obtained from fitting all Q_1 values to equation 1. and thus are valid for solutions with (Cl$^-$) = 0. The Q_2 values are those observed at (Cl$^-$) $\cong$ 4.2. The $\bar{Q}_1$ and $\bar{Q}_3$ values were obtained under the assumption that the dependence of Q_1 upon (Cl$^-$) is due to reaction 3. [b] Obtained from ultraviolet spectrophotometric studies on freshly prepared solutions.

Outer-sphere Association of $Cr(OH_2)_6^{+3}$ and Cl^-.—The absorbancy of a freshly prepared solution of chromium(III) perchlorate in hydrochloric acid is indistinguishable at $\lambda > 280$ mμ from the absorbancy of a similar solution containing perchloric acid instead of hydrochloric acid. Thus absorbancy measurements at the wave lengths used in the analysis of equilibrated solutions do not disclose the presence of the species $Cr(OH_3)_6^{+3}{\cdot}Cl^-$. If the occurrence of reaction 3 is the cause of the dependence of Q_1 upon (Cl$^-$), however, the relevant equation is

$$1/Q_1 = 1/\bar{Q}_1 + \bar{Q}_3(\text{Cl}^-)/\bar{Q}_1 \qquad (2)$$

where $\bar{Q}_1$ and $\bar{Q}_3$ are the apparent equilibrium quotients for reactions 1 and 3 under the assumption that reaction 3 does occur and is the sole cause of the dependence of Q_1 upon (Cl$^-$).[21]

The values of $\bar{Q}_1$ and $\bar{Q}_3$ obtained from the fitting of equation 2 to the data are given in Table I. Now it is true, of course, that the Q_1 values cannot be perfectly consistent with both equations 1 and 2. One manifestation of this is the disagreement between the values of Q'_1 and $\bar{Q}_1$, each of which is an intercept at (Cl$^-$) = 0 in the appropriate plot.[22] The values of $\bar{Q}_3$ are seen to be much lower than the limit considered necessary by Redlich[23] to constitute proof of specific ion association as the cause of abnormal activity coefficient behavior.

At wave lengths shorter than 250 mμ, the absorbancy of a freshly prepared solution of chromium(III) perchlorate in hydrochloric acid is much greater than the absorbancy of a similar solution containing perchloric acid and no chloride ion. Such spectral changes in other systems have been interpreted in terms of the formation of a new species, an outer-sphere complex of the anion and the metal ion with its first coördination shell of water molecules (or ammonia molecules) intact.[24] This interpretation for some of these systems is rendered relatively certain by the presence of a new peak attributable to the outer-sphere complex. In some of the systems studied and in the present study, however, there is not this type of evidence for reality of the outer-sphere complex. One may nevertheless attempt a correlation of the spectral data in terms of reaction 3 with the parameters a_0 which is determined independently and a_3 and $\bar{Q}_3$ which are evaluated from the dependence of A upon (Cl$^-$).[11] The method of Newton and Arcand[25] has been used in treating the data obtained at 25° from 20 solutions with ($Cr(OH_2)_6^{+3}$) = 0.009 to 0.09 and (Cl$^-$) = 0.00 to 4.02. The value of $\bar{Q}_3$ so obtained is 0.30$_5$ ± 0.03. (This is the average of the values of $\bar{Q}_3$ obtained at each of the six wave lengths; the stated uncertainty is the average difference be-

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[19] For summaries see: H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, Chap. 14, and R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Buttersworth Scientific Publications, London, England, 1955, Chap. 15.

[20] At a concentration of 4 molal the mean activity coefficients of perchloric acid and hydrochloric acid are 2.08 and 1.76, respectively.

[21] In deriving equation 2, it is assumed that (Cl$^-$) $\gg$ ($Cr^{+3}{\cdot}Cl^-$). This is approximately true. In the actual treatment of the data account was taken of the chloride ion tied up as $Cr^{+3}{\cdot}Cl^-$.

[22] That both equations 1 and 2 fit the same data reasonably well is not surprising since equation 2 can be written in a form

$$\log Q_1 = \log \bar{Q}_1 - 0.434\bar{Q}_3(\text{Cl}^-) + 0.217\bar{Q}_3{}^2(\text{Cl}^-)^2 - \ldots$$

having much in common with equation 1.

[23] O. Redlich, *Chem. Revs.*, **39**, 333 (1946); T. F. Young and A. C. Jones, *Ann. Revs. Phys. Chem.*, **3**, 279 (1952).

[24] (a) M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944); (b) E. H. Katzenellenbogen, Paper No. 23, Div. of Physical and Inorganic Chem., Am. Chem. Soc. Meeting, Sept., 1950; (c) M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **266**, 73 (1951); (d) H. Taube and F. A. Posey, THIS JOURNAL, **75**, 1463 (1953); (e) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953); (f) A. W. Adamson and R. G. Wilkins, THIS JOURNAL, **76**, 3379 (1954); (g) H. Yoneda, *Bull. Chem. Soc., Japan*, **28**, 125 (1955); (h) F. A. Posey and H. Taube, THIS JOURNAL, **78**, 15 (1956); (i) A. L. Phipps and R. A. Plane, *ibid.*, **79**, 2458 (1957).

[25] T. W. Newton and G. M. Arcand, *ibid.*, **75**, 2449 (1953).

tween the individual values and the average value.) The values of a_3 consistent with this average value of $\bar{Q}_3$ and the values of a_0 are

λ(mμ)	230	232	234	236	238	240
a_0[26]	0.82	0.82	0.94	1.11	1.34	1.65
a_3	24.7	18.2	13.6	10.3	8.17	6.55

The absorbancy values calculated with these values of the parameters have an average difference of 2.8% from the average of observed values on duplicate samples. That no more than ~50% of the chromium(III) is calculated to be present as outer-sphere complex in any of the solutions studied indicates the values of a_3 and Q_3 are relatively uncertain. More important still is the relative uncertainty of interpreting a spectral change of this sort in terms of the formation of a new species.[27] This interpretation is given some support, albeit only very mild support, by the agreement of $\bar{Q}_3$ with the values obtained at other temperatures from the dependence of Q_1 upon (Cl^-) and with the value obtained by Connick and Tsao[28] ($\bar{Q}_3 = 1.5$ at $I = 1$ at 25°) from the dependence of the potential of the silver-silver chloride electrode upon the concentration of hexaaquochromium(III) ion.

Discussion

Before the discussion of that which was surely established by this work, the stabilities of the inner-sphere chlorochromium(III) species, that which is much less certain, the existence and the stability of the outer-sphere complex $Cr(OH_2)_6^{+3}\cdot Cl^-$ will be discussed. Do the data presented make it possible to say anything more about this species than could have been said before the experiments were run? The presence of an anion in the shell around some of the hexaaquochromium(III) ions is to be expected simply on the basis of statistical considerations (appropriately modified for electrostatic interactions). A 3 Å. thick spherical shell around a hexaaquochromium(III), assumed to have a radius of 3 Å., has a volume of 800 Å.^{3}. In a 3 *m* chloride solution, there are only eighteen water molecules per one chloride ion. If chloride ions occupy only their statistical share of the space in this shell, and if one water molecule and one chloride occupy the same volume, the chloride ion's share of this shell is 42 Å.^{3}, which is much more than enough volume for one chloride ion. But the values of $\bar{Q}_3$ obtained lead to the conclusion that only one-half of the hexaaquochromium(III) ions are associated with chloride ion at 3 *m* chloride. Another way in which to make a calculation of this type has been suggested to the authors by R. E. Connick, who pointed out the close possible approach to the central metal ion of water molecules or anions into the eight dimples in the octahedral faces. If these eight positions constitute the second coördination shell, the statistical share of such sites around $Cr(OH_2)_6^{+3}$ occupied by chloride at 3 *m* chloride would correspond to 44% of the $Cr(OH_2)_6^{+3}$ ions being associated with chloride ion. The $\bar{Q}_3$ value suggested by the work of Connick and Tsao[28] at lower ionic strength makes a considerably stronger case for the species $Cr(OH_2)_6^{+3}\cdot Cl^-$ having a stability in excess of that suggested by statistical calculations of the type just presented. It seems reasonable to conclude, however, that the reality of $Cr(OH_2)_6^{+3}\cdot Cl^-$ as a chemically interesting species is not well-founded.

Their inertness makes the reality of the inner-sphere species $Cr(OH_2)_5Cl^{++}$ and $Cr(OH_2)_4Cl_2^+$ unequivocal despite the low values of Q_1 and Q_2. The values of ΔH and ΔS derived from the temperature coefficients of Q_1 and Q_2 are, thus, of considerable interest. These values and the values of ΔH determined by calorimetric means[29] are given in Table II.

TABLE II

THERMODYNAMIC QUANTITIES FOR CHROMIUM(III) CHLORIDE COMPLEX ION FORMATION REACTIONS[a]

Reaction	Q (at 25°)	ΔH, kcal.	ΔS, e.u.
1 (at (Cl^-) = 4.4)	0.105	4.5	10.6
(at (Cl^-) = 0)	.202	6.1	17.2
(at (Cl^-) ≅ 0)[b]		6.6 ± 0.5	
2 (at (Cl^-) ≅ 4.2)	.0303	4.3	7.5
(at (Cl^-) ≅ 0)[b]		5.0 ± 0.2	

[a] For an aqueous solution in which the total stoichiometric anion molality is 4.44. [b] Determined by calorimetric means in solutions of ionic strength ≅ 5 molar, the principal electrolyte being sodium perchlorate. In the case of reaction 1, this value is less accurate than the value determined from the temperature coefficient of the equilibrium quotient; in the case of reaction 2, this value is probably more accurate than the value determined by the temperature coefficient of the equilibrium quotient. It is to be noted, however, that the calorimetric experiments involved *trans*-$CrCl_2^+$ while the equilibrium experiments involved the equilibrium mixture of the isomers. The heat of isomerization is indicated to be small.[5]

It is interesting to note that the small decrease in ΔF of 0.39 kcal. which occurs upon replacing chloride ion in the medium with perchlorate ion is the consequence of much larger changes in ΔH and ΔS which almost cancel one another. The increase in Q_1 with this medium change is due to the relatively large increase in ΔS. The smaller value of Q_2 relative to Q_1 is a consequence of a less positive value of ΔS for reaction 2.

While the temperature coefficients of $\bar{Q}_1$ and $\bar{Q}_3$ can be treated to obtain values of ΔH and ΔS, the questionable significance of the interpretation involving the species $Cr(OH_2)_6^{+3}\cdot Cl^-$ renders the meaning of such values even more questionable.

A comparison of the thermodynamic quantities associated with the chromium(III) chloride complex ion reactions and the analogous iron(III) reactions would be of interest, particularly in view of the change in coördination number which occurs at some step in the successive iron(III) chloride complex ion formation reactions.[30] It is unfortunate

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(26) It is to be noted that these values of a_0 are considerably lower than values reported recently (P. J. Elving and B. Zemel, THIS JOURNAL, **79**, 1281 (1957); R. A. Plane and J. P. Hunt, *ibid.*, **79**, 3343 (1957)); the solutions studied in the present work were apparently more free of polymeric species.

(27) T. W. Newton and F. B. Baker (*J. Phys. Chem.*, **61**, 934 (1957)) have discussed the general question of medium effects upon absorbancy indices and their influence on interpretations such as that presented here.

(28) M. S. Tsao, Ph.D. thesis, University of California, Berkeley, 1952; R. E. Connick and M. S. Tsao, Paper No. 9, Division of Physical and Inorganic Chemistry, 123rd meeting of the American Chemical Society, March, 1953.

(29) K. Schug and E. L. King, THIS JOURNAL, **80**, 1089 (1958).

(30) (a) H. L. Friedman, *ibid.*, **74**, 5 (1952); (b) G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1435 (1953); (c) H. Taube, *J. Phys. Chem.*, **58**, 528 (1954).

that the values of ΔH and ΔS reported for the iron(III) chloride reactions[31] depend upon the very questionable assumption that the absorbancy indices are independent of temperature.[32] When the values of ΔH and ΔS for the iron(III) reactions are accurately known, the comparison with the values for the chromium(III) reactions will be particularly significant since in the latter system there is no change in coördination number with complexing.

Acknowledgment.—The authors wish to acknowledge both the financial assistance already cited[2] and helpful discussions regarding this subject with Professor H. Taube.

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[31] E. Rabinowitch and W. H. Stockmayer, THIS JOURNAL, **64**, 335 (1942).

[32] Some species for which this assumption has been demonstrated to be invalid were studied in ref. 24h. It has been shown recently that the absorbancy of hydrated metal ions in the solid state increases with an increase in temperature and that this temperature dependence has a theoretical basis (O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957)).

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

The Isomeric Dichlorotetraaquochromium(III) Ions; their Separation, Spectra and Relative Stabilities[1]

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The previously unresolved geometrical isomers of dichlorotetraaquochromium(III) ion have been separated by ion-exchange methods. The more easily eluted isomer is demonstrated on the basis of its spectrum and elution characteristics to be the same isomer as that present in the green solid $(Cr(OH_2)_4Cl_2)Cl{\cdot}2H_2O$. This more easily eluted isomer is assigned the *trans* configuration in view of the precedent for an ion with such a configuration being less strongly held in the resin phase than the corresponding *cis* isomer. The spectra of the two isomers are reported. In conformity with the ligand-field theory, the unsymmetrical *cis* isomer has a greater absorbancy than the *trans* isomer. The *trans* isomer is slightly less stable than the *cis* isomer.

Octahedral dichlorotetraaquochromium(III) ion can exist in *cis* and *trans* isomeric forms. The solid green chromium(III) chloride which crystallizes from previously heated solutions of chromium(III) in concentrated hydrochloric acid has long been known to contain dichlorochromium(III) ion as its only chromium(III) species[2]; which isomer this is has not been definitely established.[3] The ion-exchange method, by which the *cis* and *trans* isomers of a number of octahedral complex ions have been separated,[4,5] has been used successfully in the present study.

Experimental Methods

Reagents.—Reagent grade chemicals were used and all solutions were prepared using doubly distilled water. The Dowex-50W resin was treated as described elsewhere.[5]

Equipment Used.—Both a Beckman model DU spectrophotometer and a Cary model 14 recording spectrophotometer were used. An eight foot long ion-exchange column with a jacket for the circulation of water at 3–6° was used. The low temperature was necessary to minimize the aquation and/or isomerization of the chromium(III) species.

Analytical Methods.—The quantitative determination of total chromium was carried out by the spectrophotometric measurement of the concentration of chromate ion[6] formed from chromium(III) species by the action of peroxide in alkaline solution. The analysis of eluent portions for total chloride ion was carried out by the conventional titration with silver nitrate using chromate ion as an indicator: the chromium(III) chloride species were first decomposed by base.

Experimental Results

Preliminary Studies.—Although the initial ion-exchange experiments failed to yield evidence for two different ions with the elution characteristics of a +1 ion, the species or mixture of species with this charge so isolated from an equilibrated solution was found to have a spectrum different from that exhibited by the species of charge +1 found in a solution prepared by dissolving $(Cr(OH_2)_4Cl_2)Cl{\cdot}2H_2O$. This suggested that the cold concentrated hydrochloric acid solution from which $(Cr(OH_2)_4Cl_2)Cl{\cdot}2H_2O$ precipitates would be enriched in the isomer[7] of $CrCl_2^+$ not present in the solid compound, it being assumed that isomerization occurs slowly at 0°. This was found to be the case. These preliminary experiments demonstrated the ratio of the molar absorbancy indices at 450 and 635 mμ for the two ions believed to have a charge of +1 to be different, 0.9 for the dichlorochromium(III) ion in the solid and 1.4 for the species (or mixture of species) of charge +1 in this mother liquor.

The Ion-exchange Separation of the Isomers.—The relative instability of $CrCl_2^+$ in solution ($Q_2 = (CrCl_2^+)/(CrCl^{++})(Cl^-) = 0.12$ at I (the ionic strength) $\cong 4$ at 95°)[8] imposed certain limitations upon the ion-exchange procedure. The presence, in an equilibrated solution, of a relatively high concentration of the ions of charge +3 and +2, Cr^{+3} and $CrCl^{++}$, was the complicating factor. In being taken into the resin phase, these ions

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[2] A. Werner and A. Gubser, *Ber.*, **34**, 1579 (1901).

[3] The recent assignment of the *cis* configuration to this isomer (ref. 13) on the basis of certain spectral characteristics suffers the disadvantage that but one of the isomers was studied.

[4] (a) E. L. King and R. R. Walters, THIS JOURNAL, **74**, 4471 (1952); (b) M. Mori, M. Shibata and J. Azami, *J. Chem. Soc. Japan*, **76**, 1003 (1955); (c) M. Mori, M. Shibata and M. Nanasawa, *Bull. Chem. Soc., Japan*, **29**, 947 (1956).

[5] J. T. Hougen, K. Schug and E. L. King, THIS JOURNAL, **79**, 519 (1957).

[6] G. W. Haupt, *J. Research Natl. Bur. Standards*, **48**, 414 (1952).

[7] Water molecules in the first coördination shell of chromium(III) species in solution will not, in general, be shown. It is assumed that chromium(III) has coördination number 6 in all species under consideration.

[8] H. S. Gates and E. L. King, THIS JOURNAL, **80**, 5011 (1958).