sure of the gas samples was between 30 to 34 mm. this small amount would not affect the vapor pressure measurements.

Acknowledgment.—The assistance of Mr. J. Baudian of the Perkin–Elmer Corp., and Mrs. Elsie Dupre and Mr. R. J. O'Connor of the Southern Utilization Research Branch, Agricultural Research Service, U.S.D.A., in obtaining the infrared spectra is gratefully acknowledged.

NEW ORLEANS 18, LA.

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

Absorption in the Ultraviolet and Visible Regions of Chloroaquochromium(III) Ions in Acid Media

BY PHILIP J. ELVING AND BERNARD ZEMEL

RECEIVED OCTOBER 10, 1956

The absorption spectra of the hexaaquo-, chloropentaaquo- and dichlorotetraaquochromium(III) ions were observed in the presence of high hydrogen ion concentration to minimize the contribution of basic and polymeric chromium species. In solutions of high perchloric acid concentration the positions of the band maxima for the three ions shifted toward the red in a regular manner with increase in the number of complexed chloride ions. In the presence of 12 *M* hydrochloric acid, the absorption spectra obtained fitted this pattern in a way consistent with the formation of a new species in solution: trichlorotriaquochromium(III); the latter does not occur to any extent in concentrations of hydrochloric acid much below 12 *M*. Since this species was not formed in saturated (5 *M*) calcium chloride solution, its formation is apparently highly hydrogen-ion dependent; a mechanism for formation of the $[Cr(H_2O)_3Cl_3]$ species is suggested. The structure of its spectrum indicates $[Cr(H_2O)_4Cl_2]^+$ to be the *cis* form.

The absorption bands of complexes of the transition metals in the visible and ultraviolet are generally of two kinds: those due to electron transfer processes between metal and ligand, and those arising from transitions within the d-shell of the ion.[1] The relatively intense bands in the ultraviolet having molar absorptivities of 10^3 or greater are considered to be electron transfer bands; bands having molar absorptivities below *ca.* 10^2 are treated as transition spectra. It is these relatively weak transition bands which are of particular interest in the chromium(III) complexes and which account for the characteristic colors of chromium(III) solutions, *e.g.*, the violet of the hexaaquo ion, the light green of the chloropentaaquo ion and the dark green of the dichlorotetraaquo ion. The chromium(III) ion lies within a negative field due to its coördinated ligands. In the presence of this field, the degeneracy of the ground state is removed, and the d-orbital set is split into two multiplet levels. The two absorption bands in the visible correspond to the two allowed transitions between these levels.

Following the isolation and identification of the chloroaquochromium(III) complexes, several investigators[2] reported absorption spectra for them; this work was qualitative in nature and served merely to confirm the existence of absorption bands. Bjerrum[3] in a very carefully performed set of experiments, reported molar absorptivity values for the wave length region from 450 to 700 mμ; however, this region includes only one of the two transition bands. Later, Sueda[4] published absorption curves for the 250 to 470 mμ region; unfortunately, he had difficulty with impurities in solution, and some, if not all, of his results seem questionable. Since the hexaaquochromium(III) ion is a starting material for the substituted ammino and thiocyanato complexes, its spectrum has been reported in connection with investigations on these systems.[5]

The objective of the present investigation was to examine and correlate the absorption spectra of the chloroaquochromium(III) ions in aqueous solution under such circumstances that the state of the chromium(III) species would be well-defined. Consequently, the absorption spectra of the hexaaquo-, the chloropentaaquo- and the dichlorotetraaquochromium(III) ions were investigated in solutions of high perchloric acid and high hydrochloric acid concentration; under such conditions, the contributions of basic and condensed chromium species are negligible, and the only ligands available in solution for complexing chromium are the chloride ion and the solvent water.

Absorption Spectra of the Chloroaquochromium(III) Complexes

Perchloric Acid Solution.—Absorption spectra of $[Cr(H_2O)_6]^{+3}$ ion in perchloric acid solution in the region from 200 to 800 mμ show the expected broad bands (Figs. 1 and 2). In addition to maxima at 407 mμ (a_M = 16.1) and 575 mμ (a_M = 13.9), there is a shoulder at 670 mμ and a steep cutoff in the far ultraviolet with a shoulder at 260 mμ. Above 350 mμ, the spectrum is independent of perchloric acid concentration up to 6 *M* and follows Beer's law for concentrations below 0.08 *M* in chromium. The spectrum in the far ultraviolet is a function of both perchloric acid and chromium concentrations.

The absorption bands in the spectra of $[Cr(H_2O)_5Cl]^{++}$ and $[Cr(H_2O)_4Cl_2]^+$ ions, obtained under similar conditions, show the expected bathochromic effect (Figs. 1 and 2); the band shapes are, however, different. The $[Cr(H_2O)_5Cl]^{++}$ ion shows

---

(1) E. Rabinowitch, *Revs. Modern Phys.*, **14**, 112 (1942); H. Hartmann and H. L. Schlafer, *Angew. Chem.*, **66**, 768 (1954).

(2) A. Byk and H. Jaffe, *Z. physik. Chem.*, **68**, 323 (1909); H. C. Jones and W. W. Strong, *Physik. Z.*, **10**, 499 (1909); H. C. Jones and J. A. Anderson, "The Absorption Spectra of Solutions," Carnegie Publication 89, Washington, 1923.

(3) N. Bjerrum, *Z. anorg. Chem*, **63**, 140 (1909).

(4) H. Sueda, *Bull. Chem. Soc. Japan*, **12**, 480, 524 (1937).

(5) (a) R. I. Coleman and F. W. Schwartz, THIS JOURNAL, **54**, 3206 (1932); (b) E. L. King and E. B. Dismukes, *ibid.*, **74**, 1674 (1952); (c) J. Bjerrum and A. Lamm, *Acta Chem. Scand.*, **9**, 216 (1955).

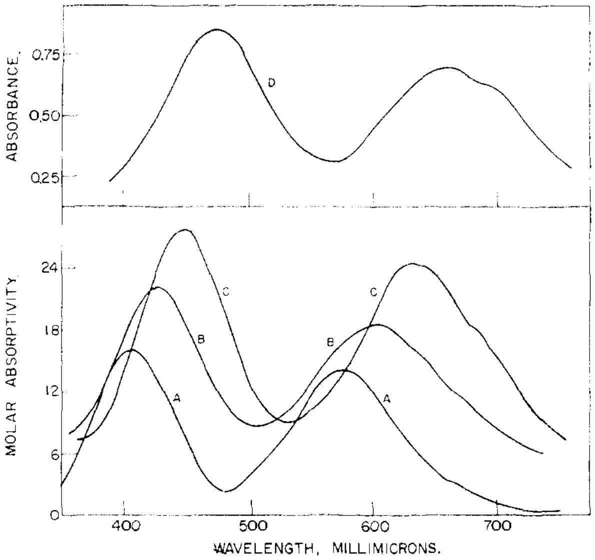

Fig. 1.—Molar absorptivity of chloroaquochromium(III) ions in 6 *M* perchloric acid: (A) hexaaquochromium(III) ion; (B) chloropentaaquochromium(III) ion; (C) dichlorotetraaquochromium(III) ion; (D) absorbance of chromium(III) in 12 *M* hydrochloric acid.

maxima at 430 mμ (a_M = 21.6) and 605 mμ (a_M = 17.8); the latter band is obviously complex and contains several components. The $[Cr(H_2O)_4Cl_2]^+$ ion shows maxima at 450 mμ (a_M = 27.9) and 635 mμ (a_M = 23.9); the latter band has shoulders at 650 and 690 mμ, indicating its complex nature. Beer's law is followed for concentrations below 0.06 *M* in the region above 350 mμ; at higher concentrations, the molar absorptivities are lower than expected, the short-wave band decreasing proportionately somewhat more. The far ultraviolet spectra for both ions are dependent on both acid and ion concentrations.

Hydrochloric Acid Solution.—Although the conversion to lower, *i.e.*, less chloride present, complexes is inhibited in acid solution, a slow transformation of the higher complexes involving loss of chloride goes on even in concentrated acid solutions. It is of interest to compare the spectra of the chromium complexes in acid media of high chloride concentration.

Absorption spectra for solutions of hexaaquochromium(III) perchlorate and of dichlorotetraaquochromium(III) chloride in 12 *M* hydrochloric acid were measured over the range of 350 to 800 mμ immediately after mixing and at intervals for several days. The resultant spectra showed a strong bathochromic effect (Fig. 1) similar to that observed in building up the lower chloro complexes. A shift in the spectra was noticeable within a few minutes after mixing; the change was essentially complete within 3 to 4 hr. The final spectrum was independent of the nature of the starting chromic complex and showed no further change on standing. Dilution of the greenish-yellow solution with water caused a rapid degradation to the green dichloro species. The positions of the absorption band maxima in the spectra of the lower chromic chloride complexes are compared with those of the species present in concentrated hydrochloric acid in Table I.

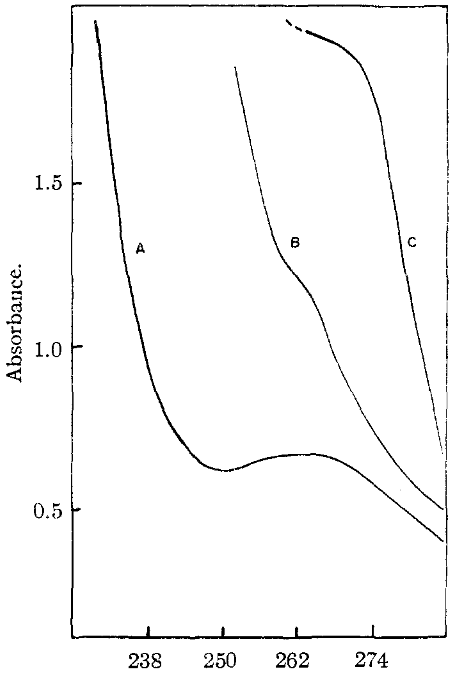

Fig. 2.—Ultraviolet absorbance of chloroaquochromium (III) ions in 6 *M* perchloric acid: (A) hexaaquochromium (III) ion; (B) chloropentaaquochromium(III) ion; (C) dichlorotetraaquochromium(III) ion.

The trichlorotriaquochromium(III) complex has been prepared[6] as a brown solid; its solution is originally greenish yellow in color and rapidly turns to the dark green of the dichloro complex. No compound of the ion $[Cr(H_2O)_2Cl_4]^-$ has been reported; ions of the composition $[Cr(H_2O)Cl_5]^{=}$ [7a]

TABLE I

ABSORPTION MAXIMA FOR THE CHLOROAQUOCHROMIUM(III) COMPLEXES[a]

Species	Position of band maxima,[c] mμ I	Position of band maxima,[c] mμ II	Bathochromic shift in maxima, mμ I	Bathochromic shift in maxima, mμ II
$[Cr(H_2O)_6]^{+++}$	407	575		
	(16.1)	(13.9)		
$[Cr(H_2O)_5Cl]^{++}$	430	605	23	30
	(21.6)	(17.8)		
$[Cr(H_2O)_4Cl_2]^+$	450	635	20	30
	(27.9)	(23.9)		
(in 12 *M* HCl)[b]	475	665	25	30

[a] In 6 *M* perchloric acid media except as indicated. Determined with a Cary Model 11 spectrophotometer at 23°. The molar concentrations of the Cr(III) species in the perchloric acid experiments varied in different runs between 0.02 and 0.05 *M*, and in the hydrochloric acid experiments were uncertain, but between 0.01 and 0.04 *M*. [b] Species is considered to be $[Cr(H_2O)_3Cl_3]$. The a_M values are somewhat higher, perhaps by about 30%, than those for the dichloro species in perchloric acid solution. [c] Values of the molar absorptivity, a_M, are given in parentheses below the appropriate wave lengths.

---

(6) G. Brauer, "Handbuch der Präparativen anorganischen Chemie," Enke, Stuttgart, 1954, p. 1032.

(7) (a) A. Werner and A. Gubser, *Ber.*, **34**, 1579 (1901); (b) R. Abegg and F. Auerbach, "Handbuch der anorganischen Chemie," Vol. 4, Hirzel, Leipzig, 1921, p. 100.

and $[CrCl_6]^{---}$ [7b] have been reported as red crystalline alkali metal salts, the transiently red solutions of which yield only the green dichloro species. Hydrochloride complexes, $Cr(HCl)_x^{+++}$, have been reported at −50°, but are unstable at room temperature.[8] Since the addition of concentrated perchloric acid involving a higher hydrogen ion activity than that in 12 *M* HCl produces no spectral shift in the green dichloro complex, it seems highly improbable that hydrochloride complexes are involved in the present situation.

From the foregoing discussion and from comparison with the spectra of the lower members of the series (Table I), it appears reasonable to assign to the complex species present in concentrated hydrochloric acid the formula $[Cr(H_2O)_3Cl_3]$.

Calcium Chloride Solution.—The polarographic half-wave potential observed for chromic chloride in saturated calcium chloride solution (*ca.* 5.6 *M*) is over 0.1 v. more negative than that found in 1 *M* potassium chloride solution.[9] Since this type of behavior is often associated with complex formation, the spectrum of the $[Cr(H_2O)_4Cl_2]$ ion in saturated calcium chloride solution was measured; it was identical to that in perchloric acid; positions of the band maxima agreed within experimental error. The shift in half-wave potential is apparently associated in this case with phenomena other than the formation of a new complex. There remains, however, the possibility that the transition is merely very slow.

Discussion of Spectrophotometric Data

In perchloric acid solutions the absorptivities of the hexaaquo-, the chloropentaaquo- and the dichlorotetraaquochromium(III) ions were measured for the region from 750 to 200 mμ; the spectral profiles are different from those reported in the literature. Each spectrum consists of three bands: one band in the far ultraviolet, due to electronic transitions, extends beyond the ultraviolet cutoff of the spectrophotometers used, but has a shoulder in the region between 200 and 350 mμ; one band in the region between 400 and 450 mμ; and a complex band in the region between 575 and 650 mμ. There is a regular shift of about 30 mμ for the long-wave band for each chloride ion complexed. The molar absorptivities for the dichloro species for the wave length region of 350 to 750 mμ are given in Table II; the solutions follow Beer's law for concentrations below 0.05 *M*.

In the region below 300 mμ all three species show the very steeply rising electron transfer band (Fig. 2) which acts as a cutoff in the ultraviolet; the maxima all lie below 200 mμ. Both the hexaaquo and the chloropentaaquo electron transfer bands have shoulders, but the bands all change markedly with both perchloric acid and chromium(III) concentration so that it is difficult to analyze them.

Although the absorption spectra of $[Cr(H_2O)_4Cl_2]^+$ ion follow Beer's law for a given Cr(III) concentration range, the spectral profile varies with perchloric acid concentration; the relative absorbance of the second band increases with increasing acid concentration. When the solvent composition is changed from 6.0 to 8.7 *M* in perchloric acid, the ratio of the absorbance at 450 mμ to that at 635 mμ is changed from 1.18 to 1.32 (Table II). These effects indicate the probable formation of other species.

TABLE II

MOLAR ABSORPTIVITIES OF THE DICHLOROTETRAAQUOCHROMIUM(III) ION IN PERCHLORIC ACID[c]

Wave length, mμ	a_M for different chromium concn.			
	0.025 *M*[a]	0.037 *M*[a]	0.049 *M*[a]	0.04 *M*[b]
350	0.6		2.7	
380	2.2	2.2	2.2	3.1
400	8.50	8.4	8.67	11.95
420	18.2	18.2	18.35	23.2
440	26.9	27.0	26.8	28.2
450	27.85	27.80	27.90	30.4
460	26.1	26.30	25.85	29.4
480	18.25	18.50	18.25	22.1
500	9.30	9.45	9.17	12.9
520	4.81	4.97	4.87	
540	4.32	4.48	4.32	
560	7.17	7.02	7.19	
580	11.81	11.90	11.65	11.79
600	18.10	18.20	17.92	17.35
620	22.8+	22.7	22.65	21.6
630	23.65	23.8	23.70	22.7
640	23.22	23.55	23.4+	22.5
650	22.40	22.8	22.6	21.9
660	20.8	21.2	21.1	20.7
670	18.25	18.4	18.25	18.35
680	15.75	15.90	15.95	16.2
690	13.45	13.60	13.52	
700	11.81	12.03	12.15	
710	9.1	9.3	9.1	
730	4.8	4.9	5.1	
750	2.4	2.4	2.5	

[a] Measured in 6 *M* $HClO_4$ solution. [b] Measured in 8.7 *M* $HClO_4$ solution. [c] Determined with a Cary Model 11 spectrophotometer at 23°.

The replacement of water by other ligands in the complex Cr(III) ions may show two different kinds of spectral dependence: a bathochromic shift as in the chloroaquo complexes, or an alteration in the molar absorptivity as in thiocyanato complexes[5b] and the "ol" compounds.[10] The mean activity coefficient of 6.0 *M* perchloric acid is 4.76, and that of 9.0 *M* acid is 19.1.[11] Under these conditions, the extraordinarily high hydrogen ion activity may cause a "loosening" of the layer of water dipoles oriented about the Cr(III) complex ion, which would permit the formation of outer sphere complexes with other ions in solution. It is noteworthy that the spectrum of hexaaquochromium(III) perchlorate solutions is independent of perchloric acid concentration, whereas the spectrum of the dichlorotetraaquochromium(III) chloride changes with the acid concentration (Table II). This effect may well be due to the formation of ion pairs between the chloride ions in solution and the

---

(8) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, Longmans, Green and Co., London, 1931, p. 386.

(9) R. L. Pecsok and J. J. Lingane, THIS JOURNAL, **72**, 189 (1950).

(10) Ch. Jorgensen, *Acta Chem. Scand.*, **8**, 175 (1954)

(11) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 601.

Cr(III) complex, the tendency for complex formation being considerably less in the case of perchlorate ions than in that for chloride ions.

While a mechanism of the type indicated in the previous paragraph is certainly speculative, it does present a possible explanation for the formation of $[Cr(H_2O)_3Cl_3]$ under two very divergent sets of circumstances.

Formation of $[Cr(H_2O)_3Cl_3]$.—Trichlorotriaquochromium(III) may be prepared by the solution of anhydrous dichlorotetraaquochromium(III) chloride in anhydrous ether.[7b] The dichloro complex disproportionates to give a solution of the brownish-red trichloro complex; a transiently greenish-yellow solution is formed if water is added. It has been demonstrated in the present study that, in the presence of concentrated (12 *M*) hydrochloric acid, the dichloro complex also converts to the trichloro species, forming a greenish-yellow solution; on dilution with water, the solution color rapidly changes back to the green of the dichloro complex. Since this reaction does not appear to take place in 5.6 *M* calcium chloride solution, chloride ion by itself is not sufficient to drive the reaction forward. The trichloro complex may thus be formed from the dichloro ion either by the complete elimination of solvent water in a non-aqueous medium or by the presence in aqueous solution of high hydrogen ion and chloride ion concentrations.

From the equivalence between high hydrogen ion concentration and the removal of solvent water, one may postulate that the high hydrogen ion concentration functions to decrease the interaction between the solvent water and the Cr(III) complex in the manner indicated. If the change in the spectral profile of the solution of the dichloro ion in concentrated perchloric acid is indeed due to outer sphere complex formation

$$[Cr(H_2O)_4Cl_2]^+ + Cl^- \overset{[H^+]}{\rightleftarrows} [Cr(H_2O)_4Cl_2]^+ \ldots . Cl^- \quad (1)$$

it appears reasonable to assume that the ion pair formed may then react further in the presence of sufficient chloride ion with the outer chloride ion exchanging with a complexed water molecule

$$[Cr(H_2O)_4Cl_2]^+ \ldots . Cl^- \rightleftarrows [Cr(H_2O)_3Cl_3] + H_2O \quad (2)$$

thus providing a mechanism for the formation of $[Cr(H_2O)_3Cl_3]$ in concentrated hydrochloric acid.

Configuration of $[Cr(H_2O)_4Cl_2]^+$.—The green dichlorotetraaquochromium(III) ion may exist as either the *cis* or *trans* form. There is at present no experimental verification of either form. Some efforts have been made to determine complex ion configuration from absorption spectra. Tsuchida attempted to correlate the position of a "third" band with *cis–trans* configuration; the results did not, however, stand the test of time.[12]

The development of the crystal field theory has been applied with some success to the spectra of the transition element complexes in solution.[12b,13] It has been shown that, for symmetrical hexacoördinated complexes such as the $[Cr(H_2O)_6]^{+3}$ ion, the longer wave length band of the two transition bands which appear, should be relatively simple, but that in the unsymmetrical ions, this band may be split into components. The nature of the spectra reported in the present investigation substantiates this.

For compounds of the type $[Cr(H_2O)_4Cl_2]^+$, the short wave length component of the split band for *cis* compounds has been shown to be *ca.* twice as intense as the long wave length component.[12b] The spectrum of the $[Cr(H_2O)_4Cl_2]^+$ ion has a maximum at 635 mμ with an a_M of 23.9 and a shoulder at 690 mμ ($a_M = 13.5$). Since this band represents the superposition of two gaussian curves in which the intensity contributions of the two are superimposed, the ratio of the two intensities may qualitatively be considered to be in the neighborhood of two so that by this criterion the species involved appears to be the *cis* rather than the *trans* form.

Experimental

Apparatus.—A Cary Model 11 spectrophotometer, kept in a constant-temperature room maintained at 23 ± 0.5°, was used for recording absorbancies greater than one. The Beckman model DU spectrophotometer used was equipped with Beckman No. 2180 double thermospacers through which water was circulated from a constant-temperature bath maintained at 25 ± 0.1°. Stoppered quartz 1-cm. cells were used. The spectrophotometric sample was balanced against a solution of the same electrolyte composition as that used in sample preparation, except for the presence of chromium species.

Photometric Nomenclature.—The Bouguer–Beer law was used in the form of $A = a_M bC = -\log (I/I_0)$, where A = absorbance, a_M = molar absorptivity, C = concentration (moles/liter), and b = path length (cm.).

Preparation and Purification of Compounds. 1. **Dichlorotetraaquochromium(III) Chloride.**—Green chromic chloride is available (Merck) as a reagent grade salt; the color and the ratio of free to complexed chloride indicate it to be largely dichlorotetraaquochromium(III) chloride. There is, however, some variation with different samples, so that in order to have a consistent starting material, the salt was purified.

A saturated solution of the salt in 3.0 *M* hydrochloric acid, maintained at 0° with an ice–salt mixture, was saturated with hydrogen chloride. After precipitation was complete, the green crystals were filtered with suction and then dried in a current of clean dry air. The dry salt was washed well with acetone and then with anhydrous ether, the ether removed by suction, and the salt stored in a vacuum desiccator over Dehydrite. The final product is the pale green anhydrous salt, $[Cr(H_2O)_4Cl_2]Cl$.

Solutions of the purified salt gave consistently reproducible spectra which showed none of the rapid initial changes observed in the unpurified material. Since there is only a small change in the percentage of complexed chloride ion, the difference probably is due to the elimination of polynuclear and/or other types of complexes from the unpurified salt.

2. **Chloropentaaquochromium(III) Chloride.**—This salt was prepared initially by Weinland's classical method.[14] A saturated solution of dichlorotetraaquochromium(III) chloride was aged at room temperature for 24 hr. A slight excess of 70% sulfuric acid was added, and the precipitated $[Cr(H_2O)_5Cl]SO_4$ filtered. The precipitate was dissolved in a minimum amount of water, five volumes of ether added, and the chloride precipitated by passing in dry hydrogen chloride at 0°.

In the latter stages of the present investigation, an alternative method was devised which seems particularly convenient for the preparation of solutions containing known concentrations of $[Cr(H_2O)_5Cl]^{++}$ ion. An aqueous solution of dichlorotetraaquochromium(III) chloride is titrated

---

(12) (a) R. Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388, 436 (1938); (b) F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

(13) H. Hartmann and H. L. Schlafer, *Z. Naturforsch.*, **6A**, 760 (1951); L. E. Orgel, *J. Chem. Phys.*, **23**, 1004 (1955).

(14) R. F. Weinland and T. Schumann, *Ber.*, **40**, 3094 (1907).

potentiometrically at 0° with standard silver perchlorate solution. An additional amount of silver, exactly equivalent to that consumed by the solution, is then added; after the reaction is complete, the silver chloride formed is removed. The concentration of $[Cr(H_2O)_5Cl]^{++}$ ion is given by the original silver titration. In acid solution, the rate of transformation of this ion to the hexaaquo ion is relatively low; in addition, the use of perchlorate media eliminates the presence of other complexing ions. Solutions of the monochloro salt were used after preparation.

3. **Hexaaquochromium(III) Perchlorate.**—This material was prepared by two different methods in order to check the removal of complexed ligands and impurities.

In one method, reagent grade Merck green chromic chloride was dissolved in 1.0 *M* perchloric acid. The solution was heated to boiling and refluxed for about one hour in order to convert the chromium(III) complexes to the hexaaquo form. The hot solution was treated with an excess of sodium hydroxide; the gelatinous precipitate formed was digested on the hot plate for about an hour, and, after cooling to room temperature, was centrifuged, washed several times with water and dissolved in perchloric acid. Chromic hydroxide was reprecipitated, centrifuged, washed and dissolved; this process was repeated until the washings showed an absence of chloride ion on treatment with silver nitrate. Hexaaquochromium(III) perchlorate was recovered from the perchloric acid solution by evaporating the latter to a small volume. The violet salt was recrystallized first from 10% perchloric acid and finally from water.

In the second method, a solution of the chromic chloride in distilled water was refluxed for 1 to 2 hr., then cooled to 0° with a salt–ice mixture and saturated with hydrogen chloride. The blue-gray hexaaquochromium(III) chloride precipitate was filtered under suction, washed with a small amount of fuming hydrochloric acid, redissolved in the minimum amount of 6 *M* hydrochloric acid, and reprecipitated at 0° by passing in hydrogen chloride gas. The supernatant liquid was poured off, and the precipitate washed several times with acetone by decantation, filtered and washed first with acetone and then with dry ether.

The hexaaquochromium(III) chloride[15] thus prepared was dissolved in water and its chloride ion content determined by titrating an aliquot with a standard silver perchlorate solution; a stoichiometric amount of silver perchlorate was then added to the main solution to precipitate all of the chloride. In order to avoid excess reagents, addition of the silver perchlorate was followed potentiometrically with a Ag/AgCl indicating electrode. The solution was filtered, the filtrate made strongly acid with perchloric acid, and the hexaaquochromium(III) perchlorate precipitated by evaporation to a small volume. The salt was recrystallized first from 10% perchloric acid solution and then from water.

The hexaaquochromium(III) perchlorate prepared by either of the two methods described proved indistinguishable on elemental analysis and comparison of absorption spectra.

4. **Silver Perchlorate.**—This salt was prepared by dissolving silver carbonate in perchloric acid, boiling the solution to concentrate the acid, cooling with ice to precipitate silver perchlorate and filtering through sintered glass. The salt was recrystallized from dilute perchloric acid and dried over Dehydrite in a vacuum desiccator.

5. **Perchloric Acid.**—The perchloric acid was obtained by dilution of the G. F. Smith Chemical Company redistilled grade 72% acid as normally supplied.

Analysis of Compounds. 1. Chromium.—Solutions were analyzed for chromium by conventional procedures. Chromium was oxidized to Cr(VI) by persulfate in the presence of a trace of silver ion; in solutions containing excess chloride, the oxidation was performed by boiling with perchloric acid. The solution was then titrated with standard ferrous sulfate solution (standardized against National Bureau of Standards dichromate); the equivalence point generally was determined potentiometrically or amperometrically using a platinum electrode.

2. **Perchlorate.**—Perchlorate ion was determined by precipitation and weighing as the tetraphenylphosphonium perchlorate.[16]

3. **Chloride.**—Uncomplexed chloride ion was determined by potentiometric titration in strongly acid medium (3 to 4 *M* $HClO_4$) at 0° with standard silver perchlorate solution, using a Ag/AgCl indicating electrode and a glass reference electrode; the potential was measured by a Beckman model G or model H *p*H meter.

Total chloride was determined by refluxing the sample solution for several hours in the presence of a known excess of standard silver perchlorate, cooling to room temperature and back-titrating the excess silver potentiometrically with a standard chloride solution. The difference between total and free chloride was taken to be the complexed chloride.

Silver perchlorate was preferable to silver nitrate as a titrant in strong perchloric acid solution due to attack of the silver electrode by the nitric acid formed. In the absence of nitrate, no attack was observed at ordinary temperatures. The silver perchlorate solution, which was about 0.1 *M* in perchloric acid, was standardized against a standard sodium chloride solution. In order to prevent chloride contamination during potentiometric titrations, a glass electrode was used as a reference in the very high hydrogen ion activity solutions involved; in neutral systems a potassium nitrate bridge connected the titration vessel to a reference saturated calomel electrode.

4. **Salt Purity.**—The hexaaquochromium(III) perchlorate was analyzed for purity by determining the mole ratio of perchlorate ion to chromium in a solution of the salt; the values found differed by only 0.1% from the theoretical ratio. The compositions of other complexes were similarly verified using the mole ratio of complexed chloride to chromium. Solutions of varying concentrations were prepared by dilution of known solutions. Analysis for concentration was based on determination of either chromium or chloride depending on the dissolved salt.

Acknowledgment.—One of the authors (B.Z.) gratefully acknowledges the aid given him in the form of a fellowship sponsored by the Minnesota Mining and Manufacturing Company.

ANN ARBOR, MICHIGAN

---

[15] Ref. 6, p. 1010.

[16] H. H. Willard and L. R. Perkins, *Anal. Chem.*, **25**, 1634 (1953).