field effects and the electron affinities. Assuming a seven-coordinated intermediate and allowing for $Dq' = 1.5Dq$, crystal field theory gives the theoretical order $Ru > Cr > Co > Rh$. The electron affinity term may be considered as causing a higher bond strength between the metal ion and the halide ion for a higher electron attraction. This produces the predicted rate sequence $Cr > Ru > Rh > Co$ if bond breaking is more important than bond making as all other available evidence suggests.[20] The conclusion is that Co(III) is more reactive and Ru(III) less reactive than theory predicts. It is also noticeable that the activation energies of all four metal ions are always rather similar, though that for cobalt is usually some 2 kcal. higher than that for chromium[21] and that for rhodium some 2 kcal. higher than that for cobalt.[11] These changes are not nearly as large as those predicted from crystal field theory.[22] It is not clear whether the difference between theory and experiment is due to changes in the details of the mechanism or to the inadequacy of simple crystal field theory.[23]

The results of Table III clearly indicate that the mechanism for the sulfation reaction of $[Ru(NH_3)_5Cl]^{2+}$ is a slow aquation followed by a fast anation.

$$[Ru(NH_3)_5Cl]^{2+} + H_2O \xrightarrow{\text{slow}} [Ru(NH_3)_5H_2O]^{3+} + Cl^- \quad (8)$$

$$[Ru(NH_3)_5H_2O]^{3+} + SO_4^{2-} \xrightarrow{\text{fast}} [Ru(NH_3)_5SO_4]^+ + H_2O \quad (9)$$

The over-all rate is the same as that for acid hydrolysis. Sulfate ion is not a nucleophilic reagent for ruthenium(III) complexes, in agreement with the behavior found for many other nucleophiles and chloroammine complexes of cobalt(III), chromium(III), and rhodium(III).

The value of the equilibrium constant for acid hydrolysis at 25° extrapolated from the data of Table II is about 140. This is not in very good agreement with the preliminary figure of 43 at ionic strength 0.10 given by Endicott and Taube.[3] There is some error in our spectrophotometric data in that the equilibrium is reached slowly and it is known that some irreversible decomposition occurs. In the earlier work[3] equilibration was achieved rapidly by using ruthenium(II) catalysis. It should be noted, however, that we kave checked our results by using three independent methods.

An examination of Lamb's data[24] shows that the equilibrium constant for the formation of $[Rh(NH_3)_5Cl]^{2+}$ from $[Rh(NH_3)_5H_2O]^{3+}$ is nearly the same as for the ruthenium complex at the same ionic strength. For both metals this constant is very much larger than for $[Co(NH_3)_5Cl]^{2+}$ and $[Cr(NH_3)_5Cl]^{2+}$, where acid hydrolysis is essentially complete. Thus for the second transition series there is a preference for binding to chloride ion rather than water. The reason for this is not clear, but it may be due to a greater degree of covalent binding. Whatever the reason, it represents an additional factor which determines the rate of acid hydrolysis.

---

[20] See ref. 12. Also R. G. Wilkins, *Quart. Rev.* (London), **16**, 316 (1962); D. R. Stranks, "Modern Coordination Chemistry," R. G. Wilkins and J. Lewis, Ed., Interscience Publishers, New York, N. Y., 1960.

[21] D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, **1**, 20 (1962).

[22] W. Plumb and G. M. Harris, private communication, report an activation energy of 33 kcal. for water exchange in $[Rh(H_2O)_6]^{3+}$ compared to 27.6 kcal. for $[Cr(H_2O)_6]^{3+}$.

[23] R. G. Pearson and R. D. Lanier, *J. Am. Chem. Soc.*, **86**, 765 (1964), have a discussion of this problem.

[24] A. B. Lamb, *ibid.*, **61**, 699 (1939).

CONTRIBUTION FROM THE CHEMISTRY DIVISION,
ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

The Association between Chromium(VI) and Aquopentaamminecobalt(III) in Aqueous Perchlorate Media[1]

BY JAMES C. SULLIVAN AND JAMES E. FRENCH[2]

Received January 6, 1964

From combined spectrophotometric and pH measurements we have obtained a value of $K = 9.82 \times 10^{-2}$ for the reaction $Co(NH_3)_5H_2O^{+3} + HCrO_4^- = C + H^+$ at 25° and $\mu = 0$. Here C represents the 1:1 complex between the cobalt(III) and CrO_4^{-2} ions. Kinetic evidence is presented which indicates it is a mixture of inner-sphere and outer-sphere species.

The reasons underlying this investigation are derived from the following observations: Taube and Posey[3] have demonstrated that the aquopentaamminecobalt(III) ion forms both inner- and outer-sphere complexes with sulfate ion; Tong and King[4] have shown that the Ce(IV)–Cr(VI) complex is more stable than the corresponding sulfate complex and have pointed out that in general Cr(VI) complexes should be more stable than the corresponding sulfate complexes; in a study of the interaction between Cr(III) and Cr(VI), King and Neptune[5] concluded that both inner- and outer-sphere complex ions might be present even though equilibrium was rapidly established.

---

[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Participant from Knox College in the Argonne Semester Program of the Associated Colleges of the Midwest.

[3] (a) H. Taube and F. A. Posey, *J. Am. Chem. Soc.*, **75**, 1463 (1953); (b) F. A. Posey and H. Taube, *ibid.*, **78**, 15 (1956).

[4] J. Y.-P. Tong and E. L. King, *ibid.*, **76**, 2132 (1954).

[5] E. L. King and J. A. Neptune, *ibid.*, **77**, 3186 (1955).

This work reports the results obtained in the study of the reaction[6]

$$R + HCrO_4^- = C + H^+ \qquad (1)$$

where R represents the aquopentaamminecobalt(III) ion and C the complex formed between CrO_4^{-2} and $Co(NH_3)_5H_2O^{+3}$.

Values have been obtained for the association constant

$$K = [C][H^+]/[HCrO_4^-][Co(NH_3)_5H_2O]^{+3} \qquad (2)$$

by combined spectrophotometric and pH measurements.

Experimental

Reagents.—The preparation and standardization of stock solutions of perchloric acid and lithium and sodium perchlorates have been described in a previous publication.[7] Reagent grade sodium dichromate (Baker) was recrystallized, centrifugally washed, and dissolved in triple-distilled water. The solution was standardized spectrophotometrically.[8] Carbonatopentaamminecobalt(III) nitrate, used as an intermediate in the preparation of the aquopentaamminecobalt(III) perchlorate, was synthesized by the procedure described in the literature.[9] Aquopentaamminecobalt(III) perchlorate was prepared using the procedure described by Posey.[10] Weighed amounts of the dried salts were dissolved in dilute perchloric acid solution. The molar extinction coefficients (l. mole^{-1} cm.$^{-1}$) of such solutions are 47.2 ± 0.3, 44.3 ± 0.4, and 1666 ± 31 at 4910, 3450, and 2350 Å. These results at 25° agree well with previously published values.[8] The uncertainties listed are the standard deviations from a set of eight independent determinations.

An additional determination of the purity of the starting material utilizes a potentiometric titration method developed by Appelman.[11] In this procedure a weighed quantity of the salt is titrated with NaOH (see eq. 3). For example, a solution analyzed by this method to be 0.0867 *M* in the Co(III) salt was calculated to be 0.0864 *M* based on the known weight of the salt dissolved.

Spectrophotometric Measurements.—All measurements were made with a Cary Model 14 recording spectrophotometer. Cylindrical cells of 0.5, 1, 2, 5, and 10 cm. path lengths were employed. The cell compartment was thermostated to within ±0.2°.

Preliminary observations provided definite evidence of optical enhancement, *i.e.*, the observed optical density was greater than the sum of the optical densities of the two absorbing species. It was not possible to carry out detailed measurements in the visible region. At concentrations of $Co(NH_3)_5H_2O^{+3}$ and $HCrO_4^-$ large enough to provide significant information precipitation occurred in the cells. It was feasible to carry out the measurements at 2550 and 2600 Å. At these wave lengths there is a shoulder of an intense absorption band of the $HCrO_4^-$ and a relative minimum in the spectrum of the cobalt compound.

Three sets of optical density measurements were made for each determination of *K*, with all measurements referred to a blank of triple-distilled water: (1) Solutions of known $HCrO_4^-$, $Co(NH_3)_5H_2O^{+3}$, and perchloric acid concentrations at a constant ionic strength. From 6 to 8 samples of varying $Co(NH_3)_5H_2O^{+3}$ concentration were included in each set. (2) Solutions of known $HCrO_4^-$ concentration. (3) Solutions of known $Co(NH_3)_5H_2O^{+3}$ concentration. The last two were measured under conditions of ionic strength and acidity identical with (1).

The weight-density method was used in the preparation of all solutions for the equilibrium studies.

pH Measurements.—The hydrogen ion concentration of the equilibrium solutions containing $Co(NH_3)_5H_2O^{+3}$ and $HCrO_4^-$ is determined not only by the initial perchloric acid and reaction 1 but also by the equilibrium

$$Co(NH_3)_5H_2O^{+3} = Co(NH_3)_5OH^{+2} + H^+ \qquad (3)$$

In nitrate or chloride media p*K* values of *ca.* 6 are reported[12] for this reaction.

To minimize the probability of introducing additional uncertainties into the study, a direct determination of [H$^+$] was made from the pH of the equilibrium solutions. Measurements were made at room temperature (25 ± 2°) with a Beckman Model G pH meter. Solutions of known acidity at the same ionic strength (maintained with $LiClO_4$) as the test solutions were used for calibration.

Treatment of Data.—Assuming the concentration of the reactant in excess $Co(NH_3)_5H_2O^{+3}$ to remain constant, it can readily be shown that

$$\frac{D - D_1}{\Sigma HCrO_4^-} = \frac{e_0 + e_1K[Co(NH_3)_5H_2O^{+3}]/[H^+]}{1 + K[Co(NH_3)_5H_2O^{+3}]/[H^+]} \qquad (4)$$

where *D* is the total optical density of the test solution/cm. path length, D_1 the optical density contribution of the cobalt salt, e_0 the molar extinction coefficient of $HCrO_4^-$, e_1 the molar extinction coefficient of the complex, and $\Sigma HCrO_4^-$ the initial Cr(VI) concentration. The other symbols appearing in (4) have been defined previously.

Initial estimates of the parameters e_1 and *K* were determined graphically. An IBM 704 program, which provides a least-squares adjustment of the functional form $y = a + bx/1 + cx$ was then used to obtain a second approximation to e_1K. The value obtained for this parameter was then used in (4) to evaluate *K*. Generally, one more iteration was carried out to obtain the final values of e_1 and *K*.

The iterative procedure was necessary since the 704 program is based on the premise that *x* is free of error compared to *y*, a condition that is not true in this investigation. This means that: (a) the estimates of the parameters may be biased because of improper weighing and (b) one of the important results of the least-squares treatment, *i.e.*, an estimate of the uncertainty to be assigned each parameter, is not available.

We estimate the uncertainty in the calculated values of *K* to be ±10%. This is based on the uncertainties in the measured optical densities and pH determinations and the spread in the value of *K* calculated for each set of experiments.

Results

Equilibrium Results. A.—Preliminary experiments indicated that, under the conditions to be described, the optical densities remained constant for periods of from 20 sec. to 48 hr. after mixing the reactants. Results obtained for variation of the concentrations of $HCrO_4^-$, $Co(NH_3)_5H_2O^{+3}$, and H^+ at an ionic strength of 0.102 (maintained with $LiClO_4$), 25°, are summarized in Table I.

The invariance of *K*, over the concentration ranges indicated, is consistent with the equilibrium expression presented in eq. 2.

The spread in the values of e_0 and e_1 demonstrates the precision of the direct measurements compared to a derived quantity. For example, the average value of

---

[6] The structure of the complex is not specifically delineated since evidence will be presented that is consistent with the interpretation that both inner- and outer-sphere complexes are present in the equilibrated solutions.

[7] J. C. Sullivan, A. J. Zielen, and J. C. Hindman, *J. Am. Chem. Soc.*, **82**, 5288 (1960).

[8] G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

[9] F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).

[10] F. A. Posey, Ph.D. Dissertation, University of Chicago, 1955.

[11] Dr. E. H. Appelman, private communication.

[12] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941, p. 280.

TABLE I

Set	Concentrations, M^a: $[HCrO_4^-] \times 10^5$	$[Co(NH_3)_5H_2O]^{+3} \times 10^3$	$[H^+] \times 10^4$	2550 Å.: $e_0 \times 10^{-3}$	$e_1 \times 10^{-3}$	$K \times 10^2$	2600 Å.: $e_0 \times 10^{-3}$	$e_1 \times 10^{-3}$	$K \times 10^2$
A	11.4	12.2–2.7	2.7–1.1	2.03	6.31	1.43	2.02	5.36	1.44
B	11.4	10.9–2.7	2.9–1.6	2.09	6.29	1.44	2.08	5.28	1.45
C	5.7	12.2–2.7	2.5–1.1	2.12	6.44	1.46	2.11	5.41	1.42
D	11.6	12.2–2.7	3.0–1.5	2.11	6.54	1.40	2.09	5.49	1.38
E	5.7	10.9–2.7	2.2–1.2	2.06	5.97	1.43	2.05	5.03	1.44
F[b]	11.5	10.1–2.0	2.1–0.79	2.10	5.73	1.45	2.09	4.85	1.44
G	11.4	12.2–2.7	7.4–6.0	2.06	6.31	1.44	2.05	5.36	1.36

[a] $HCrO_4^-$ and $Co(NH_3)_5H_2O^{+3}$ concentrations are initial values. Hydrogen ion concentrations are the measured equilibrium values. [b] $NaClO_4$ was used to maintain the ionic strength in this set.

TABLE II

VARIATION OF K WITH IONIC STRENGTH AT 25°

Concentrations, M: $\mu \times 10^2$	$[HCrO_4^-] \times 10^5$	$[Co(NH_3)_5H_2O]^{+3}$	$[H^+] \times 10^4$	2500 Å.: $e_0 \times 10^{-3}$	$e_1 \times 10^{-3}$	$K \times 10^2$	$K \times 10^2$ (calcd.)[c]
48.8	23.1	32.6–6.6	2.58–0.43	2.14	5.52	0.915	0.952
25.0	13.3	10.0–1.1	2.50–0.62	2.11	6.09	0.98	0.943
10.24[a]	11.6–5.7	12.2–2.0	7.4 –0.79	2.08	6.23	1.44	1.39
1.51	9.54	2.1–0.42	1.2 –0.85	2.08	5.45	3.64	3.68
1.00	6.70	1.2–0.20	1.2 –0.92	2.07	5.85	4.07	4.32
0.25	2.87	0.329–0.083	0.27–0.17	*b*		6.40	6.33

[a] Average of the values presented in Table II. [b] The two wave lengths used in this determination were 2450 and 2500 Å. [c] Calculated according to eq. 5.

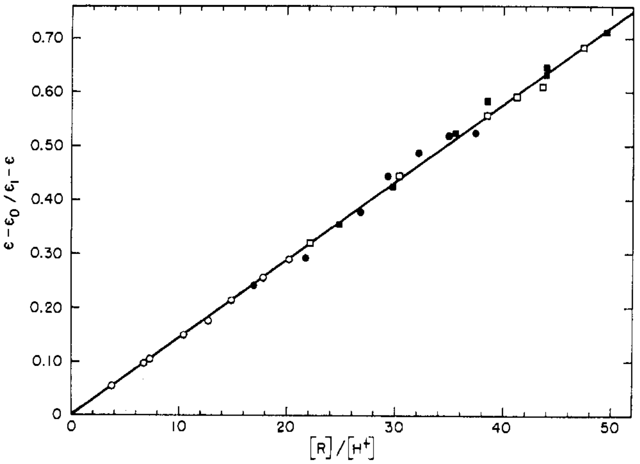

Fig. 1.—$(t - t_0)/(t_1 - t)$ as a function of $[R]/[H^+]$; 2550 Å., μ = 0.102, T = 25°. See Table I for set identification. ●, set B; □, set E; ■, set D; O, set G.

$e_0 = 2.08 \pm 0.03 \times 10^3$ at 2550 Å. may be compared to that for $e_1 = 6.23 \pm 0.28 \times 10^3$.

An additional test of the consistency, and an indication of the experimental uncertainties, of the data is presented in Fig. 1. Here we have plotted $(e - e_0)/(e_1 - e)$ *vs.* $[Co(NH_3)_5H_2O]/[H^+]$ for B, D, E, and G using the average value of e_1 for the four sets. The line is constrained to pass through the origin and has the appropriate slope of 1.44×10^{-2}.

As defined by eq. 2, K is not a thermodynamic quantity since it includes the unevaluated ratio of activity coefficients. The results presented for set F indicate that this ratio is the same when either lithium or sodium perchlorate is substituted for the Co(III) salt at constant ionic strength.

B.—A summary of the experimental conditions and results obtained with variation of ionic strength are presented in Table II. Values listed for K are averages of the results at two wave lengths, generally 2550 and 2600 Å.

Values for the molar extinction coefficients of the Cr(IV) and the complex which are listed in the table are consistent with the interpretation that within any given set these quantities will remain invariant.

The variation of K with ionic strength is adequately correlated by the expression[13]

$$\log K = \log K_0 + \frac{A\Delta Z^2\sqrt{\mu}}{1 + \sqrt{\mu}} + B\mu \qquad (5)$$

We ascribe physical significance to only one of the two adjustable parameters. The value attained by K at zero electrolyte concentration is K_0. The value of ΔZ^2 is determined by the reaction (−8 in this case), and A is obtained from published values of the Debye–Hückel limiting slope.[14]

A weighted least-squares adjustment of the data, after an obvious rearrangement of eq. 5, resulted in values for $K_0 = (9.82 \pm 0.27) \times 10^{-2}$ and $B = 1.36 \pm 0.06$. An estimated uncertainty of 10% for each K was used in assigning the weights. That this is a reasonable estimate is confirmed by the results of the least-squares adjustment, which assign a 7% uncertainty to each K based on external consistency.

The goodness of fit may be more readily judged by the comparison of the last two columns in Table II.

C.—Table III summarizes the results obtained at various temperatures. The concentrations of the reactants varied over the same range as reported in Table II for the set at ionic strength 1.0×10^{-2}.[15]

---

[13] E. A. Guggenheim and J. C. Torgeon, *Trans. Faraday Soc.*, **51**, 1747 (1955).

[14] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Co., New York, N. Y., 1958, Chapter 5.

[15] Equilibrium values of the hydrogen ion concentration determined at 25° were used for all temperatures. The uncertainties this introduces into the results should be minimal since there is not a marked change in the equilibrium hydrogen ion concentrations at 25°.

Values of K that are listed represent an average of the determination at two wave lengths, generally 2500 and 2550 Å.

TABLE III

VARIATION OF K WITH TEMPERATURE; $\mu = 1 \times 10^{-2}$

T, °C.	$K \times 10^2$	$K \times 10^2$ (calcd.)
35.0	3.62	3.61
25.0	4.07	4.02
15.0	4.32	4.51
10.0	4.94	4.80

Although there were marked changes in the apparent molar extinction coefficient of $Co(NH_3)_5H_2O^{+3}$ with variation in temperature (a fact noted by Taube[3]), the values measured for $HCrO_4^-$, $e_0 = (2.15 \pm 0.06) \times 10^3$, and derived for the complex, $e_1 = (5.81 \pm 0.26) 10^3$, do not exhibit this behavior. This is probably a reflection of the point that the observations reported here are in a region of an intense, broad maximum in the spectrum of $HCrO_4^-$.

A weighted least-squares adjustment of the data yields a value of $\Delta H = -1.96 \pm 0.23$ kcal. The last column in Table III provides an opportunity to compare the calculated and average experimental values of K.

A Slowly Established Equilibrium. A.—The results of a limited number of kinetic experiments at 5° are presented in Table IV. The values for k were obtained from a plot of log $(D_e - D)$ *vs.* time. The approach to equilibrium is an apparent first-order process since the concentration of $Co(NH_3)_5H_2O^{+3}$ is always in large excess over the $HCrO_4^-$.

TABLE IV

SUMMARY OF KINETIC DATA[a]

Initial concentrations, M			
R × 10^3	Cr(VI) × 10^5	[H$^+$] × 10^4	$k \times 10^3$, sec.$^{-1}$
1.584	3.35	1.00	2.25
1.623	2.75	1.00	1.85
1.623	2.75	2.00	1.89
1.636	1.38	1.00	0.937

[a] $\mu = 1 \times 10^{-2}$, 5°, 2550 Å.

An additional pertinent observation is that when hexaamminecobalt(III) is substituted for $Co(NH_3)_5H_2O^{+3}$ (under the same concentration conditions as described in Table IV) there are no detectable changes in absorbancy for comparable periods.

Although it is probable that the time-dependent spectral changes indicate the formation of an inner-sphere complex (presumably by substitution on the Cr(VI)), the results presented are not extensive enough to warrant presentation of a detailed mechanism. The point of interest for the present is that the observations are consistent with the concept that both inner-sphere and outer-sphere complexes are present in the equilibrium solutions examined.

B.—Attempts to prepare the chromatopentaamminecobalt(III) perchlorate by a variation of the method reported by Briggs[16] for the preparation of the corresponding chloride and nitrate were not successful. However, a solid compound with a ratio of Co:Cr = 1:3 was prepared.

For example, a solution 10^{-3} M in aquopentaamminecobalt(III) perchlorate which is 10^{-4} M in perchloric acid is heated to *ca.* 50°. To this a solution of Cr(VI) at the same acidity is added and a red-orange precipitate is observed to form. The mixture is heated for about 1 hr. and after storing overnight (5–10°) the product is filtered, washed with water, alcohol, and ether, and then dried in a vacuum desiccator.

Analysis of one such preparation gave: 11.8% Co, 14.02% N, and 31.73% Cr.[17] Since there are three isomers consistent with these results, including $Co(NH_3)_5H_2O(Cr_2O_7)(HCrO_4)$ with 11.9% Co, 14.15% N, and 31.51% Cr, the following observations are pertinent.

(1) When this sparingly soluble salt is dissolved in 10^{-4} M $HClO_4$, at 5°, the absorptivity at 2500 Å. decreases. $D - D_e$ decreases by a factor of 2 in 7 min. It must be noted that the first observation was taken *ca.* 4 min. after the initial addition of the solid to the perchloric acid.

(2) Anion and cation exchange studies of fresh solutions of the product, at room temperature in 10^{-4} M $HClO_4$, as well as precipitation studies carried out over 5–30 min. intervals, provided no evidence for the existence of an inert Co(III)–Cr(VI) species in solution.

(3) When a solution of Cr(VI) in 10^{-4} M $HClO_4$ is added to a solution of hexaamminecobalt(III) chloride or perchlorate a pale yellow precipitate is formed at room temperature upon mixing. This solid has a ratio of Co:Cr = 1:3. When a solution of this salt, in 10^{-4} M $HClO_4$, is examined spectrophotometrically, there is no change in the absorbancy with time.

Although these observations are consistent with the hypothesis that there is a labile inner-sphere complex of Co(III) and Cr(VI), the results are not unambiguous. Additional evidence of the structure of the solid is provided by the following observations.

Ferraro[18] has shown that there is a splitting of the ν_3 frequency of the nitrate ion in metallic compounds where this molecule is covalently bonded. In view of this, we report some preliminary results that have been obtained in the infrared studies of the solid Co(III)–Cr(VI) compounds.[19]

The ν_3 frequency of the chromate ion is observed at 900 cm.$^{-1}$ in K_2CrO_4.[20] In the compound prepared from the hexaamminecobalt(III) and Cr(VI) this frequency is observed at 930 cm.$^{-1}$. The compound prepared from the aquopentaamminecobalt(III) and Cr(VI) showed this frequency split into a number of

---

[16] S. H. C. Briggs, *J. Chem. Soc. Trans.*, **115**, 67 (1919).

[17] Analysis performed by the analytical division of this laboratory.

[18] J. R. Ferraro, *J. Mol. Spectry.*, **4**, 99 (1960).

[19] These studies were carried out by Dr. John R. Ferraro of this laboratory. Details will be incorporated in a forthcoming publication by Dr. Ferraro.

[20] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963, pp. 107–109.

components. In addition there was no evidence of the characteristic water absorption.[21]

These results indicate that some of the chromate ions in the latter compound find themselves in surroundings different from that provided solely by the crystal field of the solid.

Discussion

The data we have presented can be represented by the reaction scheme

$$[Co(NH_3)_5H_2O]^{+3} + HCrO_4^- = [Co(NH_3)_5H_2O]^{+3}\cdot CrO_4^{-2} + H^+ \quad (6)$$

$$[Co(NH_3)_5H_2O]^{+3}\cdot CrO_4^{-2} = [Co(NH_3)_5CrO_4]^+ + H_2O \quad (7)$$

but it should be emphasized that the tabulated values of the equilibrium constant refer to reaction 1.

At 25°, we combine the value obtained for K_0 with the enthalpy change obtained at an ionic strength of 1×10^{-2} to compute $\Delta F° = 1.37$ kcal./mole, $\Delta H° = -1.96$ kcal./mole, and $\Delta S° = -11.2$ e.u. for reaction 1.

To compare the affinities of sulfate and chromate ions for the aquopentaamminecobalt(III) ion we write eq. 1 as in eq. 8.

$$Co(NH_3)_5H_2O^{+3} + CrO_4^{-2} = C \quad (8)$$

From the value of 3.20×10^{-7} for the dissociation constant of $HCrO_4^-$,[22] combined with the value of $\Delta H° = -0.7$ kcal./mole[23] for that process, we find (for reaction 9 at 25°) $\Delta F° = -7.48$ kcal./mole, $\Delta H° = -1.3$ kcal./mole, and $\Delta S° = 20.9$ e.u.

The value obtained by Taube and Posey[3] for the outer-sphere association between aquopentaamminecobalt(III) and sulfate ion is 1.89×10^3. Since the value reported here for the association between that cation and chromate is 3.07×10^5, it is evident that the latter complex is more stable by a factor of *ca.* 10^2.

This result is qualitatively consistent with the arguments previously cited.[4] It is, however, interesting to note (although not amenable to quantitative rationalization) that in a similar comparison between $CeCrO_4^{+2}$ and $CeSO_4^{+2}$, Tong and King[4] found the chromate complex to be more stable by a factor of 10^7.

Acknowledgment.—We wish to express our appreciation to Dr. J. Ferraro for allowing us to quote the results of the infrared studies. Conversations with Professors H. Taube and E. L. King during the course of this investigation have been stimulating.

---

[21] The spectra were recorded with a Perkin-Elmer Model 14. The samples were dried at 100° overnight prior to pressing in a KBr pellet.

[22] J. D. Neuss and W. Rieman, *J. Am. Chem. Soc.*, **56**, 2238 (1934).

[23] L. G. Hepler, *ibid.*, **80**, 6181 (1958).

CONTRIBUTION FROM THE CHEMISTRY DIVISION,
ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Octahedral Absorption Spectra of the Dipositive 3d Metal Ions in Molten Aluminum Chloride[1]

BY HARALD A. ØYE AND DIETER M. GRUEN

Received December 9, 1963

The absorption spectra of dipositive Ti, V, Cr, Mn, Fe, Co, Ni, and Cu in molten $AlCl_3$ were measured in the wave number range 4000–34,000 cm.$^{-1}$ at 227° and 5.6 atm. All the spectra which were obtained using the $AlCl_3$ solvent can be interpreted on the basis of octahedral configurations of chlorides about the central transition metal ions. These observations are in contradistinction to the situation in alkali chloride melts where, with the exception of V^{2+}, the dipositive 3d ions display fourfold coordination. A discussion of the possible reasons for the different coordination behavior in various chloride solvent systems is presented.

Introduction

The coordination chemistry of the di- and tripositive 3d metal ions in alkali chloride melts was discussed in a recent paper.[2] Briefly, the situation in alkali chloride melts appears to be the following: the di- and tripositive 3d ions can exist in either a four- or a six-coordinated form with a mobile equilibrium between the two forms. It was postulated that for each ion, the equilibrium constant of the octahedral–tetrahedral (O–T) transformation in alkali chloride melts is determined primarily by two factors: the octahedral site stabilization energy [o.s.s.e. (M^{n+})] depending on the number of unpaired electrons in the 3d shell and an electrostatic factor $[E^{n+}]$ depending on the charge of the 3d ion. (Entropy changes were found to be small, the $T\Delta S$ terms being of the order 1–2 kcal./mole, and were neglected.)

Only for the ions Ti^{3+}, V^{3+}, and V^{2+} was it possible experimentally to study the O–T transformation. For all the other 3d ions, the equilibrium constants in alkali chloride melts favor either the six- or the four-coordinate form so strongly that the energetically unstable form is present in amounts too small to be measured using presently available techniques.

It would clearly be of importance to find conditions

---

[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963).