

In no case are the values of the parameters changed significantly. However, the values of K_3 , K_4 , and the absorptivities of HgI_4^{2-} changed by 10–15% if all activity coefficients were set equal to unity. Since $\chi^2/115$ did not increase appreciably, this suggests that the fit is, statistically, equally good whether or not activity corrections are included. Since the weight of chemical experience requires that the variation of the activity coefficients be included over this ionic strength range ($0 < \mu < 0.05$), we regard the results obtained with the Davies equation as the more accurate.

The distribution of Hg(II) among the three iodide complexes is given in Table II along with the experimental absorbances of the solutions and the calculated residuals. A residual is the amount to be subtracted from the measured absorbance to give agreement with the absorbance calculated from the best values of the equilibrium constants and the molar absorptivities. More than 90% of the calculated absorbances agree with the measured values to within better than 5% over the more than 1000-fold change in ligand concentration.

Examination of the partial correlation coefficients²⁰ indicates that the parameters are not strongly correlated. This is a consequence of the widely separated values of K_3 and K_4 which minimizes the overlap of species as the iodide ion concentration is increased. As may be seen from Table II, 12% of the solutions contain mainly HgI_2 , nearly 20% contain over 90% HgI_3^- , and the solutions at the higher KI concentrations are mainly HgI_4^{2-} . Because the parameters are not strongly correlated, the errors quoted above are probably realistic estimates of the 50% confidence intervals for the parameters.

Acknowledgments.—R. J. Peterson wishes to thank the NSF Undergraduate Research Participation Program for its support, and P. J. Lingane wishes to thank the University of Minnesota Computing Center for a grant of computer time.

(20) W. C. Hamilton, "Statistics in Physical Science," The Ronald Press Co., New York, N. Y., 1964, Section 5.9.

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A Potentiometric Study of Cobalt(III) Perchlorate Solutions^{1a}

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There is some uncertainty, and even controversy,² concerning the species present in acidic cobalt(III)

(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission. (b) On leave from the Royal Institute of Technology, Stockholm, Sweden.

(2) C. F. Wells, *Discussions Faraday Soc.*, **46**, 197 (1968), and references cited therein.

perchlorate solutions. There seems to be fairly general agreement that solutions of $[\text{Co}^{\text{III}}] \gtrsim 10^{-2} M$ and $[\text{H}^+] < 0.5 M$ contain di- and/or polynuclear hydrolyzed species.³ However, it has also been suggested on the basis of kinetic studies² that a (hydrated) dimer of Co^{III} predominates even in solutions of $[\text{Co}^{\text{III}}] \lesssim 1 \times 10^{-3} M$ at high acidities.

Also, there is a paucity of standard potential (E°_{Co}) data for the $\text{Co}^{\text{III}}\text{--Co}^{\text{II}}$ couple in perchlorate solutions. Two values, at 25° in 4 M HClO_4 — $1.92 \pm 0.02 V$ (measured directly)⁴ and $1.95 \pm 0.10 V$ (indirect estimate)⁵—are the only ones found in the literature.

If cobalt(III) exists in solution in the form of dimeric ions, this should be supported by electromotive force measurements with the (reversible) $\text{Co}^{\text{III}}\text{--Co}^{\text{II}}$ redox electrode; the "Nernst slope" would be half of that expected for monomeric cobalt(III) (at constant cobalt(II) concentration).^{6,7}

If both monomeric and dimeric Co^{III} species are present in equilibrium



one has

$$[\text{Co}^{\text{III}}_2][\text{Co}^{\text{III}}]^{-2} = K_D \quad (1a)$$

Here brackets are used to denote concentrations, and K_D is an overall dimerization quotient. If hydrolysis occurs, K_D will be a constant at constant $[\text{H}^+]$ ($\equiv h$). If K_D in eq 1 is finite, then the Nernst equation for the emf, E (expressed as a reduction potential), is given by

$$E = E_0 + \frac{RT \ln 10}{F} \log \{ [(1 + 8K_D[\text{Co}^{\text{III}}]_T)^{1/2} - 1]/4K_D[\text{Co}^{2+}] \} \quad (2)$$

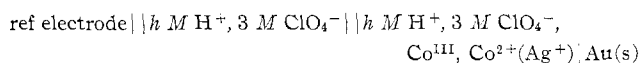
where E_0 is a constant, which includes *inter alia* the reference half-cell emf and liquid junction potentials (assumed to be constant); $[\text{Co}^{\text{III}}]_T$ is the total concentration of Co^{III} ; other symbols have their conventional meaning. For the case of a very high K_D (practically all dimer) eq 2 reduces to

$$E = E_0 + \frac{RT \ln 10}{2F} \log \{ ([\text{Co}^{\text{III}}]_T/2K_D[\text{Co}^{2+}])^2 \} = E_0' + \frac{RT \ln 10}{2F} \log \{ ([\text{Co}^{\text{III}}]_T/[\text{Co}^{2+}])^2 \} \quad (2a)$$

Experimental Section

Cobalt(III) perchlorate solutions in 3 M $(\text{Na}^+, \text{H}^+)\text{ClO}_4^-$ were prepared by electrolytic oxidation near 0° of cobalt(II) perchlorate which had been prepared from reagent grade cobalt carbonate and perchloric acid. Sodium perchlorate was prepared from chloride-free sodium carbonate and perchloric acid. Water was triply distilled. Other reagents were of reagent grade.

The cell used for the emf measurements was



The reference electrode was a commercial calomel electrode in which the KCl had been replaced with 4.0 M NaCl. An HClO_4^-

(3) L. H. Sutcliffe and J. R. Weber, *J. Inorg. Nucl. Chem.*, **12**, 281 (1960).

(4) B. Warnqvist, quoted by H. Diebler and N. Sutin, *J. Phys. Chem.*, **68**, 174 (1964); D. H. Huchital, N. Sutin, and B. Warnqvist, *Inorg. Chem.*, **6**, 838 (1967).

(5) D. A. Johnson and A. G. Sharpe, *J. Chem. Soc.*, 3490 (1964).

(6) A. Ogg, *Z. Physik. Chem.*, **27**, 285 (1898).

(7) B. D. Blaustein and J. W. Gryder, *J. Am. Chem. Soc.*, **79**, 540 (1957).

TABLE I
VARIATION OF EMF WITH Co(III) AND Co(II) CONCENTRATIONS AT 3°, $h = 0.50 M$, AND $\mu = 3 M ((Na^+)ClO_4^-)$

$10^3[Co^{III}]_M$	$10^3[Co^{II}]_M$	$E - 1019.3^b$ mV	$\Delta E(\text{obsd})$, mV	$\Delta E(\text{mono})$, mV	$\Delta E(\text{di})$, mV	E°_{Co} , mV
0.26	23.19	453				1828
			32	29.7	15.4	
0.85	22.15	485.0				1830
			28.3	29.0	16.1	
2.51	19.29	513.3				1830
			18.0	17.8	11.2	
4.41	15.99	531.3				1830
			12.7	14.0	9.8	
6.26	12.62	544.0				1829
						$Av \ 1829 \pm 1^a$

^a Not including the 10–20-mV uncertainty on the hydrogen electrode scale, due to liquid junction potentials. ^b The emf read on the instrument was the actual cell emf (E) minus the emf of a standard Weston cell (1019.26 mV).

NaClO₄ solution and a glass frit were placed between the reference electrode and the cobalt half-cell to prevent reaction between cobalt(III) and chloride. As noted by Noyes and Deahl,⁸ it was found preferable to use a gold foil, instead of platinum, as the inert electrode, and it was also necessary to add silver ion (a few drops of AgClO₄ solution) as a potential mediator, in order to obtain electrode equilibrium quickly.

The concentration range of cobalt(III) was typically $\sim 0.5 \times 10^{-3}$ to $\sim 5 \times 10^{-3} M$ and the Co^{III}:Co^{II} ratio was ~ 0.01 – 0.25 . Emfs were measured with a Beckman Research pH meter (Model 1019).

The cobalt(III) concentration was determined by quickly adding an aliquot to a known amount of iron(II) sulfate solution and then titrating the excess iron(II) with standard cerium(IV) sulfate. Ferroin was used as an indicator. The cobalt(II) concentration was then obtained by subtraction from the known total cobalt concentration. Measurements were carried out at two temperatures, 23 ± 1 and $3 \pm 1^\circ$, and at a number of acidities, h . At 23° , the rapid reduction of cobalt(III) by water precluded measurements at $h < 0.5 M$.

Results and Calculations

As a preliminary, one may compare the experimentally observed emf change, $\Delta E(\text{obsd})$, between two experimental points of different cobalt(III) (and cobalt(II)) concentrations with: (a) that computed from the usual Nernst equation, $\Delta E(\text{mono})$, and (b) that computed from eq 2a, $\Delta E(\text{di})$. A typical example of results is presented in Table I (data for 3° ; $h = 0.5 M$). It can be seen that $\Delta E(\text{obsd})$ values are generally within ± 1 – 2 mV, or better, of the corresponding $\Delta E(\text{mono})$ values and in general are significantly different from the $\Delta E(\text{di})$ values. Similar results were obtained in other experiments, with $h = 0.05$ – $3 M$ at 3° and with $h = 3 M$ at 23° . For $h = 0.5 M$ at 23° (where the reduction of Co^{III} by water is fairly rapid and makes it difficult to obtain reproducible results) the deviation from $\Delta E(\text{mono})$ was larger for some points but still within 5 mV. The maximum deviation ($\Delta E(\text{mono}) - \Delta E(\text{obsd})$) was used, with the aid of eq 2, to estimate upper limits of K_D compatible with these results. This is shown in Table II, which also contains values for the formal standard potential, E°_{Co} , on the hydrogen electrode scale, for the Co^{III}–Co²⁺ couple in the various media. The electrode reaction is assumed to be $Co^{III} + e^- \rightleftharpoons Co^{2+}$. In computing E°_{Co} , potentials of 0.242 V at 23° and 0.249 V at 3° , relative to the standard hydrogen electrode, were assumed for the calomel electrode with NaCl.

(8) A. A. Noyes and T. J. Deahl, *J. Am. Chem. Soc.*, **59**, 1337 (1937).

Because the true values of the liquid junction potentials are not known precisely, the E°_{Co} values can only be quoted to within ± 0.01 – 0.02 V. At a given acidity, on the other hand, liquid junction potentials are essentially constant, and E°_{Co} values are obtained experimentally with a precision of ± 1 mV, as can be seen in Table I.

Discussion

From these results one may conclude that cobalt(III) is mainly monomeric (*e.g.*, Co³⁺(aq)) in the acidity, temperature, and concentration ranges of these experiments. As seen in Table II, an upper limit for K_D of

TABLE II
UPPER LIMIT ESTIMATES OF COBALT(III) DIMERIZATION QUOTIENT, K_D , AND STANDARD POTENTIALS FOR Co^{III}–Co^{II} IN $3 M (Na^+)ClO_4^-$

Temp, °C	h, M	K_D (approx upper limit), M^{-1}	E°_{Co}, V^a
23	3	20	1.86
23	0.5	500	1.85
3	3	10	1.83
3	0.5	20	1.83
3	0.1	20	1.82
3	0.05	10	1.83

^a Error estimated at $\pm (0.01$ – $0.02) V$.

10 – $20 M^{-1}$ is estimated in all cases, except for $h = 0.5 M$ at 23° , where a lower experimental accuracy (*vide infra*) leads to an estimated upper limit of $\sim 500 M^{-1}$. If $K_D = 20 M^{-1}$, then, to take an example, at $[Co^{III}]_T = 3 \times 10^{-3} M$, 10% of the total Co^{III} exists as a dimer; at $0.5 \times 10^{-3} M$, only 2% is dimeric.

It is unfortunate that no data could be obtained at 23° in the interesting acidity range $< 0.5 M$. However, using a plausible maximum enthalpy change, ΔH , for the dimerization, *i.e.*, $\sim +20$ kcal (which is about equal to the ΔH for the reaction $2Cr^{3+} + 2H_2O \rightleftharpoons Cr(OH)_2Cr^{4+} + 2H^+$),⁹ one may estimate a probable upper limit for K_D of 250 – $500 M^{-1}$ at 23 – 25° . Even with a K_D value of this order, one would have $< 40\%$ cobalt(III) in the form of dimers at $[Co^{III}]_T = 10^{-3} M$. (This estimate would, of course, not be valid if actually higher polymers are formed and/or equilibrium is not attained.)

Since E°_{Co} seems to be constant (within ± 0.01 V) in the range 0.05 – $0.5 M H^+$ at 3° , one may estimate an

(9) J. E. Earley and R. D. Cannon, *Transition Metal Chem.*, **1**, 67 (1965).

approximate upper limit for the first hydrolysis constant, $*K_1$, for the Co^{3+} ion: $*K_1 \leq 0.01 M$. If ΔH for the hydrolysis reaction ($\text{Co}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{CoOH}^{2+} + \text{H}^+$) is about 10 kcal mol $^{-1}$, as estimated by Sutcliffe and Weber,¹⁰ then, at 25°, $*K_1 \leq 0.05 M$.

In conclusion, the results presented in this note suggest that some kinetic mechanisms that have been proposed,² involving a large proportion of dimeric cobalt(III), may require reconsideration.

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(10) L. H. Sutcliffe and J. R. Weber, *Trans. Faraday Soc.*, **62**, 1225 (1956).

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Fluoro-Containing Complexes of Chromium(III). IV. The Reactions of *trans*-Fluoroaquo-bis(ethylenediamine)-chromium(III) Perchlorate Monohydrate with Ammonium Chloride and Ammonium Bromide¹

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Fluoro-containing complexes of chromium(III) of the type $[\text{Cr}(\text{AA})_2\text{FX}]\text{Y}$ (AA is a diamine) which involve a *trans* arrangement of the FX ligands are relatively rare and have not been investigated in detail. The confirmed *trans* complexes of this type with AA = ethylenediamine appear to be restricted to the $\text{F}(\text{H}_2\text{O})$,³ $\text{F}(\text{ONO})$,¹ and F_2 ¹ complexes. When the bidentate ligand is changed from ethylenediamine to 1,3-propanediamine the *trans* FCl, FBr, F(NCS), and $\text{F}(\text{H}_2\text{O})$ complexes can be prepared.⁴ *cis* complexes of the type $[\text{Cr}(\text{en})_2\text{FX}]\text{Y}$ are slightly more numerous than the corresponding *trans* materials. The series of *cis* complexes which have been isolated as solids include the FF,⁵ FCl,¹ and F(NCS)¹ compounds.

The investigation described in this paper was undertaken to develop a suitable method for the preparation of a *trans* complex of the type $[\text{Cr}(\text{en})_2\text{FX}]\text{Y}$ which involved a halogen other than fluorine as the X ligand and to establish its structure.

Experimental Section

Caution! Perchlorate salts of metal complexes with reducing ligands such as amines are potentially explosive and care should be exercised when working with these materials.

(1) For the previous publication in this series see J. W. Vaughn, O. J. Stvan, Jr., and V. E. Magnuson, *Inorg. Chem.*, **7**, 736 (1968).

(2) National Science Foundation Undergraduate Research Participant, 1968–1969.

(3) W. Dahme, Dissertation, Clausthal Bergakad, Germany, 1957, p 36; A. Katowski, Ed., "Gmelins Handbuch der Anorganischen Chemie, VIII Auflage, Chrom," Vol. 52, Part C, Verlag Chemie, Weinheim/Bergstr., Germany, 1965, p 190.

(4) J. W. Vaughn, *Inorg. Nucl. Chem. Letters*, **4**, 183 (1968).

(5) K. R. A. Fehrmann and C. S. Garner, *J. Am. Chem. Soc.*, **82**, 6294 (1960).

trans- $[\text{Cr}(\text{en})_2\text{F}(\text{H}_2\text{O})](\text{ClO}_4)_2$.—This complex was prepared by the method of Dahme.³ *Anal.* Calcd for $[\text{Cr}(\text{en})_2\text{F}(\text{H}_2\text{O})](\text{ClO}_4)_2$: C, 11.8; H, 4.4; N, 13.7; F, 4.7. Found: C, 11.9; H, 4.5; N, 13.7; F, 4.7.

trans- $[\text{Cr}(\text{en})_2\text{FCl}]\text{ClO}_4$.—A 3-g sample of *trans*- $[\text{Cr}(\text{en})_2\text{F}(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ was suspended in 200 ml of methanol and mechanically shaken for about 1 hr. At the end of this time, the undissolved material was removed by filtration and the orange-red solution treated with 1.5 g of solid ammonium chloride. The flask and contents were mechanically shaken for another 18 hr at room temperature. At the end of this time the pink crystals were collected, washed with methyl alcohol, and dried at 75°. *Anal.* Calcd for *trans*- $[\text{Cr}(\text{en})_2\text{FCl}]\text{ClO}_4$: Cr, 15.9; H, 4.9; N, 17.1; C, 14.73; F, 5.8; Cl, 21.60. Found: Cr, 15.5; H, 5.0; N, 17.1; C, 15.0; F, 5.7; Cl, 21.45.

In aqueous solution at room temperature the complex exhibited absorption maxima at 553, 460, and 381 nm with molar absorptivities of 19.9, 21.5, and 27.4 $M^{-1} \text{cm}^{-1}$, respectively.

The solid-state absorption spectrum of the complex was determined in the 700–300-nm region by the potassium bromide pellet method. This spectrum exhibited two well-defined peaks and a shoulder in this region. The infrared spectrum in the 400–600- cm^{-1} region exhibited bands at 445, 492, 517, and 560 cm^{-1} . A $10^{-3} M$ aqueous solution of the complex exhibited a molar conductance of 142 ohms $^{-1}$ at 25°.

Reaction of *trans*- $[\text{Cr}(\text{en})_2\text{F}(\text{H}_2\text{O})](\text{ClO}_4)_2$ with Ammonium Bromide.—A 3-g sample of *trans*- $[\text{Cr}(\text{en})_2\text{F}(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ was suspended in 200 ml of methanol and mechanically shaken for 1 hr. At the end of this time, the undissolved material was removed by filtration and the orange-red solution treated with 1.5 g of solid ammonium bromide. The flask and contents were mechanically shaken for 18 hr at room temperature. At the end of this time, no product had precipitated from solution. The reaction mixture was allowed to stand for 10 days at room temperature before the pink precipitate was collected by filtration, washed with methanol, and dried at 75° for 12 hr.

The infrared spectrum in the 400–600- cm^{-1} region was characterized by absorptions at 445, 495, 520, and 570 cm^{-1} , while the electronic spectrum in aqueous solution at room temperature exhibited absorptions at 525, 466, 400, and 350 nm. The molar absorptivities were 20.0, 23.2, 16.7, and 17.7 $M^{-1} \text{cm}^{-1}$, respectively. *Anal.* Calcd for *trans*- $[\text{Cr}(\text{en})_2\text{F}_2]\text{Br}$: C, 16.6; H, 5.5; N, 19.3; F, 13.1; Br, 27.6. Found: C, 16.7; H, 5.5; N, 19.1; F, 13.1; Br, 27.5.

Synthesis of *trans*- $[\text{Cr}(\text{en})_2\text{F}(\text{H}_2\text{O})]\text{Br}_2 \cdot \text{DMF} \cdot \text{H}_2\text{O}$.—Since it was not possible to prepare the bromofluoro complex in methyl alcohol, the solvent was changed to dimethylformamide and the reaction repeated. A 1.0-g (0.0025 mol) sample of *trans*- $[\text{Cr}(\text{en})_2\text{F}(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ was dissolved in 4–5 ml of Spectro grade dimethylformamide and 0.49 g (0.005 mol) of solid ammonium bromide was added. The solution was mechanically stirred for 10 min before a small amount of precipitate was removed by filtration and discarded. The filtrate was allowed to stand at room temperature for 5 hr before the dark red crystals were collected by filtration, washed with cold ethanol, followed by acetone, and air dried. This method produced *trans*- $[\text{Cr}(\text{en})_2\text{F}(\text{H}_2\text{O})]\text{Br}_2 \cdot \text{DMF} \cdot \text{H}_2\text{O}$ in 30% yield. *Anal.* Calcd for *trans*- $[\text{Cr}(\text{en})_2\text{F}(\text{H}_2\text{O})]\text{Br}_2 \cdot \text{DMF} \cdot \text{H}_2\text{O}$: C, 18.3; H, 5.9; N, 15.3; F, 4.2; Br, 34.8. Found: C, 18.0; H, 6.0; N, 15.2; F, 4.2; Br, 34.9.

The electronic spectrum of the product obtained by this reaction in the 350–700-nm range was identical with that of the *trans*- $[\text{Cr}(\text{en})_2\text{F}(\text{H}_2\text{O})]^{2+}$ ion.

The electronic spectrum of *trans*- $[\text{Cr}(\text{en})_2\text{F}(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ was determined both in water and in dimethylformamide. The spectrum was markedly solvent dependent. In aqueous solution the complex exhibited absorption bands at 371 (31.2), 454 (25.6), and 519 nm (24.2 $M^{-1} \text{cm}^{-1}$) while in dimethylformamide the initial time spectrum was characterized by bands at 394 (34.0), 463 (28.7), and 524 nm (31.7 $M^{-1} \text{cm}^{-1}$). The spectrum of the dimethylformamide solution changed with time, and after 48 hr peaks were found at 506 (76.5) and 390 nm (31.2 $M^{-1} \text{cm}^{-1}$)