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The Kinetics of the Formation and Dissociation of the Monochloro Complex of Cobalt(III)[1]

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The rates of the reactions $Co^{3+} + Cl^- \rightleftharpoons CoCl^{2+}$ have been studied in the concentration ranges $[Co(III)] = 3.0$ to 5.0×10^{-4} M, $[Co(II)] = 5.0$ to 33.0×10^{-2} M, $(Cl^-) = 4.8$ to 105×10^{-3} M, $(H^+) = 0.4$ to 3.0 M, ionic strength $= 3.0$ M. The approach to equilibrium is given by $k_{obsd} = k'(Cl^-) + k''$ where $k' = [k_{1f}(H^+) + k_{2f}K_{1h} + k_{3f}K_4(Co^{2+})(H^+)]/[(H^+) + K_{1h}]$ and $k'' = [k_{1d}(H^+) + k_{2d}K_{2h} + k_{3d}(Co^{2+})(H^+)]/(H^+)$. The values of the constants are $k_{1f} \leqslant 2$ M^{-1} sec.$^{-1}$, $k_{2f} = (2 \pm 1) \times 10^2$ M^{-1} sec.$^{-1}$, $K_{1h} = 0.22 \pm 0.05$ M, $k_{3f}K_4 = 26 \pm 5$ M^{-2} sec.$^{-1}$, $k_{1d} \leqslant 0.05$ sec.$^{-1}$, $k_{2d}K_{2h} = 1.5 \pm 0.5$ M sec.$^{-1}$, $k_{3d} = 1.0 \pm 0.2$ M^{-1} sec.$^{-1}$ at 25.0° and ionic strength $= 3.0$ M. The measurements suggest that $Co(H_2O)_6{}^{3+}$ undergoes water exchange relatively slowly and thus that the stable state of $Co(H_2O)_6{}^{3+}$ is the low-spin form.

Although numerous studies of substitution reactions have been reported in recent years, very few have dealt with reactions of cobalt(III).[3] The paucity of data on such reactions is probably related to the instability of free cobaltic ions in solution.[4,5] This instability precludes precise equilibrium measurements of its complexing with anions. The problem, however, appears somewhat more tractable by kinetic measurements and we have studied the reactions of cobalt(III) with chloride using a flow technique. A preliminary report of these studies has appeared elsewhere.[6] We wish to present here a more detailed account of these investigations and to report the forward and reverse rate constants for the reaction

$$Co^{3+} + Cl^- \rightleftharpoons CoCl^{2+}$$

at 25.0°.

Experimental Section

Solutions of cobalt(II) perchlorate were prepared by dissolving cobalt carbonate (Baker and Adamson) in perchloric acid (Baker Analyzed Reagent). Cobalt(III) solutions were prepared by electrooxidation of the cobalt(II) at 0° and a current density of about 20 ma. cm.$^{-2}$. Sodium perchlorate was prepared from sodium carbonate and perchloric acid. The perchloric acid (70%) and hydrochloric acid (37.8%) were obtained from the J. T. Baker Chemical Co. The cobalt(II) and cobalt(III) solutions were standardized spectrophotometrically (ϵ_{max}[cobalt(III)] = 37.0 at 605 mμ and ϵ_{max}[cobalt(II)] = 4.84 at 509 mμ). The concentration of cobalt(III) was also checked by adding an excess of standardized iron(II) solution to an aliquot of the electrolyzed solution and titrating the excess iron(II) with cerium(IV).

The kinetics were studied at 25.0° and an ionic strength of 3.0 M using the flow techniques and apparatus described previously.[7,8] On mixing solutions of cobalt(III) and hydrochloric acid, each adjusted to the same acidity and ionic strength with perchloric acid and sodium perchlorate, two distinct changes in absorbance are observed in the wave length range 280 to 330 mμ. A photograph of an oscilloscope trace showing these changes is reproduced in Figure 1. The initial increase in absorbance is associated with the formation of the monochloro complex of cobalt(III) and the subsequent slow decrease with the reduction of cobalt(III) by chloride. In order to study the complex-formation step, the reduction can be slowed down markedly by decreasing the chloride and increasing the cobalt(II) and perchloric acid concentrations of the solutions. The following concentration ranges were used: $[Co(III)] = 3.0$ to 5.0×10^{-4} M, $[Co(II)] = 5.0$ to 33.0×10^{-2} M, $(Cl^-) = 4.8$ to 105×10^{-3} M, $(HClO_4) = 0.4$ to 3.0 M. Under these conditions (provided the higher chloride concentrations were used with the higher cobalt(II) and perchloric acid concentrations) the oxidation–reduction reaction is relatively slow and the formation of $CoCl^{2+}$ is essentially complete before any significant reduction of cobalt(III) takes place. Another factor which limited the acidity range that could be used in this work is the high hydrolysis constant of Co^{3+}.

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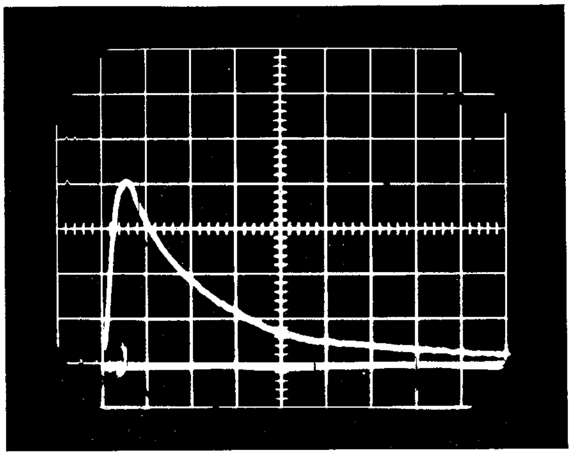

Figure 1.—The absorbance of the cobalt(III)-chloride system as a function of time at 25.0°; [Co(III)] = 7.5×10^{-5} *M*, [Co(II)] = 2.4×10^{-4} *M*, $(Cl^-) = 5.0 \times 10^{-2}$ *M*, $(HClO_4)$ = 1.0 *M*, λ = 280 mμ. The abscissa scale is 500 msec. per major division and the ordinate scale is in arbitrary units of absorbance. The bottom trace corresponds to the absorbance of the solution at "infinite" time.

Results

The kinetic data are consistent with the assumption that at the higher acidities the formation and dissociation of $CoCl^{2+}$ involves the reactions

$$Co(H_2O)_6{}^{3+} + Cl^- \underset{k_{1d}}{\overset{k_{1f}}{\rightleftharpoons}} (H_2O)_5CoCl^{2+} + H_2O \qquad K_1$$

$$Co(H_2O)_6{}^{3+} \rightleftharpoons (H_2O)_5CoOH^{2+} + H^+ \qquad K_{1h}$$

$$(H_2O)_5CoOH^{2+} + Cl^- \underset{k_{2d}}{\overset{k_{2f}}{\rightleftharpoons}} (H_2O)_4CoOHCl^+ + H_2O \qquad K_2$$

$$Co(H_2O)_5Cl^{2+} \rightleftharpoons (H_2O)_4CoOHCl^+ + H^+ \qquad K_{2h}$$

$$Co(H_2O)_6{}^{3+} + (H_2O)_5CoCl^+ \underset{k_{3d}}{\overset{k_{3f}}{\rightleftharpoons}} Co(H_2O)_6{}^{2+} + (H_2O)_5CoCl^{2+} \qquad K_3$$

$$Co(H_2O)_6{}^{2+} + Cl^- \rightleftharpoons (H_2O)_5CoCl^+ + H_2O \qquad K_4$$

Provided the hydrolysis reactions and the formation and dissociation of $CoCl^+$ are sufficiently rapid, the rate of formation of $CoCl^{2+}$ is given by

$$\frac{d(CoCl^{2+})}{dt} = k_{1f}(Co^{3+})(Cl^-) - k_{1d}(CoCl^{2+}) + \frac{k_{2f}K_{1h}}{(H^+)}(Co^{3+})(Cl^-) - \frac{k_{2d}K_{2h}}{(H^+)}(CoCl^{2+}) + k_{3f}K_4(Co^{2+})(Co^{3+})(Cl^-) - k_{3d}(Co^{2+})(CoCl^{2+}) \qquad (1)$$

At equilibrium, $d(CoCl^{2+})/dt = 0$ and the concentrations are related by the equation

$$k_{1f} = \left[k_{1d} + \frac{k_{2d}K_{2h}}{(H^+)} + k_{3d}(Co^{2+})\right]\frac{(CoCl^{2+})_{eq}}{(Co^{3+})_{eq}(Cl^-)} - \left[k_{3f}K_4(Co^{2+}) + \frac{k_{2f}K_{1h}}{(H^+)}\right] \qquad (2)$$

where $(H^+) = (H^+)_{eq}$, $(Cl^-) = (Cl^-)_{eq}$, and $(Co^{2+}) = (Co^{2+})_{eq}$. The mass balance equation for Co(III) gives

$$(Co^{3+}) + (CoCl^{2+}) + (CoOH^{2+}) = (Co^{3+})_{eq} + (CoCl^{2+})_{eq} + (CoOH^{2+})_{eq} \qquad (3)$$

where the concentrations of $CoOHCl^+$ and of more highly hydrolyzed species of cobalt(III) have been neglected. Upon substitution for k_{1f} and (Co^{3+}) eq. 1 becomes

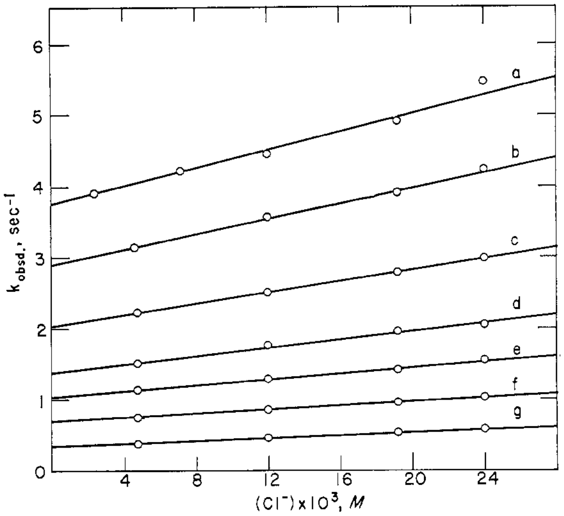

Figure 2.—Plots of k_{obsd} *vs.* (Cl^-) at 25.0° and ionic strength 3.0 *M*: (a) 0.40 *M* H^+; (b) 0.50 *M* H^+; (c) 0.70 *M* H^+; (d) 1.00 *M* H^+; (e) 1.30 *M* H^+; (f) 2.00 *M* H^+; (g) 3.00 *M* H^+. [Co(II)] = 5.0×10^{-2} *M*, [Co(III)] = 3.0×10^{-4} to 5.0×10^{-4} *M*.

$$\frac{d(CoCl^{2+})}{dt} = \left\{\left[\frac{k_{1f}(H^+) + k_{2f}K_{1h} + k_{3f}K_4(Co^{2+})(H^+)}{(H^+) + K_{1h}}\right](Cl^-) + \left[\frac{k_{1d}(H^+) + k_{2d}K_{2h} + k_{3d}(Co^{2+})(H^+)}{(H^+)}\right]\right\}[(CoCl^{2+})_{eq} - (CoCl^{2+})] \qquad (4)$$

The observed first-order rate constant is therefore given by

$$k_{obsd} = \frac{0.693}{t_{1/2}} = k'(Cl^-) + k'' \qquad (5)$$

where

$$k' = \left[\frac{k_{1f}(H^+) + k_{2f}K_{1h} + k_{3f}K_4(Co^{2+})(H^+)}{(H^+) + K_{1h}}\right]$$
$$k'' = \left[\frac{k_{1d}(H^+) + k_{2d}K_{2h} + k_{3d}(Co^{2+})(H^+)}{(H^+)}\right] \qquad (6)$$

In Figure 2 values of k_{obsd} are plotted *vs.* (Cl^-) at constant (Co^{2+}) and at various (H^+) concentrations. Values of k' and k'' calculated from the slopes and intercepts of these plots are presented in Table I. It follows from eq. 6 that

$$\frac{k''}{k'} = \frac{K_{1h}}{K_1(H^+)} + \frac{1}{K_1} \qquad (7)$$

and, therefore, that K_{1h} and K_1 can be evaluated from the slope and intercept of a plot of k''/k' *vs.* $1/(H^+)$. This plot gives $K_1 = 26 \pm 3$ M^{-1} and $K_{1h} = 0.22 \pm 0.05$ *M* at 25.0° and ionic strength 3.0 *M*.

In Figure 3, k'' and $k'[1 + K_{1h}/(H^+)]$ are plotted against $1/(H^+)$. It will be seen that the rates of the reaction at lower acidities are faster than predicted by

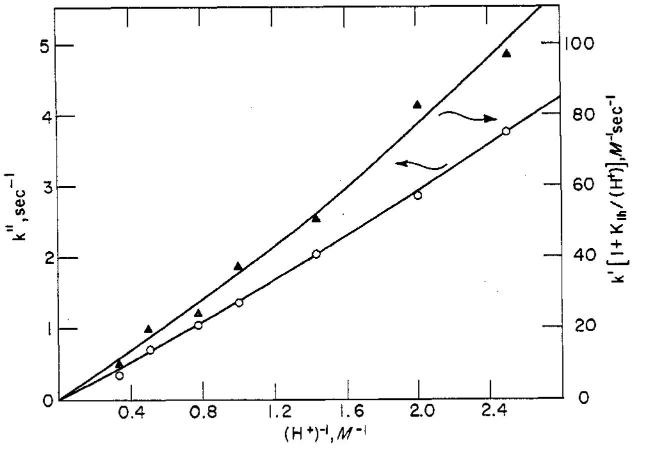

Figure 3.—Plots of k'' and $k'[1 + K_{1h}/(H^+)]$ *vs.* $1/(H^+)$ at 25.0° and ionic strength 3.0 *M*.

TABLE I

VALUES OF k' AND k'' AS A FUNCTION OF (H^+) AT 25.0° AND IONIC STRENGTH 3.0 *M*; [Cobalt(II)] = 5.0×10^{-2} *M*

(H^+), *M*	k', M^{-1} sec.$^{-1}$	k'', sec.$^{-1}$	k'/k'', M^{-1}
0.40	62.5	3.75	16.7
0.50	57.0	2.84	20.0
0.70	38.5	2.03	19.0
1.00	30.5	1.36	22.4
1.30	20.5	1.04	19.7
2.00	17.5	0.69	25.4
3.00	9.0	0.35	25.7

eq. 6. This deviation may be due to contributions of reaction paths involving species which are more highly hydrolyzed than $CoOH^{2+}$. The values of $k_{2f}K_{1h}$ estimated from the initial slopes of the plots in Figure 3 are 36 ± 4 sec.$^{-1}$ and 1.5 ± 0.5 M^{-1} sec.$^{-1}$, respectively, at 25.0° and ionic strength 3.0 *M*. Substituting $K_{1h} = 0.22 \pm 0.05$ *M* gives $k_{2f} = (2 \pm 1) \times 10^2$ M^{-1} sec.$^{-1}$. The upper limits of $[k_{1f} + k_{3f}K_4(Co^{2+})]$ and $[k_{1d} + k_{3d}(Co^{2+})]$ estimated from the intercepts are 3 M^{-1} sec.$^{-1}$ and 0.1 sec.$^{-1}$, respectively. Unfortunately, a more precise determination of k_{1f} and k_{1d} cannot be made because $k_{1f}(H^+) << k_{2f}K_{1h}$ and $k_{1d}(H^+) << k_{2d}K_{2h}$ even at the highest acidity used in this work.

In order to set more definite limits on k_{1f} and k_{1d}, it is necessary to determine the effect of Co^{2+} on the complex formation and dissociation. The rate law may be rearranged to give

$$k_{obsd} = \left[\frac{k_{1f}(H^+) + k_{2f}K_{1h}}{(H^+) + K_{1h}}\right](Cl^-) + \left[\frac{k_{1d}(H^+) + k_{2d}K_{2h} + k_{3d}(H^+)}{(H^+)}\right] + \left[\frac{k_{3f}K_4(H^+)(Cl^-)}{(H^+) + K_{1h}} + k_{3d}\right](Co^{2+}) \qquad (8)$$

Provided (H^+) and (Cl^-) are constant, a plot of k_{obsd} *vs.* (Co^{2+}) should yield a straight line. Such plots are shown in Figure 4. The values of k_{3d} and $k_{3f}K_4$ obtained from these plots are 1.0 ± 0.2 M^{-1} sec.$^{-1}$ and 26 ± 5 M^{-2} sec.$^{-1}$, respectively, at 25.0° and ionic strength 3.0 *M*. If these values of k_{3f}, k_{3d}, and K_4 are substituted into the equation for k' and k'', we find that $k_{1f} \leqslant 2$ M^{-1} sec.$^{-1}$ and $k_{1d} \leqslant 0.05$ sec.$^{-1}$.

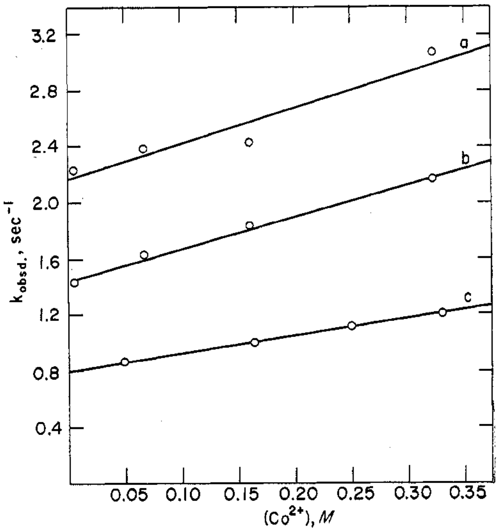

Figure 4.—Plots of k_{obsd} *vs.* (Co^{2+}) at 25.0° and ionic strength 3.0 *M*: (a) 0.105 *M* Cl^-; (b) 0.053 *M* Cl^-; (c) 0.012 *M* Cl^-; $(H^+) = 2.0$ *M*.

TABLE II

THE REDUCTION OF COBALT(III) BY CHLORIDE IONS IN 3.0 *M* PERCHLORIC ACID AT 25.0°

[Co(III)] × 10^3, M^a	$(Cl^-) \times 10^2$, M^a	$(Co^{2+}) \times 10^3$, M^a	$t_{1/2}$, min.^{b}
1.06	0.51	2.86	10.4
0.95	0.51	13.0	65
1.03	0.68	2.89	7.7
1.06	1.02	2.86	4.2
1.12	1.02	3.78	5.5
1.18	1.02	6.22	7.6
1.14	1.02	8.76	12.4
1.14	1.02	10.3	14.5
1.14	1.02	13.8	32
1.05	2.04	2.87	2.0
1.12	2.04	3.78	2.7

[a] Initial concentrations of reactants. [b] The $t_{1/2}$ values are approximate only and were obtained from the initial slopes of plots of log (absorbance) against time.

The Reduction of Cobalt(III) by Chloride.—The reduction of cobalt(III) by chloride was studied by following the decrease in the absorbance at 605 mμ as a function of time. Plots of log (absorbance) *vs.* time were not linear; the slopes decreased with time. Values of $t_{1/2}$, estimated from the initial slopes, are presented in Table II. It will be seen that the rate of the oxidation–reduction reaction decreases as the cobalt(II) concentration is increased and that it is more than first order in the total chloride concentration, at least in the concentration ranges used. These data are not sufficiently extensive to justify a detailed kinetic analysis of the oxidation–reduction reaction at the present time.

Discussion

The extent of hydrolysis of cobalt(III) ions in solution has been debated for some time. From a spectrophotometric study of cobalt(III) perchlorate solutions, Hargreaves and Sutcliffe[9] concluded that no appreciable hydrolysis occurs above an acidity of 1 M. Earlier, Bawn and White[10] had explained the kinetics of decomposition of cobalt(III) sulfate solutions at an acidity below about 1 M in terms of reactions involving both a hydrolyzed species, $(H_2O)_5CoOH^{2+}$, and a dimeric species, $(H_2O)_5CoOCo(H_2O)_5{}^{4+}$, resulting from the association of two $CoOH^{2+}$ ions. After a study of the effect of acidity on the reaction between cobalt(III) and cerium(III), Sutcliffe and Weber[11] revised their previous findings and concluded that a hydrolyzed species must be present at 1 M acidity; the hydrolysis constant of cobalt(III) was given as 1.75×10^{-2} M at 25.0°. More recently, Baxendale and Wells[5] have shown that cobalt(III) is present mainly in a dimeric form in such solutions. In the light of this evidence, Sutcliffe and Weber[4] made a spectrophotometric reexamination of cobalt(III) perchlorate solutions at acidities up to 1 M and suggested that rapid hydrolysis of the cation is followed by slow formation of a dimer. Since dimerization was ignored in their previous work, their estimate of K_{1h} is probably in error. The value of $K_{1h} = 0.22 \pm 0.05$ M found in the present work from measurements over a much wider range of acidity is considered to be more reliable than the previous estimates. The high hydrolysis constant of Co^{3+} is similar to that of Mn^{3+} and recalls the powerful oxidizing properties of these ions in solution.[12,13] It has been suggested that because these oxidizing agents attract electrons so strongly they polarize the coordinated water molecules to such an extent that dissociation of a proton can readily occur.[12]

There is also considerable uncertainty concerning the rate of water exchange of $Co(H_2O)_6{}^{3+}$. Friedman, Taube, and Hunt[14] have observed a rapid water exchange. However they suggested that the exchange might be catalyzed by the Co^{2+} ions present in their solutions. Since Co^{2+} undergoes rapid water exchange, electron exchange between Co^{2+} and Co^{3+} could account for the fast apparent water exchange of $Co(H_2O)_6{}^{3+}$. Our studies allow an indirect estimate of the rate of water exchange of $Co(H_2O)_6{}^{3+}$. In order to do this it is necessary to assume that, in common with many other complex-formation reactions, the formation of $(H_2O)_5CoCl^{2+}$ from $Co(H_2O)_6{}^{3+}$ and Cl^- proceeds in two steps

$$Co(H_2O)_6{}^{3+} + Cl^- \rightleftharpoons (H_2O)_5CoH_2OCl^{2+} \quad K_0$$

$$(H_2O)_5CoH_2OCl^{2+} \xrightarrow{k_1} (H_2O)_5CoCl^{2+} + H_2O$$

with $k_{1f} = K_0k_1$.[3] The value of K_0, the outer-sphere association constant, cannot readily be calculated from first principles particularly at the ionic strengths used in this work. We will therefore assume that K_0 is the same in the cobalt(III) and iron(III) systems. Moreover k_1, the first-order rate constant for water exchange of the outer-sphere complex, is probably not too different from k_{ex}, the rate constant for water exchange of $Co(H_2O)_6{}^{3+}$.[8] Using the data presented in Table III an approximate value of the water exchange rate of $Co(H_2O)_6{}^{3+}$ can now be estimated from the relation

$$\frac{k_{ex,Co^{3+}}}{k_{ex,Fe^{3+}}} = \frac{k_{1f,Co^{3+}}}{k_{1f,Fe^{3+}}} \tag{9}$$

provided the water exchange rate of $Fe(H_2O)_6{}^{3+}$ is known. According to Connick and Stover[15] this rate constant is 3×10^3 sec.$^{-1}$ at 25.0°. Substitution in eq. 9 gives k_{ex} for $Co(H_2O)_6{}^{3+} \leqslant 1 \times 10^3$ sec.$^{-1}$ at 25.0°. The rate constant for water exchange of $(H_2O)_5FeOH^{2+}$ is, very roughly, 3×10^5 sec.$^{-1}$,[16] substitution of this value and the appropriate kinetic data in eq. 9 gives k_{ex} for $(H_2O)_5CoOH^{2+} \approx 3 \times 10^3$ sec.$^{-1}$ at 25.0°. The water exchange of $(H_2O)_5CoOH^{2+}$ thus appears to be about one hundred times slower than the exchange of $(H_2O)_5FeOH^{2+}$. This conclusion is very tentative for although the value of $k_{2f}K_{1h}$ is known with some confidence the value of k_{2f} depends on K_{1h}. As mentioned above, the value of K_{1h} is by no means well-established. However even if K_{1h} were as low as 1.8×10^{-2} M (the value determined by Sutcliffe and Weber[4]) the rate of water exchange of $(H_2O)_5CoOH^{2+}$ would still be some ten times slower than water exchange of $(H_2O)_5FeOH^{2+}$. Moreover, as in the corresponding iron(III) system, it is likely that water exchange of $(H_2O)_5CoOH^{2+}$ is much faster than water exchange of $Co(H_2O)_6{}^{3+}$ and therefore that k_{ex} for the latter ion is much lower than 1×10^3 sec.$^{-1}$. The slow exchange rates suggested by these comparisons are not unreasonable in view of the evidence that $Co(H_2O)_6{}^{3+}$ has a low spin configuration.[17]

TABLE III

COMPARISON OF THE COBALT(III)–CHLORIDE AND IRON(III)–CHLORIDE SYSTEMS AT 25.0°; IONIC STRENGTH 3.0 M

	Co(III) system	Fe(III) system[a]
K_1, M^{-1}	26 ± 3	8.2
k_{1f}, M^{-1} sec.$^{-1}$	$\leqslant 2$	9 ± 2
k_{1d}, sec.$^{-1}$	$\leqslant 0.05$	1.1 ± 0.2
k_{2f}, M^{-1} sec.$^{-1}$	$(2 \pm 1) \times 10^2$	$(2.1 \pm 0.3) \times 10^4$
$k_{2d}K_{2h}$, M sec.$^{-1}$	1.5 ± 0.5	3.4 ± 0.6
$k_{2f}K_{1h}$, sec.$^{-1}$	40 ± 1.5	28 ± 5
k_{3d}, M^{-1} sec.$^{-1}$	1.0 ± 0.2	12.1 ± 1.6
$k_{3f}K_4$, M^{-2} sec.$^{-1}$	26 ± 5	96 ± 12

[a] R. J. Campion, T. J. Conocchioli, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 4591 (1964).

Finally it should be noted that the cobalt(II)-catalyzed reactions provide a path for the chloride-catalyzed cobalt(II)–cobalt(III) electron exchange. It is apparent from Table III that electron transfer between $CoCl^{2+}$ and Co^{2+} is about ten times slower than the

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corresponding $FeCl^{2+}$–Fe^{2+} reaction. This difference in rates is small and may be due to differences in the standard free energy changes of the reactions. This suggests that spin multiplicity restrictions have, at most, a small effect on the rate of the $CoCl^{2+}$–Co^{2+} electron-transfer reaction.

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The Crystal Structure, Visible, and Ultraviolet Spectra of Potassium Hexachloromanganate(IV)[1]

BY P. C. MOEWS, JR.

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Powder diffraction patterns of potassium hexachloromanganate(IV) can be indexed on the basis of a cubic cell with $a_0 = 9.6445 \pm 0.0020$ Å. Systematic extinctions indicate that potassium hexachloromanganate(IV) is isostructural with potassium hexachloroplatinate(IV) and has the antifluorite structure [space group No. 225, Fm3m-O_h^5; with four Mn in (a) 000 + F.C.; eight K in (c) $\pm(^1/_4{}^1/_4{}^1/_4)$ + F.C.; and 24 Cl in (e) $\pm(x00, 0x0, 00x)$ + F.C.]. Intensity data were collected, and the structure was refined by the method of least squares. Individual temperature parameters B_{Mn}, B_K, and B_{Cl} were determined to be 1.9 ± 0.3, 3.0 ± 0.4, and 2.55 ± 0.1 Å.^{2}, respectively, and the single structural parameter, x, was determined to be 0.2360 ± 0.0004. The Mn–Cl bond distance is 2.276 ± 0.004 Å., and the K–Cl bond distance is 3.412 ± 0.004 Å. The ammonium ($a_0 = 9.80 \pm 0.02$ Å.), rubidium ($a_0 = 9.82 \pm 0.02$ Å.), cesium ($a_0 = 10.17 \pm 0.02$ Å.), and tetramethylammonium ($a_0 = 12.70 \pm 0.02$ Å.) hexachloromanganate(IV) salts were also prepared and have similar structures. The visible and ultraviolet spectra of potassium hexachloromanganate(IV) were determined and are discussed.

Introduction

Potassium hexachloromanganate(IV), K_2MnCl_6, was first prepared by Meyer and Best[2] in 1899. Weinland and Dinkelacker[3] later prepared the compound by the reaction of potassium permanganate with fuming hydrochloric acid

$$2KMnO_4(s) + 16HCl \longrightarrow K_2MnCl_6(s) + 4Cl_2(g) + 8H_2O + Mn^{2+} + 2Cl^-$$

and also reported the preparation of the ammonium and rubidium salts. The hexachloromanganate(IV) salts are described as black solids which rapidly decompose on standing. Individual crystals appear "deep dark red" under a microscope. The magnetic susceptibility of K_2MnCl_6 has been determined,[4] but apart from this the hexachloromanganate(IV) salts have not been studied.

Very few manganese compounds in which the manganese atom has an oxidation number of +4 are known. It is therefore of interest to characterize these compounds further. Although the hexachloromanganate(IV) salts are not stable for long periods, it was possible to determine the structure of K_2MnCl_6 by X-ray powder techniques. The visible and ultraviolet spectra of K_2MnCl_6, as well as the unit cell dimensions of the ammonium, rubidium, cesium, and tetramethylammonium salts, were also obtained.

Experimental Section

Analyses.—Available chlorine, the chlorine liberated when the manganese in higher oxidation states is reduced to manganous ion by chloride ion, was determined by an iodometric titration. An acidic potassium iodide solution was added to a sample of the hexachloromanganate(IV) salt, and the liberated iodine was titrated with a standard sodium thiosulfate solution. The solution remaining from the available chlorine analysis was analyzed for manganese by adjusting the pH to 10 and titrating with a standard ethylenediaminetetraacetic acid solution using the "copper–PAN system" as an indicator.[5]

Preparation of Compounds.—Potassium hexafluoromanganate(IV) was prepared by the reduction of potassium permanganate with ether in a solution of hydrofluoric acid.[6]

Potassium hexachloromanganate(IV) was prepared by the method of Weinland and Dinkelacker.[3] The following detailed procedure gives good results.

Concentrated hydrochloric acid (50 ml.) was cooled to 0° and saturated with hydrogen chloride gas. Finely powdered potassium permanganate (5 g.) was added; a vigorous reaction occurred, and the temperature rose to 15°. The solution was allowed to stand for 15 min. at 15° and then was poured into a sintered-glass funnel. The black solid which collected was thoroughly washed with glacial acetic acid and dried by drawing air through it for 30 min. The yield of potassium hexachloromanganate(IV) was 4.5 g., 82% based on potassium permanganate.

Anal. Calcd. for K_2MnCl_6: available Cl, 20.5; Mn, 15.9; mole ratio available Cl/Mn, 2.00. Found 1 hr. after preparation: available Cl, 20.1; Mn, 15.7; mole ratio of available Cl/Mn, 1.98. Found 16 hr. after preparation: available Cl, 19.3; Mn, 15.3; mole ratio of available Cl/Mn, 1.96. Found 96 hr. after preparation: available Cl, 19.1; Mn, 15.9; mole ratio of available Cl/Mn, 1.87.

The ammonium, rubidium, cesium, and tetramethylammonium salts of hexachloromanganate(IV) were prepared by adding the

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[1] Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.

[2] R. J. Meyer and H. Best, *Z. anorg. allgem. Chem.*, **22**, 169 (1899).

[3] R. F. Weinland and P. Dinkelacker, *ibid.*, **60**, 173 (1908).

[4] S. S. Bhatnagar, B. Prakash, and J. C. Maheshwari, *Proc. Indian Acad. Sci.*, **A10**, 150 (1939).

[5] H. Flaschka and H. Abdine, *Chemist-Analyst*, **45**, 58 (1956).

[6] W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, London, 1954, p. 484.