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Electron-Transfer Reactions of Multidentate Ligand Cobalt(III) Complexes. I. The Reductions of Some Chloro(triethylenetetramine)cobalt(III) Complexes by Iron(II)

Yoshimi Kurimura, Kousaburo Ohashi,* Toshio Ohtsuki,* and Katsumi Yamamoto*
College of General Education, Ibaraki University, Mito
**Department of Chemistry, Ibaraki University, Mito*

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The kinetics of Fe^{2+} reductions of *cis*-α-Co(trien)Cl_2^+, *cis*-α-Co(trien)OH_2Cl^{2+} and *cis*-β_1-Co(trien)OH_2Cl^{2+} (trien=triethylenetetramine) have been studied at 25°C, $[H^+]=0.10$ M and $\sum[ClO_4^-]=1.0$ M. The second-order rate constants obtained are 4.0×10^{-4} M^{-1} sec^{-1}, 1.6×10^{-4} $M^{-1}sec^{-1}$, and 9.8×10^{-5} M^{-1} sec^{-1} for *cis*-α-Co(trien)Cl^{+2}, *cis*-α-Co(trien)OH_2Cl^{2+}, and *cis*-β_1-Co(trien)OH_2Cl^{2+} respectively. It is demonstrated, by comparing with other rate data for the Fe^{2+} reductions of *cis*-CoN_4XCl^{n+} ($N=NH_3$, 0.5 en and 0.25 trien, and $X=H_2O$ and Cl^-) that the rate decreases with an increase in the number of chelate rings in the Co(III) complexes. The chelate effect of the nonbridging ligand on the electron-transfer reactions of Co(III) complexes is discussed on the basis of a model which involves the ligand-field strength of the *trans*-ligand to the bridging one, the energy needed for stretching the *trans*-group away from the Co(III) center, and the effect of the solvation.

The iron(II) reductions of Co(en)$_2$XY^{n+} [1,2] and Co$(NH_3)_4$XCl^{n+} [3] and electron-transfer reactions between aquochromium(II) ion and chromium(III) complexes[4–10] have been studied in order to investigate the effect of the nonbridging ligand on the rate of electron-transfer reactions. The effect of the nonbridging ligand on the electron-transfer reactions of Co(en)$_2$XY^{n+} can be classified in the following three categories[2]: i) the effect of the geometry, ii) the effect of changing the nature of one nonbridging ligand, and iii) the effect of chelation. The investigation was also carried out on the effect of chelation by nonbridging ligands on the reductions of aquo-, sulfato- and chlorocobalt(III) complexes by chromium(II) and vanadium(II).[11,12] Fraser[12] introduced the solvation theory to explain the results obtained by these reactions. However, it has since been suggested that the results for the reactions of *cis*- and *trans*-Co(en)$_2$XCl^{n+} complexes with iron(II) did not conform to this solvation treatment of the chelation effect.[2]

The present authors wish now to report the effects encountered in the reductions of some Co(trien)XCl^{n+} complexes by iron(II).

Experimental

Preparation of Complexes. The *trans*-[Co(trien)Cl_2]Cl, *cis*-α-[Co(trien)Cl_2]Cl, and *cis*-β-[Co(trien)Cl_2]Cl were prepared in a manner previously described.[13] The identity and purity of the complexes were confirmed analytically and spectrophotometrically.

Materials. A solution of iron(II) perchlorate was prepared by dissolving analytical-grade iron wire in an excess of perchloric acid. The concentration of the iron(II) was determined by titration with a standared potassium permanganate solution. The iron(III) concentration was calculated

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6) D. E. Pennington and A. Haim, *ibid.*, **5**, 1887 (1966).
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11) R. T. M. Fraser, *Proc. Chem. Soc.*, **1963**, 262.
12) R. T. M. Fraser, *Inorg. Chem.*, **2**, 954 (1963).
13) a) A. M. Sargeson and G. H. Seale, *ibid.*, **6**, 787 (1967). b) D. A. Buckingham, P. A. Mazill, and A. M. Sargeson, *ibid.*, **6**, 1032 (1967).

from the difference in the amonts of the total iron and that of the iron(II) found. In all cases, the amounts of iron(III) were less than 5% of the total iron. The perchlorate concentration was analyzed by the titration of the hydrogen-ion concentration when an aliquot of the iron(II) solution was passed through a column of cation-exchange resin in the hydrogen form. The hydrogen-ion concentration of the iron(II) solution was calculated from the concentrations of perchlorate, ion(II), and iron(III). In most cases, the hydrogen-ion and perchlorate concentrations of the iron(II) solution were adjusted to 0.20 M and 2.0 M respectively by the addition of perchloric acid and sodium perchlorate solutions. All the other chemicals were of a reagent grade.

Kinetic Measurements. Erlenmeyer flasks containing the iron(II) solution, redistilled water, and weighed amounts of the solid complex respectively were kept in a thermostat. A 5-m*l* portions of the water was pipeted into the flask, and, after the complete dissolution of the complex had been achieved, 5-m*l* of the iron(II) solution were added by means of an injection syringe. Then, this solution was rapidly transferred into a spectrophotometer cell of a Hitachi Model 125 spectrophotometer. The reaction rate was measured at a sufficiently high concentration of iron(II) in order to minimize the complications arising from aquation.

Reductions of cis-α-*Co(trien)*Cl_2^+ *and* cis-α-*Co(trien)* OH_2Cl^{2+}. The aquation processes and the rate constants for the aquation reactions of the Co(III) complexes under investigation have been given by Sergeson and Searle.[14,15] The rate constant for the aquation of the first chloride ion in *cis*-α-RCl_2^+, where R represents $Co(trien)^{3+}$, is 9.4×10^{-3} min^{-1} at 25°C. Since *cis*-α-ROH_2Cl^{2+} is formed in a 100% retention by aquation of the *cis*-α-RCl_2^+ and since the rate of aquation of the second chloride ion in the *cis*-α-ROH_2Cl^{2+} is very slow,[2] a kinetic scheme for the iron(II) reductions of *cis*-α-RCl_2^+ and *cis*-α-ROH_2Cl^{2+} is given by:

$$\begin{tikzcd}
cis\text{-}\alpha\text{-}RCl_2^+ \arrow[r, "k_{a_1}"] \arrow[d, "k_1"', "Fe^{2+}"] & cis\text{-}\alpha\text{-}ROH_2Cl^{2+} \arrow[d, "k_2"', "Fe^{2+}"] \\
Co(II) + Fe(III) & Co(II) + Fe(III)
\end{tikzcd}$$

The rate constant of k_{a1} is known, and the two rate constants to be determined are k_1 and k_2. Since the rate of the aquation of *cis*-α-RCl_2^+ is relatively large as compared with the reduction rates of *cis*-α-RCl_2^+ and *cis*-α-ROH_2Cl^{2+} even at high iron(II) concentrations, k_1 and k_2 were determined in a manner similar to that used by Benson and Haim.[2] The absorbance of the reaction mixture was measured at 525 nm, which is the isosbestic point for *cis*-α-RCl_2^+ and *cis*-α-ROH_2Cl^{2+}, as a function of the time. Then, values of $\log(A_t-A_\infty)$, where A_t is the absorbance at time t, and A_∞, the absorbance after all the Co(III) complex has been reduced to Co(II), were plotted as a function of the time. One of the plots is illustrated in Fig. 1. After a certain period of time, the plots conformed to linearity; the slope of the linear portion gives a measure of the pseudo-fist-order rate constant for the disappearance of *cis*-α-ROH_2Cl^{2+}. The linear behavior begins when the *cis*-α-RCl_2^+ has been exhausted and the only Co(III) species present in an appreciable concentration is *cis*-α-ROH_2Cl^{2+}. The linear portion of the $\log(A_t-A_\infty)$ *vs.* t plot gives a slope which is equal to $-k_2[Fe^{2+}]/2.303$. When A_c is defined as the value of A_t obtained by extrapolating the linear portion of the $\log(A_t-A_\infty)$ *vs.* t plot to zero time, the plot of $\log(A_t-A_c)$ *vs.* t gives a slope which is equal to $-\{k_{a1}+k_1[Fe^{2+}]\}/2.303$.

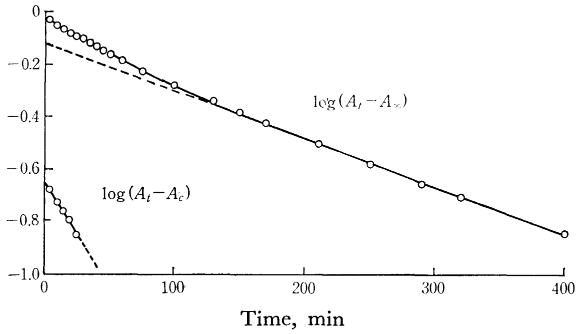

Fig. 1. Plots of log (A_t-A_∞) *vs.* time and log (A_t-A_c) *vs.* time for iron(II) reduction of *cis*-α-$Co(trien)Cl_2^+$.
8.28×10^{-3} M *cis*-α-$[Co(trien)Cl_2]Cl$, 0.415 M Fe^{2+}, $[H^+]=$ 0.10 M, $\sum(ClO_4^-)=1.0$ M, 525 nm, 25°C.

The values of k_1 and k_2 were calculated from the known values of k_{a1}, $[Fe^{2+}]$, and the slope.

Reduction of cis-β_1-*Co(trien)*OH_2Cl^{2+}. Our attempt to determine the rate constant for the ion(II) reduction of *cis*-β-RCl_2^+ by this method failed because of the fast aquation ($k=8.7\times10^{-2}$ min^{-1} at 25°C)[14] of this complex. Since the aquation of the *cis*-β-RCl_2^+ gives two different species of the mono-aquo complexes (94% of *cis*-β_1-ROH_2Cl^{2+} and 4% of *cis*-β_2-ROH_2Cl^{2+}),[14] the rate constants for the iron(II) reductions of these complexes could not be determined separately either by the method in which *cis*-β-RCl_2^+ was used as a starting material. A rapid first aquation of *trans*-RCl_2^+ ($k=21.1\times10^{-2}$ min^{-1} at 25°C)[14] gives only *cis*-β_1-ROH_2Cl^{2+}, and the rate of aquaion of the latter species is relatively slow ($k=1.40\times10^{-3}$ min^{-1} at 25°C).[14] The *trans*-species is almost completely converted into the *cis*-β_1-species about 30 min after the dissolution of the *trans*-species at 25°C, and the min after the dissolution of the *trans*-species at 25°C, and the aquation of the second chloride ion of the *cis*-β_1-species produced in the aquation reaction can be neglected within this period. Therefore, the determination of the rate constant for *cis*-β_1-ROH_2Cl^{2+} could be achieved by adding the iron(II) solution to that of *cis*-β_1-ROH_2Cl^{2+} which had been prepared by keeping the pure *trans*-RCl_2^+ solution in a thermostat for 30 min at 25°C. The kinetic scheme for the iron(II) reduction of *cis*-β_1-ROH_2Cl^{2+} is given as follows:

$$\begin{tikzcd}
trans\text{-}RCl_2^+ \arrow[r, "25°C,\ 30\ min"] & cis\text{-}\beta_1\text{-}ROH_2Cl^{2+} \arrow[r, "k_{a_2}"] \arrow[d, "k_3"', "Fe^{2+}"] & cis\text{-}\beta\text{-}R(OH_2)_2^{3+} \\
 & Co(II) + Fe(III) &
\end{tikzcd}$$

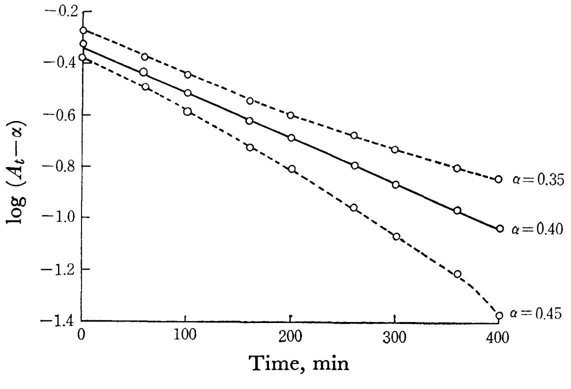

Fig. 2. Plots of log $(A_t-\alpha)$ *vs.* time for iron(II) reduction of *cis*-β_1-$Co(trien)OH_2Cl^{2+}$.
9.1×10^{-3}M *cis*-β_1-$[Co(trien)OH_2Cl]Cl_2$, 0.448M Fe^{2+}, $[H^+]=$ 0.10M, $\sum(ClO_4^-)=1.0$M, 488 nm, 25°C.

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14) A. M. Sargeson and G. H. Searle, *Nature*, **200**, 356 (1963).
15) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 2172 (1967).

As will be shown in the Appendix, the following equation can be derived when the width of the cell used is 1-cm:

$$A_t - \alpha = (E'_i - E')\{[\mathrm{ROH_2Cl}]_0 - A\}e^{-Bt}$$

In this equation, the A_t is the absorbance of the reaction mixture at the isosbestic point (488 nm) for the ROH_2Cl^{2+} and $R(OH_2)_2{}^{3+}$, and E_i' and E' are the molar extinction coefficients of these species, and that of aquo-cobalt(II) ion at this wavelength, respectively. The A, B, and α are obtained by means of the equations shown in the Appendix. Since the value of α was unknown, the value of k_3 was determined as follows: as may be seen in Fig. 2, a straight line is obtained by adjusting the α value so that a plot of the $\log(A_t - A_\infty)$ *vs.* t becomes linear. Since the linear plot gives a slope which is equal to $-(ka_2 + k_3[Fe^{2+}])/2.303$, k_3 can be obtained from the known values of k_{a_2} and $[Fe^{2+}]$.

Results and Discussion

Since $CoCl^{2+}$ [16] and, probably, $Co(en)_2XCl^{n+}$ ($X = H_2O$ and Cl^-)[2] react with Fe^{2+} *via* the chloride-bridged activated complex, it is reasonable to assume a similar mechanism for our reactions.

TABLE 1. RATE CONSTANTS[a)] FOR REDUCTIONS OF $RXCl^{n+}$ BY Fe(II)
($R = $Co (trien), $X = H_2O$ and Cl^-)

Complex	Rate constant ($M^{-1}sec^{-1}$)
cis-α-$RCl_2{}^+$	4.0×10^{-4}
cis-α-ROH_2Cl^{2+}	1.6×10^{-4}
cis-β_1-ROH_2Cl^{2+} [b)]	9.8×10^{-5}

a) At 25° C, $\sum(ClO_4{}^-) = 1.0$ M, $[H^+] = 0.10$ M

b) Starting material is *trans*-$RCl_2{}^+$.

The values of the measured second-order rate constants and the specific rates of *cis*-CoN_4XCl^{n+} with Fe^{2+} are represented in Tables 1 and 2 respectively. The relatively low reduction rate of the $CoN_4OH_2Cl^{2+}$ as compared with that of the corresponding $CoN_4Cl_2{}^+$ may be mainly due to its dipositive charge.

In the *cis*-$CoN_4Cl_2{}^+$ system, the order of effectiveness is $Co(en)_2Cl_2{}^+ > Co(trien)Cl_2{}^+$, while in the *cis*-$CoN_4OH_2Cl^{2+}$ system it is $Co(NH_3)_4OH_2Cl^{2+} > Co(en)_2OH_2Cl^{2+} > \alpha$-Co(trien)$OH_2Cl^{2+} > \beta_1$-Co(trien)$OH_2Cl^{2+}$. The configurations of the *cis*-α- and *cis*-β_1-ROH_2Cl^{2+} have been determined by Sergeson *et al.*[13,14] As the rate constants for the *cis*-α- and *cis*-β_1-ROH_2Cl^{2+} are in the same order, the rate seems not to be strinkingly affected by their configurations with respect to the ligand of trien.

TABLE 2. RATE CONSTANTS FOR Fe^{2+} REDUCTIONS OF *cis*-$CoN_4Cl_2{}^+$ AND *cis*-$CoN_4OH_2Cl^{2+}$
($N = NH_3$, 0.5 en and 0.25 trien)

Complex	Rate constant[a)]	R_{NH3}[b)]	R_{en}[c)]
$Co(en)_2Cl_2{}^+$	16[e)]		1
$Co(trien)Cl_2{}^+$	4.0		0.25
$Co(NH_3)_4OH_2Cl^{2+}$	353[d)]	1	
$Co(en)_2OH_2Cl^{2+}$	4.5[e)]	0.013	
α-Co(trien)OH_2Cl^{2+}	1.6	0.0045	
β_1-Co(trien) OH_2Cl^{2+}	0.98	0.0028	

a) At 25° C, $\sum(ClO_4{}^-) = 1.0$ M, $[H^+] = 0.10$ M, units are 10^{-4} M^{-1} sec^{-1}.

b) Ratio of rate constant to the rate constant for $Co(NH_3)_4OH_2Cl^{2+}$.

c) Ratio of rate constant to the rate constant for $Co(en)_2Cl_2{}^+$.

d) From Ref. 3.

e) From Ref. 2.

The results indicate that the relative effectiveness is decreased with an increase in the number of the chelate ring, so the trend in the rate can be ascribed to the chelate effect of the nonbridging ligand on the electron-transfer reactions. Orgel[17] and Taube[18] suggested that electron-transfer to the unoccupied d_{z^2} orbital on the Co(III) will take place more rapidly the lower the energy of the d_{z^2} orbital. The orbital energy would be lower by: (i) a *trans*-ligand to the bridgnig one with a weak ligand field,[2,17,18] and (ii) the removal of the *trans*-ligand in the z direction away from the Co(III) center.[2]

The rate of the Cr^{2+} reductions of $CoN_5SO_4{}^+$($N_5 = (NH_3)_5$, $(en)_2NH_3$, and tetren[19]) is rather decreased with an increase in the number of the chelate ring in the Co(III) complexes, whereas the rate is hardly affected by an increase in the number of the chelate ring in the Cr^{2+} reductions of CoN_5OAc^{2+} and perhaps $CoN_5Cl.^{2+}$ [12] Fraser explained these results on the basis of solvation. Such a solvation effect is now represented by the effect (c).

The effects of the ligand-field strength of the *trans*-ligand (represented by the effect (a)) and the energy for the bond stretching in the Co–N bond in the z direction (represented by the effect (b)) appear to be of little importance in such reaction as the Cr^{2+} reductions of *cis*- and *trans*-$Co(en)_2NH_3Z^{2+}$($Z = Cl^-$ and OH^-),[19] nor as has been described above, in the Cr^{2+} reductions of CoN_5Cl^{2+}, CoN_5OAc^{2+}, and, possibly, $CoN_5SO_4{}^+$.[12] This may be ascribed to the fact that the relative bond-stretching energies in the Co-N bonds in such reactions as CoN_5Cl^{2+}, CoN_5OAc^{2+}, and $CoN_5SO_4{}^+$ with Cr^{2+}

TABLE 3. ANALYSIS OF CHELATE EFFECT IN ELECTRON-TRANSFER REACTIONS

Type of reaction	Example	$\Delta F_s / \Delta F^{\ddagger}$	Effects[c),d)] a	b	c	Effects of chelation[b)]
A	$Cr^{2+}-CoN_5Cl^{2+}$ [a)]	small	−	−	−	−
	$Cr^{2+}-CoN_5OAc^{2+}$ [a)]		−	−	−	−
	$Cr^{2+}-CoN_5SO_4{}^+$ [a)]		−	−	+	+
B	$Fe^{2+}-CoN_4Cl_2{}^+$ [b)]	large	+	+	+	+
	$Fe^{2+}-CoN_4OH_2Cl^{2+}$ [b)]		+	+	−	+

a) $N_5 = (NH_3)_5$, $(en)_2$ NH_3, and tetren.

b) $N = NH_3$, 0.5 en and 0.25 trien.

c) + indicates that effect is relatively large, —, effect is negligible small.

d) a, b, and c indicate that the effect of ligand field strength of the *trans*-ligand, effect of removal of the *trans*-ligand away from the Co(III) center and effect of solvation, respectively.

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[16] T. J. Concochioli, G. Nancollas, and N. Sutin, *J. Amer. Chem. Soc.*, **86**, 1453 (1953).

[17] L. Orgel, Report of the Tenth Solvay Conference, Brussels, 289 (1956).

[18] H. Taube, *Adv. Inorg. Chem. Radiochem.*, **1**, 1 (1959).

[19] tetren=tetraethylenepentamine.

(type-A reactions) would be small compared with those in such reactions as the Fe^{2+} reductions of *cis*-CoN_4XCl^{n+} (type-B reactions). In fact, it was demonstrated by Green *et al.*[20] that there is little stretching of the Co-N bonds in the reactions of *cis*- and *trans*-$Co(en)_2NH_3Z^{2+}$ complexes with Cr^{2+}. The relative bond-stretching energy mentioned above is defined as: $\Delta F_s/\Delta F^{\ne}$ where ΔF_s is a free-energy change to stretch the Co-N bond in the z direction away from the Co(III) center prior to the transfer of an electron.

An analysis of the chelate effect on the electron-transfer reactions of the CoN_5X^{n+} and CoN_4XCl^{n+} complexes is shown in Table 3. In the Fe^{2+} reductions of *cis*-$CoN_4OH_2Cl^{2+}$, where the relative bond-stretching energy would be important and where the effect of solvation energy may be less important since the resulting cobalt(II) and iron(III) in the reactions have over-all charges of +2, there should be no change in the $\Delta F^{\ne}$ as the chelation is increased;[12] the results obtained can be explained mainly by the (a) and (b) effects. Since the order of the increasing ligand-field strength may be: $NH_3 <$ en $<$ trien and that of the increasing energy for the removal of the *trans*-ligand seems to be: $NH_3 <$en $<$ trien, it is expected that the relative rate will decrease with an increase in the number of the chelate ring in the Fe^{2+} reductions of CoN_4XCl^{n+}. It is considered that the energy required to stretch the metal-ligand bond along the z axis in the *cis*-CoN_4XCl^{n+} is increased as the stability of the complex increases, though the approximation is poor because of the lack of information about the force constants for the Co-N bonds discussed.

Appendix

The kinetic scheme for the Fe^{2+} reductions of *cis*-β_1-ROH_2Cl^{2+} is:[21]

$$ROH_2Cl + Fe^{2+} \xrightarrow{k_3} Co(II) + Fe(III) \quad (1)$$

$$ROH_2Cl + H_2O \xrightarrow{k_{a_1}} R(OH_2)_2 + Cl^- \quad (2)$$

The integrated rate equations for reactions (1) and 2) are:

$$[ROH_2Cl]_t = [ROH_2Cl]_0e^{-Bt} \quad (3)$$

$$[R(OH_2)_2] = A - Ae^{-Bt} \quad (4)$$

where:

$$A = \frac{k_{a_1}[ROH_2Cl]_0}{k_{a_1} + k_3[Fe^{2+}]}$$

$$B = k_{a_1} + k_3[Fe^{2+}]$$

By stoichiometric considerations, the absorbance at the isosbestic point of ROH_2Cl and $R(OH_2)_2$ at time t is found to be:

$$A_t = E_i'[ROH_2Cl]_t + E_i'[R(OH_2)_2]_t + E'[Co(II)]_t$$

where E_i' is the molar extinction coefficient for ROH_2Cl and $R(OH_2)_2$ at the isosbestic point and where E' is the molar extinction coefficient for the Co(II) ion.

Since

$$[Co(II)]_t = [ROH_2Cl]_0 - [ROH_2Cl]_t - [R(OH_2)_2]_t$$

$$A_t = E'[ROH_2Cl]_0 + (E_i'-E')\{[ROH_2Cl]_t + [R(OH_2)_2]_t\} \quad (5)$$

from Eqs. (3), (4), and (5), we obtain:

$$A_t - \alpha = (E_i'-E')\{[ROH_2Cl]_0 - A\}e^{-Bt}$$

where:

$$\alpha = E'[ROH_2Cl]_0 + (E_i'-E')A$$

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[20] M. Green, K. Schung, and H. Taube, *Inorg. Chem.*, **4**, 1184 (1956).

[21] The charges of the Co(III) complexes in the following equations are omitted for the sake of simplicity.