Electron-Transfer Reactions of Multidentate Ligand Cobalt(III) Complexes. II. The Effect of Nonbridging Ligands

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The specific rates for the Fe^{2+} reductions of *cis*-$Co(en)_2ACl^{2+}$ (A=methyl-, ethyl-, propyl-, butyl-, ethanol-, and propanolamine), $Co(dien)(en)Cl^{2+}$ and $Co(tetren)Cl^{2+}$ have been determined. The observed rates are relatively insensitive to the *cis*-ligand of the A. The rate constant for the *cis*-$Co(en)_2ACl^{2+}$ decreases with an increase in the size of the A ligand. In such cases as that of the aminoalcohol ligand, the rate is greater than that of the corresponding alkylamine ligand complex. The effect of chelation by nonbridging ligands has been discussed by comparing the relative effectiveness for Fe^{2+} reductions of CoN_5Cl^{2+} ($N_5=(NH_3)_5$, $(en)_2NH_3$, (dien)(en), and tetren) with that for Cr^{2+} reductions of some Co(III) complexes.

One of the most interesting points encountered in the inner-sphere electron-transfer reactions of Co(III) complexes may be the effect of nonbridging ligands on the specific rates of the reactions. It has been demonstrated that the reactivity patterens of Co(III) complexes in the electron-transfer reactions which proceed through bridged activated complexes may be much affected by the effects of the ligand-field strength of the *trans*-ligand (the a effect)[1,2] and by the energy required to stretch the *trans*-ligand away from the Co(III) center (the b effect).[3] Another explanation has been proposed by Fraser;[4] he explained the effect of chelate formation by nonbridging ligands on the reactivity of the Co(III) complexes with a CoN_5X^{n+} configuration, where X is OAc^-, Cl^-, and SO_4^{2-}, in terms of the solvation energy (the c effect).

It has been shown in the previous paper[5] that the effects of both (a) and (b) may be important in the Fe^{2+} reductions of *cis*-CoN_4XCl^{n+} ($N_4=(NH_3)_4$, $(en)_2$, and trien, $X=H_2O$ and Cl^-), since the free energy for bond stretching for the Co-N bond, in which N is the nitrogen atom located in the *trans*-position to the chloride ion, has a relatively large portion of free energy of activation.

The effect of *cis*-ligand on the rate has also been studied, and it has been demonstrated that the size of the nonbridging *cis*-ligand of B is not the most important factor in determining the reactivity of *cis*-$Co(en)_2BCl^{2+}$.[6,7]

The purposes of this study are to investigate the effect of the nonbridging ligand in the Co(III) complexes and to obtain some detailed information about the effect of the *cis*-ligand in the Fe^{2+} reductions of *cis*-$Co(en)_2ACl^{2+}$ complexes.

Experimental

Materials. *cis*-$[Co(en)_2ACl]Cl_2$,[8,9] $[Co(tetren)Cl]Cl_2$[10] (tetren=tetraethylenepentamine), and $[Co(dien)(en)Cl]Cl_2$[10] (dien=diethlenetrianime and en=ethylenediamine) were prepared by the procedures described in the references cited. The identities of these complexes were confirmed analytically and spectrophotometrically. The preparation of the iron(II) perchlorate solution and the determinations of concentrations of iron(II), the perchlorate anion, and the hydrogen ion were carried out using procedures previously reported.[5] All the other chemicals were of a reagent grade and were used without further purification. The concentrations of perchlorate and hydrogen ions in the iron(II) solution were adjusted by the addition of sodium perchlorate and perchloric acid.

Kinetic Measurements. The general procedure was to make up the reaction mixture in a Erlenmayer flask, and then to transfer the mixture to a spectrophotometer cell, which had been placed in a thermostated cell compartment of a Hitachi Model 124 spectrophotometer, using a injection syringe. The reactions were followed by observing the decrease in the absorbance of the Co(III) complexes at the wavelength in the vicinity of the first absorption maximum. The wavelengths used were 535 nm, 525 nm, and 480 nm in the cases of *cis*-$Co(en)_2ACl^{2+}$, $Co(dien)(en)Cl^{2+}$, and $Co(tetren)Cl^{2+}$ respectively. All the measurements were carried out under pseudo-first-order conditions, in which there was much more iron(II) than Co(III) complexes. The second-order rate constant for the iron(II) reduction of the Co(III) complex defined by $-d[Co(III)]/dt=k[Co(III)][Fe(II)]$ was calculated from the concentration of iron(II) and the slope of the $\log(A_t-A_\infty)$ *vs.* time plot, which is equal to $-k[Fe^{2+}]/2.303$, where A_t is the absorbance at time t; A_∞, the absorbance after all the Co(III) complex has been reduced to Co(II), and k, the rate constant. The value of A_∞ was calculated by the $A_\infty=\varepsilon[Co(II)]$ equation, where [Co(II)] is equal to the initial concentration of the Co(III) complex and where ε is the molar extinction coefficient of the aquo-cobalt(II) ion.

Results

Reductions of cis-*$Co(en)_2ACl^{2+}$.* In all cases, the $\log(A_t-A_\infty)$ *vs.* t plots were substantially linear for at

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TABLE 1. RATE CONSTANTS FOR Fe^{2+} REDUCTIONS OF *cis*-$Co(en)_2ACl^{2+}$
$\sum(ClO_4^-)=1.0$ M, $[H^+]=0.10$ M

Exp. No.	A	[Fe(II)] M	[Co(III)] 10^{-3}M	Temp., °C (±0.1°C)	Rate constant 10^{-5} M^{-1} sec^{-1}
1	Methylamine	0.472	6.26	25.0	2.79
2	Methylamine	0.254	6.52	25.0	2.65
3	Methylamine	0.472	6.57	35.0	6.22
4	Methylamine	0.472	6.80	44.0	12.3
5	Ethylamine	0.472	6.62	25.0	2.74
6	Ethylamine	0.254	5.60	25.0	2.65
7	Ethylamine	0.472	7.47	35.0	5.91
8	Ethylamine	0.472	6.93	44.0	11.8
9	Propylamine	0.415	6.01	25.0	2.57
10	Propylamine	0.254	6.40	25.0	2.59
11	Propylamine	0.415	5.86	35.0	5.87
12	Propylamine	0.415	6.21	44.0	11.1
13	Butylamine	0.472	5.60	25.0	2.08
14	Butylamine	0.254	5.81	25.0	1.98
15	Butylamine	0.472	4.04	34.5	4.40
16	Butylamine	0.472	4.27	44.0	9.71
17	Ethanolamine	0.415	4.18	25.0	4.63
18	Ethanolamine	0.254	5.86	25.0	4.72
19	Ethanolamine	0.415	4.04	34.5	11.0
20	Ethanolamine	0.415	5.89	44.0	19.4
21	Propanolamine	0.415	6.35	25.0	3.14
22	Propanolamine	0.254	5.51	25.0	3.07
23	Propanolamine	0.415	4.19	34.5	7.67
24	Propanolamine	0.415	4.16	44.0	13.9

TABLE 2. RATE CONSTANTS AND ACTIVATION PARAMETERS FOR Fe^{2+} REDUCTIONS OF *cis*-$Co(en)_2ACl^{2+}$ AT 25°C

A	Rate constant[a) 10^{-5} $M^{-1}sec^{-1}$	$\Delta F^{\ddagger}$[b)	$\Delta H^{\ddagger}$[b)	$\Delta S^{\ddagger}$ e.u.	pK_a	
NH_3	1.8[c)				9.25	
Methylamine	2.72	23.7	13.9	−32.7	10.72,[d)	10.62[h)
Ethylamine	2.70	23.7	13.8	−33.1	10.81[e)	10.63[h)
Propylamine	2.58	23.7	13.4	−34.5		10.53[h)
Butylamine	2.03	23.8	13.8	−33.7	10.71[f)	10.61[h)
Ethanolamine	4.68	23.3	13.8	−32.0	9.74[g)	9.50[h)
Propanolamine	3.11	23.6	14.5	−30.4		

a) Except for A=NH_3, average values obtained by this work at 25 ± 0.1°C.
b) Units are kcal·mol^{-1}.
c) From Ref. 3.
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least 2 half-lives. Summeries of the kinetic measurements and activation parameters are presented in Tables 1 and 2 respectively.

Reductions of Co(dien)(en)Cl²⁺ and Co(tetren)Cl²⁺. The second-order rate constant for the Fe^{2+} reduction of $Co(dien)(en)Cl^{2+}$ was obtained from the slope of the $\log(A_t-A_\infty)$ plot (see Fig. 1) and the concentration of the Fe^{2+}. The $\log(A_t-A_\infty)$ plots were linear up to 1000 min in all cases, so the effect of aquations of the Co(III) complexes could be neglected. The reported rate constant for the aquation of $Co(dien)(en)Cl^{2+}$ is 5.2×10^{-7} sec^{-1} at 35°C and pH=1.[8) Though the rate of the disappearence of the $Co(dien)(en)Cl^{2+}$ was followed up to 1000 min, the value of A_t-A_∞ was relatively small since the reduction rate was very slow; therefore, the rate constants obtained were of poor quality. The second-order rate constants for the Fe^{2+} reduction of the $Co(dien)(en)Cl^{2+}$ are presented in Table 3. Our attempt to determine the rate constant for the Fe^{2+} reduction of $Co(tetren)Cl^{2+}$ by the above method failed because of the extremely slow reaction rate. The absorbance of a reaction mixture containing 0.46 M of iron(II) and 5.0×10^{-3} M of the complex at 580 nm under the conditions of $\sum[ClO_4^-]$

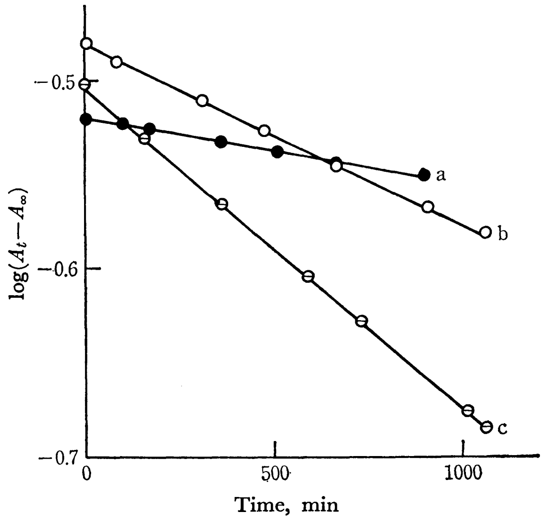

Fig. 1. Plots of $\log(A_t-A_\infty)$ vs. time for Fe^{2+} reduction of Co(dien)(en)Cl^{2+}.
a: [Co(III)]$=4.51\times10^{-3}$M, 25.0°C
b: [Co(III)]$=4.61\times10^{-3}$M, 33.0°C
c: [Co(III)]$=4.76\times10^{-3}$M, 40.0°C
[Fe^{2+}]=0.37M, $\sum[ClO_4^-]$=1.0M, [H^+]=0.10M

$=1.0$ M and [H^+]$=0.10$ M hardly decreased for 40 hr after the initiation of the reaction at 25°C. Therefore, the rate constant for the Fe^{2+} reduction of the Co(tetren)Cl^{2+} was estimated not to exceed 10^{-8}M^{-1}sec^{-1} at 45°C.

Table 3. Rate constants for Fe^{2+} reduction of Co(dien)(en)Cl^{2+} $\sum[ClO_4^-]=1.0$M

[Fe^{2+}] M	[Co(III)] 10^{-3}M	Temp., °C (±0.1°C)	Rate constant 10^{-6} M^{-1} sec^{-1}
0.13	5.57	25.0	6.2[a]
0.37	4.95	25.0	5.9[b]
0.37	4.51	25.0	6.0[b]
0.37	4.61	33.0	10[b]
0.37	4.76	40.0	16[b]

a) [H^+]=0.10M, b) [H^+]=0.26M

Discussion

Effect of the Nonbridging cis-*Ligand.* It may be reasonable to assume that all the reactions now beeing studied proceed *via* a chloride-bridged activated complex[3,5]. In such reactions of Co(III) complexes, it has been suggested that the effect of the nonbridging *cis*-ligand on the rate is of minor importance.[6] This trend also seems to be valid for the reactions of *cis*-Co(en)$_2$ACl^{2+} with Fe^{2+} (Table 1). However, detailed information about the effect of the *cis*-ligand of the A is given by the results summarized in Table 1. The specific rate of the *cis*-Co(en)$_2$NH$_3$Cl^{2+} is smaller than that of the alkylamine complexes under investigation. In such cases as the alkylamine ligands, the value of the ligand field may be slightly lowered in comparison to the ligand field for NH_3.[11,12] This may account for smaller effectiveness of the *cis*-Co(en)$_2$NH$_3$Cl^{2+} than that of the *cis*-Co(en)$_2$NH$_2$CH$_3$Cl^{2+}. In the case of the alkylamine ligand, the reactivity successively decreases with an increase in the size of the amine ligand from methylamine to butylamine. Similar behavior was also observed in the case of the aminoalcohol ligand. A distinctive correlation between pK_a and the specific rate could not be found in the reactions of *cis*-Co(en)$_2$ACl^{2+} with Fe^{2+}. A decrease in the rate with an increase in the size of the A may be due to a decrease in the stabilization of the activated state as the size of the A increases. The aminoalcohol complex is much more effective than the corresponding alkylamine complex. For example, the rate constant for the ethanolamine complex is 1.7 times that for the ethylamine complex. This suggests that the introduction of a hydroxyl group into the nonbridging *cis*-ligand facilitates the reaction rate. The presence of a hydroxyl group in the nonbridging ligand may stabilize the activated complex due to an increase in the solvation energy relative to that of the activated complex formed by the corresponding alkylamine ligand complex and Fe^{2+}.

Table 4. Rate constants for Fe^{2+} reductions of CoN$_5$Cl^{2+} complexes $\sum[ClO_4^-]=1.0$M, [H^+]$=0.10$M

Complex	Rate constant M^{-1}sec^{-1}	Ref.
Co(NH$_3$)$_5$Cl^{2+}	1.6×10^{-3} [a]	14
cis-Co(en)$_2$NH$_3$Cl^{2+}	$(1.8\pm0.1)\times10^{-5}$ [b]	3
Co(dien)(en)Cl^{2+}	6.0×10^{-6} [b]	this work
Co(tetren)Cl^{2+}	$<10^{-8}$ [b]	this work

a) 25.5°C. b) 25°C.

Effect of Chelation by Nonbridging Ligands. The relative effectiveness for Fe^{2+} reductions of the CoN$_5$Cl^{2+} is appreciably decreased with an increase in the number of chelate rings in the Co(III) complex, as is shown in Table 4. The decreasing order of the effectiveness is Co(NH$_3$)$_5$Cl^{2+}>Co(en)$_2$NH$_3$Cl^{2+}>Co(dien)(en)Cl^{2+}>Co(tetren)Cl^{2+}. Similar behavior was also observed in the Fe^{2+} reductions of *cis*-CoN$_4$OH$_2$Cl^{2+}.[5] The effect of the *trans*-ligand on the rate of the electron-transfer reactions which proceed *via* the bridged activated complexes may be classified into: a) the ligand-field strength of the *trans*-ligand[1,2] and b) the energy required to stretch the *trans*-ligand away from the Co(III) center.[3] The relative reduction rate would be smaller if the *trans*-ligand has a stronger ligand field and/or if more energy is required to stretch the metal-ligand bond along the *z* axis. The relative effectiveness for Cr^{2+} reductions of CoN$_5$X^{n+} is decreased with an increase in the number of the chelate ring when X=SO$_4^{2-}$; however, the effectiveness is almost the same when X=OAc$^-$ and perhaps also when X=Cl$^-$.[4] The solvation effect was introduced by Fraser[4] to explain such results.

If we consider that the effects of (a) and (b) mentioned above are major factors in determining the rate of the electron-transfer reactions of the Co(III) complexes, the relative effectiveness for Cr^{2+} reductions of the CoN$_5$X^{n+}, whenever X=OAc$^-$, Cl$^-$, or SO$_4^{2-}$, would

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be changed by replacing the nonbridging ligand by an other ligand, for example, by replacing NH_3 by en or en by tetren, since the ligand-field strength may be increased in the order of $NH_3 < en < tetren$ and the energy needed for the removal of these ligand from the Co(III) center may be in the same order. On the other hand, when the solvation effect is considered to be only the predominant factor in determining the rate, the relative effectiveness for the Fe^{2+} reductions of the $Co(NH_3)_5Cl^{2+}$, $Co(en)_2NH_3Cl^{2+}$, $Co(dien)(en)Cl^{2+}$, and $Co(tetren)Cl^{2+}$ would be almost the same as in the cases of Cr^{2+} reductions of the CoN_5OAc^{2+}, because the over-all charge on the Co(III) and Co(II) complexes and on the Fe(II) and Fe(III) complexes are identical, since the $FeCl^{2+}$ is the only Fe(III) species produced in the reaction:

$$CoN_5Cl^{2+} + Fe^{2+} \longrightarrow Co^{2+} + 5N + FeCl^{2+}$$

though it would dissociate into Fe^{3+} and Cl^- under the experimental conditions.[13]

Therefore, we assume that the free energies for the bond stretching of the Co–N bonds (ΔF_s) are very little in the case of CoN_5X^{n+}–Cr^{2+} reactions and large for CoN_5X^{n+}–Fe^{2+} reactions. It seems reasonably to say that the specific rates of the former reactions are hardly affected by chelate formation by nonbridging ligands if the over-all charge described above is not changed. However, the specific rates of the latter reactions are appreciably affected by the chelate formation of the nonbridging ligands, since ΔF_s may be mainly affected by the nature of the *trans*-ligand in this case. Such an assumption was reasonably accepted in 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^-) in the previous work.[5] The results obtained here account for the fact that one of the most important factors in determining the rates of the electron-transfer reactions of the Co(III) complexes is the free energy for bond stretching of the Co–N bond in the Fe^{2+} reductions of *cis*-CoN_4XCl^{n+} and CoN_5Cl^{2+}. The major factors which affect the effectiveness may be: the effect of the solvation in the Cr^{2+} reductions of $CoN_5SO_4^+$, the ligand-field strength of the *trans*-ligand, and the energy required to stretch the Co–N bond in the Fe^{2+} reductions of the CoN_5Cl^{2+}, and the effect of the solvation, the ligand-field strength of the *trans*-ligand, and the stretching energy in the Fe^{2+} reductions of the *cis*-$CoN_4Cl_2^+$.

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