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Electron-transfer Reactions of Multidentate Ligand Cobalt(III) Complexes. VI. The Effect of the Chelation of Nonbridging Ligands on the Iron(II) Reductions of Chlorocobalt(III) Complexes

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An earlier kinetic study of the reductions of several chlorocobalt(III) complexes, which proceed *via* the bridged activated states, suggested that the predominant factors controlling the rate of electron-transfer reactions are the energy for stretching the *trans*-ligand to the bridging one[1–3] and the effect of solvation.[4–6] More detailed data are necessary, however, to discuss the effect of nonbridging ligands on the rate. Therefore, the effects of the chelation of nonbridging ligands on the rate of the Fe^{2+} reductions of cobalt(III) complexes of the CoN_5Cl^{2+} and $CoN_4Cl_2^+$ types were investigated; the results will now be discussed.[7]

Experimental

trans-$[Co(en)(NH_3)_2Cl_2]Cl$,[7,8] *trans*-$[Co(en)_2Cl_2]Cl$,[9] and *cis*-$[Co(trien)NH_3Cl]Cl_2$[10] were prepared by the methods

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1) L. Orgel, Report of the Tenth Solvay Conference, Brussels, 289 (1956).

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4) Y. Kurimura, K. Ohashi, T. Ohtsuki, and K. Yamamoto, This Bulletin, **44**, 1293 (1971).

5) Y. Kurimura and K. Ohashi, *ibid.*, **44**, 1794 (1971).

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7) N=NH_3, 1/2 en, 1/2 pn, 1/2 tn, 1/3 dien, 1/4 trien, and 1/5 tetren; the abbreviations of the chelating agents are: en=ethylenediamine, pn=propylenediamine, tn=triethylenediamine, dien=diethylenetriamine, trien=triethylenetetramine, and tetren=tetraethylenepentamine.

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9) A. Werner, *Ber.*, **34**, 1733 (1901).

10) R. G. Pearson, G. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

described in the references cited. *cis*-$[Co(pn)_2NH_3Cl]Cl_2$, *trans*-$[Co(pn)_2Cl_2]Cl$, and $[Co(dien)ACl]Cl_2$ (A=pn and tn) were prepared by methods similar to those used for *cis*-$[Co(en)_2NH_3Cl]Cl_2$,[11] *trans*-$[Co(en)_2Cl_2]Cl$,[9] and $[Co(dien)(en)Cl]Cl_2$[10] respectively. The purity of the Co(III) complexes was ascertained by the elementary analysis of carbon, nitrogen, and hydrogen. The kinetics were followed by observing the change in the absorbance of the reaction mixture of the complex. The preparation of the ferrous perchlorate solution was described previously.[4] For all cases, rate studies were carried out with an excess of a reductant as pseudo-first order conditions. For the case of *trans*-$Co(en)(NH_3)_2Cl_2^+$, a lower concentration of the Co(III) ($\sim 2\times 10^{-4}$ M) was employed for the kinetic measurements because of its lower solubility; thus, scale-expander attachement for a Hitachi Model 124 spectrophotometer was used. The ionic strength of the reaction mixture was adjusted by the addition of sodium perchlorate.

Results and Discussion

The rate constants for the Fe^{2+} reduction, and the relative rates for the Fe^{2+} reduction and acid hydrolysis of the Co(III) complexes, are presented in Tables 1 and 2 respectively. It is safe to assume that the Fe^{2+} reduction of CoN_5Cl^{2+} and $CoN_4Cl_2^+$ proceeds *via* the chloride-bridged mechanism.[3,5,6]

In previous discussions it was suggested[4,5] that the free energy for the bond stretching of the Co–N bond, especially that of the *trans*-N to the bridging ligand, is an important factor in the Fe^{2+} reduction of the CoN_5Cl^{2+}, and that both free energy for the bond stretching and the solvation effect[4–6] are major factors in the Fe^{2+} reduction of the $CoN_4Cl_2^+$ in determining the rate of electron-transfer reaction.[15] It is clear from Table 2 that an increase in chelation, such as replacing two NH_3 ligands by one ethylenediamine molecule, shows a progressive decrease in the rate of the reduction.

The relative rate constant of the *cis*-$Co(en)_2NH_3Cl^{2+}$ is about four times smaller than that of the *trans*-isomer. This suggests that the reduction rate is much more sensitive to the free energy for the reorganization of the *trans*-ligand than that of the *cis*-ligand for the CoN_5Cl^{2+} type: the effectiveness of *cis*-$Co(en)_2NH_3Cl^{2+}$ would be lower than that of the *trans*-isomer, since the reorganization energy for the *trans*-N ligand (en) of the former would be greater than that for the *trans*-ligand (NH_3) of the latter.

Table 1. Rate constants for the iron(II) reduction of cobalt(III) complexes

Complex ion	k[a]/$M^{-1}sec^{-1}$
cis-$Co(pn)_2NH_3Cl^{2+}$	2.5×10^{-5}
$Co(dien)(pn)Cl^{2+}$	8.0×10^{-6}
$Co(dien)(tn)Cl^{2+}$	1.4×10^{-5}
cis-$Co(trien)NH_3Cl^{2+}$	2.5×10^{-6}
trans-$Co(en)(NH_3)_2Cl_2^+$	0.36
trans-$Co(pn)_2Cl_2^+$	2.6×10^{-2}

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

Table 2. Relative rate constants for the Fe^{2+} reduction and acid hydrolysis of Co(III) complexes of the CoN_5Cl^{2+} and CoN_4Cl^+ types

No	Complex ion	CoN_5Cl^{2+} type	
		$(R_{Fe})_1$[a]	$(R_{aq})_1$[d]
1	$Co(NH_3)_5Cl^{2+}$	1.0	1.0
2	*cis*-$Co(en)_2NH_3Cl^{2+}$	1.3×10^{-2}	0.21
3	*cis*-$Co(pn)_2NH_3Cl^{2+}$	1.9×10^{-2}	
4	*trans*-$Co(en)_2NH_3Cl^{2+}$	4.9×10^{-2}	
5	$Co(dien)(en)Cl^{2+}$	4.4×10^{-3}	0.78
6	$Co(dien)(pn)Cl^{2+}$	5.9×10^{-3}	
7	$Co(dien)(tn)Cl^{2+}$	1.0×10^{-2}	
8	*cis*-$Co(trien)NH_3Cl^{2+}$	1.9×10^{-3}	0.10
9	$Co(tetren)Cl^{2+}$	very small	0.033
No	Complex ion	*trans*-$CoN_4Cl_2^+$ type	
		$(R_{Fe})_2$[b]	$(R_{aq})_2$[e]
10	*trans*-$Co(NH_3)_4Cl_2^+$	1.0	1.0
11	*trans*-$Co(en)(NH_3)_2Cl_2^+$	0.16	0.13
12	*trans*-$Co(en)_2Cl_2^+$	1.4×10^{-2}	1.8×10^{-2}
13	*trans*-$Co(pn)_2Cl_2^+$	1.2×10^{-2}	3.4×10^{-2}
No	Complex ion	*cis*-$CoN_4Cl_2^+$ type $(R_{Fe})_3$[c]	
14	*cis*-$Co(NH_3)_4Cl_2^+$	1.0	
15	*cis*-$Co(en)_2Cl_2^+$	1.2×10^{-2}	
16	*cis*-$Co(trien)Cl_2^+$	2.9×10^{-3}	

a) Ratio of rate constant to that of $Co(NH_3)_5Cl^{2+}$ ($k=1.35\times 10^{-3}$ M^{-1} s^{-1})[12] at 25 °C and $\mu=1.0$, calculated from the rate constants listed in Refs. 12, 3, and 6, and those obtained by this work,

b) Ratio of rate constant to that of *trans*-$Co(NH_3)_4Cl_2^+$ ($k=2.21$ M^{-1} s^{-1})[13] at 25 °C and $\mu=1.0$, calculated from the rate constants listed in Refs. 3 and 13, and those obtained by this work,

c) Ratio of rate constant to that of *cis*-$Co(NH_3)_4Cl_2^+$ ($k=0.136$ M^{-1} s^{-1}),[12] calculated from the rate constants in Refs. 3, 5, and 12,

d) Ratio of rate constant for the acid hydrolysis to that of $Co(NH_3)_5Cl^{2+}$ at 35 °C, from Ref. 14.

e) Ratio of rate constant for the acid hydrolysis to that of *trans*-$Co(NH_3)_4Cl_2^+$ at 25 °C, from Ref. 14.

An appreciable decrease in the rate can also be seen when we replace the four NH_3 ligands of the *trans*-$Co(NH_3)_4Cl_2^+$ by two ethylenediamines. That is, the reduction rate is as sensitive to the chelation of the *cis*-ligands as that of the *trans*-ligand for the $CoN_4Cl_2^+$ type (Tables 2, 10 and 12, and 14 and 15). This may be due to (a) the effect of solvation, and (b) the effect of free energy on the reorganization of the non-bridging ligands. The effect of (a) may be explained as follows. The larger the complex ion, the less its solvation energy will be. Therefore, the rate is reduced by chelation because of the reduced stability of the transition state resulting from less efficient solvation.[4,6,14] A similar solvation treatment was given

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[11] a) A. Werner, *Ann. Chem.*, **386**, 165 (1912); b) A. Werner and V. L. Kino, *Ber.*, **44**, 1890 (1911).

[12] J. H. Espenson, *Inorg. Chem.*, **4**, 121 (1965).

[13] R. G. Linck, *ibid.*, **7**, 2394 (1968).

[14] F. Basolo and R. G. Pearson, "Mechanism of Inorganic reactions," John Wiley & Sons, New York (1967), p. 161.

[15] In the $CoN_5Cl^{+}+Fe^{2+}\rightarrow Co^{2+}+5N+FeCl^{2+}$ reaction the over-all charges on the Co(III) and Co(II) are not identical, so the solvation effect is considered to be an important factor in the reaction.[6]

in order to explain the effect of the chelation on the acid hydrolysis of the Co(III) complexes, though this theory does not distinguish between S_N1 and S_N2 mechanisms.[14] An interesting fact is that the values of $(R_{Fe})_2$ for *trans*-$CoN_4Cl_2^+$ are almost parallel to those of $(R_{aq})_2$: the rate constants of the Fe^{2+} reduction and those of the acid hydrolysis decrease by a factor of about one by replacing the two NH_3 ligands by one ethylenediamine. The $(R_{Fe})_1$, $(R_{Fe})_2$, and $(R_{Fe})_3$ represent the ratios of the rate constant for the Fe^{2+} reduction to those of $Co(NH_3)_5Cl^{2+}$, *trans*-$Co(NH_3)_4Cl_2^+$, and *cis*-$Co(NH_3)_4Cl_2^+$ respectively, while $(R_{aq})_1$ and $(R_{aq})_2$ represent the ratios of the rate constants for the aquation to those of $Co(NH_3)_5Cl^{2+}$ and *trans*-$Co(NH_3)_4Cl_2^+$ respectively.

Table 2 also shows the effect on the rate of increase in the size of the chelate ring from five members to six when trimethylenediamine is used instead of ethylenediamine. For both the CoN_5Cl^{2+} and $CoN_4Cl_2^+$ types, the rates are little affected by using the propylenediamine instead of ethylenediamines (Table 2, Nos 3 and 4, 5 and 6, and 12 and 13). However, the rate is doubled by replacing two ethylenediamines by two trimethylenediamines. This increase in the rate may be related to the fact that complexes with six-membered chelate rings are much less stable than those with five-membered chelate rings.[14,16]

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16) S. Chaberek and A. E. Martell, "Organic Sequestring Agents," John Wiley & Sons, New York (1959), p. 126.