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The Kinetics of the Electron-transfer Reactions between Several Chloropentakis(alkylamine)cobalt(III) Complexes and Iron(II)

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In previous papers, the effect of the *cis*-ligand to the bridging chloride ion on the reactivity of *cis*-Co(en)$_2$-ACl^{2+}[1] (A=alkylamine and aminoalcohol) and the effect of amino acid[2] as the nonbridging ligand on the reactivity of *trans*(O,Cl)-Co(dien)(am)Cl^{+} (am=amino acid, dien=diethylenetriamine) and *trans*(*N*)-Co(am)$_2$-(ox)$^-$ (ox=oxalic acid) in the iron(II) reductions of these complexes have been reported.

It was demonstrated that the reactivity of *cis*-Co(en)$_2$-ACl^{2+} decreased slightly with an increase in the size of alkylamine and that the specific reduction rate for the β-alanine cobalt(III) complex was considerably larger than that for the other amino acid cobalt(III) complexes investigated.

Buckingham *et al.*[3] found that the base and acid hydrolyses of a series of chloropentakis(alkylamine)-cobalt(III) complexes were very much accelerated by the steric interaction of the alkylamines. The reactivities of these complexes are increased with increases

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[1] Y. Kurimura and K. Ohashi, This Bulletin, **44**, 1797 (1971).

[2] K. Ohashi, K. Yamamoto, I. Hirako, and Y. Kurimura, *ibid.*, in prees.

[3] D. A. Buckingham, B. M. Foxman, and A. M. Sargeson, *Inorg. Chem.*, **9**, 1790 (1970).

Table 1. The rate constants, the activation parameters for iron(II) reductions at 25±0.1°C and absorption maximum of cobalt(III) complexes

Complex	Rate constant[a) $\mathrm{M}^{-1}\cdot\mathrm{sec}^{-1}$	$\Delta H^{\neq}$ kcal/mol	$\Delta S^{\neq}$ eu	nm λ_{max}[b)	λ_{max}[c)
$Co(NH_3)_5Cl^{2+}$	7.30×10^{-3}	16.9	−10.4	525	362
trans-$Co(NH_3)_4(CH_3NH_2)Cl^{2+}$	1.26×10^{-2}	16.3	−11.0	535	364
$Co(CH_3NH_2)_5Cl^{2+}$	4.72×10^{-2}	14.8	−13.7	550	380
$Co(n\text{-}C_3H_7NH_2)_5Cl^{2+}$	9.14×10^{-2}	13.4	−16.4	550	383
$Co(i\text{-}C_4H_9NH_2)_5Cl^{2+}$	1.63×10^{-1}	—	—	550	382

a) $[H_2SO_4]=0.050\mathrm{M}$, $\sum[SO_4^{2-}]=0.50\mathrm{M}$
b) wavelength for the first absorption maximum
c) wavelength for the second absorption maximum

in the size of the alkylamine.

It is interesting to investigate the effect of the coordinated ligands on the reactivity of chloropentakis(alkylamine)cobalt(III) complexes with iron(II). Therefore, the present author wishes to report the results observed in the electron-transfer reactions of several chloropentakis(alkylamine)cobalt(III) complexes.

Experimental

Preparation of Complexes. $[Co(CH_3NH_2)_5Cl]Cl_2$,[4) $[Co(n\text{-}C_3H_7NH_2)_5Cl]Cl_2\cdot HCl$,[3) and $[Co(i\text{-}C_4H_9NH_2)_5Cl]Cl_2\cdot HCl$[3) were prepared by the methods described in the references cited. The *trans*-$[Co(NH_3)_4(CH_3NH_2)Cl]Cl_2$ was prepared by a manner similar to that for the preparation of *trans*-$[Co(^{15}NH_3)(NH_3)_4Cl](ClO_4)_2$.[5)

The wavelengths of the first and second absorption maxima for these complexes are listed in Table 1, along with the rate constants.

Materials. The preparation of a stock solution of iron(II) sulfate and the determination of iron(II), the sulfate ion, and the hydrogen ion were carried out by a method similar to that described in a previous paper.[6) All the other chemicals were of a guaranteed reagent grade. The concentration of sulfuric acid and the total concentration of the sulfate ion of the reaction mixture were adjusted to 0.05M and 0.50M respectively by the addition of sulfuric acid and sodium sulfate solutions.

Measurement of the Reaction Rate. The reactions were followed spectrophotometrically under pseudo-first-order conditions in which the iron(II) concentration was in a large excess to that of the Co(III) complex. The absorbance at the wavelengths corresponding to the first absorption maxima for the complexes were all recorded automatically except for the case of $Co(i\text{-}C_4H_9NH_2)_5Cl^{2+}$. Since the aquation of the $Co(i\text{-}C_4H_9NH_2)_5Cl^{2+}$ proceeded in some extent during the dissolution, the reduction rates were measured at 537 nm, which is the isosbestic point for this complex and $Co(i\text{-}C_4H_9NH_2)_5OH_2^{3+}$. The rate of the aquation of this complex during electron-transfer reaction was negligible small in comparison with that of the reduction during the initial period.

The activation parameters for all the complexes except for $Co(i\text{-}C_4H_9NH_2)_5Cl^{2+}$ were obtained from the log k *vs.* $1/T$ plot, using a linear least-squares method.

Results and Discussion

In the cases of $Co(NH_3)_5Cl^{2+}$, *trans*-$Co(NH_3)_4(CH_3NH_2)Cl^{2+}$, and $Co(CH_3NH_2)_5Cl^{2+}$, the plots of log (A_t-A_∞) *vs.* time were linear for at least two half-lives, but for the $Co(n\text{-}C_3H_7NH_2)_5Cl^{2+}$ and $Co(i\text{-}C_4H_9NH_2)_5Cl^{2+}$, the reaction obeyed a pseudo-first-order sequence for a 60% reaction.

The rates for these reductions are first-order dependences on the Co(III) and Fe(II) concentrations respectively.

In spite of the lability of iron(III) complexes, it has been found, by a direct observation of the transient species $FeCl^{2+}$, that the reactions of cobalt(III) complexes, such as $Co(NH_3)_4OH_2Cl^{2+}$,[7) $Co(HEDTA)Cl^-$,[7) and $Co(OH_2)_5Cl^{2+}$,[8) with iron(II) proceed *via* the chloride-bridged activated states. Therefore, it seems reasonable to assume a similar mechanism for the present reactions. The most important factors in determining the rates of the inner-sphere electron-transfer reactions of cobalt(III) complexes may be: (1) the ligand field strength of the *trans*-ligand which is located at the *trans*-position to the bridging ligand, and (2) the energy for stretching the *trans*-ligand away from the cobalt(III) center. The greater reactivity for *trans*-$Co(NH_3)_4(CH_3NH_2)Cl^{2+}$ than $Co(NH_3)_5Cl^{2+}$ may be ascribed to the weak ligand-field strength for the *trans*-ligand (methylamine) in the former compared with that for the *trans*-ligand (ammonia) in the latter (Table 1).

The rate constants shown in Table 1 indicate that the reactivity of the cobalt(III) complexes of the CoA_5Cl^{2+} type, where A is alkylamine, increases slightly with the size of the alkylamine ligand.

In a previous work,[1) it was suggested that the reactivity of *cis*-$Co(en)_2ACl^{2+}$ in the reduction by iron(II) decreased slightly with an increase in the size of the alkylamine from methylamine to butylamine. The specific rates for CoA_5Cl^{2+} with iron(II) are increased, however, with an increase in the size of alkylamine. The ligand-field strengths of alkylamines are of almost the same degree. Consequently, the small increase in the reactivity of CoA_5Cl^{2+} may be caused by the steric interaction[3) between the coordinated alkylamines. This steric interaction would reduce the reorganization

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[4) R. Mitzner, P. Blankenburg, and W. Depkat, *Z. Chem.*, **9**, 68 (1960).

[5) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **88**, 5443 (1966).

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

[7) A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, **88**, 5343 (1966).

[8) T. J. Conochioli, G. Nancollas, and N. Sutin, *ibid.*, **86**, 1453 (1953).

energy for the reduction. No detailed explanation of such a steric effect can be made from the results thus far obtained.

The rates of the base and acid hydrolyses of chloropentakis(alkylamine)cobalt(III) complexes are very much increased with the size of alkylamine. For example, the relative reactivities for the base and acid hydrolyses of $Co(i\text{-}C_4H_9NH_2)_5Cl^{2+}$ are, respectively about 6×10^5 and 10^2 times greater than those of $Co(NH_3)_5Cl^{2+}$.

In the Fe(II) reduction reactions of chloropentakis(alkylamine)cobalt(III) complexes, the effect of the size of alkylamine is very small compared with that in the base and acid hydrolyses reactions. This indicates that the steric effect of the nonbridging ligand in the Fe(II) reduction is not very important.

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