The Effect of Axial Ligands on the Reductions of Co(III) Complexes with a Macrocyclic Schiff-base Ligand by Fe(edta)$^{2-}$

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The second-order rate constants for the reduction of cobalt(III) complexes with a macrocylic Schiff-base ligand, $Co(dop)L_2^{2+}$ (dop=*N,N'*-bis(2-hydroxyimino-1-methylpropylidene)-1,3-propanediamine and L=primary amine), by Fe (edta)$^{2-}$ are very sensitive to the nature of the axial ligands. The rate increases with a decreases in the basicity of the axial ligands: the order is methylamine, ethylamine, 2-aminoethanol, toluidine, aniline, and bromoaniline derivatives. It is shown that there is a linear relationship between the logarithmic second-order rate constant and the pK_a of the axial primary amine ligand. Among the series of primary amine derivatives, the differences in the free energy of the activation for the reduction can be considered to be mainly dependent upon those in the enthalpy of the activation for the bond stretching of the Co–N (axial ligand) prior to the electron-transfer.

Various kinetic and thermodynamic properties of cobalt(III) complexes with macrocyclic Schiff-base ligands have been well studied in view of the similarities of numerous chemical properties of these with those of the derivatives of coenzyme B_{12}.[1–16] In the ligand-substitution process of such complexes it is demonstrated that the reactive sites are essentially those in the axial ligand resulting from a very high stability of the coordination bonds between the cobalt(III) ion and the equatorial ligands.[15]

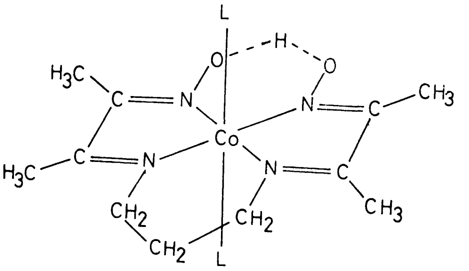

Fig. 1. $Co(dop)L_2^{2+}$.

In the redox process of the cobalt(III)–macrocyclic-ligand complexes, a linear relationship has been found between the polarographic halfwave potential of the first reduction wave and the p*K* value of the axial Lewis base ligands of the $Co(salen)L_2^+$(salen=*N,N'*-disalicylidene-ethylenediamine) and $Co(dop)L_2^{2+}$ (dop =*N,N'*-bis(2-hydroxyimino-1-methylpropylidene)-1,3-propanediamine).[14] The rate constants for the outer-sphere oxidation of $Co^{II}(N_4)X_2(N_4$=a tetradentate macrocyclic ligand) have been shown to be experimentally correlated to the standard free energy of the reactions.[17] There have been few investigations concerning the effect of the nature of the axial and equatorial ligands on the rate of the reductions of the cobalt(III) complexes with a macrocyclic Schiff-base ligand.

We wish now to report and discuss the influence of axial ligands on the reduction rate of the cobalt(III) complex ions of the $Co(dop)L_2^{2+}$ type by Fe(edta)$^{2-}$. The Fe(edta)$^{2-}$ has been shown to be a good reducing agent for several cobalt(III) complexes in the neutral pH region, and the mechanisms of these reductions have been investigated.[18]

Experimental

Materials. $[Co(dop)Cl_2]$ was prepared after the literature procedure.[19] Complexes of the $[Co(dop)L_2](ClO_4)_2$ type were synthesized by a manner similar to that used in the preparation of $[Co(dop)(NH_3)_2](ClO_4)_2$ described elesewhere.[19] The analytical data of the cobalt(III) chelates prepared are presented in Table 1. The NMR spectra were recorded in DMSO-d_6, with tetramethylsilane as the internal standard. The *trans*-structure of all the chelates were confirmed by their NMR spectra (Table 2). The buffer components, inorganic salts, and disodium salt of ethylenediamine-*N,N,N',N'*-tetraacetic acid were of a guaranteed grade and were used without further purification. The iron(II) chelate solution was prepared by a manner similar to that described previously.[18] The solutions of the iron(II) chelate and the cobalt(III) complexes were adjusted to the described pH and ionic strength by the use of acetate-buffer and potassium-chloride solutions respectively.

Kinetic Measurements. The reduction of the cobalt(III)

TABLE 1. ANALYTICAL DATA OF $[Co(dop)L_2](ClO_4)_2$

L	Found (Calcd) %		
	C	H	N
Cl^- [a]	35.78(35.73)	5.20(4.98)	15.18(15.07)
CH_3NH_2	27.55(27.92)	5.16(5.23)	14.79(15.03)
$C_2H_5NH_2$	30.33(30.68)	5.79(5.66)	14.01(13.63)
$HOC_2H_4NH_2$	29.18(29.09)	5.39(5.38)	13.58(13.57)
$C_6H_5NH_2$	40.08(40.42)	5.27(4.87)	12.24(12.30)
$CH_3C_6H_4NH_2$	42.03(42.21)	5.41(5.24)	11.79(11.81)
$BrC_6H_4NH_2$	39.94(32–84)	3.36(3.72)	9.89 (9.99)

a) $[Co(dop)Cl_2]$.

TABLE 2. NMR SPECTRAL DATA OF $[Co(dop)L_2](ClO_4)_2$ IN DMSO-d_6

L	δ /ppm		
	$(-CH_2-)_3$ [a]	$CH_3\backslash C{=}N/O-$	$CH_3\backslash C{=}N/C-$
CH_3NH_2	≈3.85	2.58	2.48
$C_2H_5NH_2$	≈3.9	2.58	2.48
$HO(CH_2)_2NH_2$	≈3.9	2.60	2.48
$C_6H_5NH_2$	≈4.0	2.55	2.24
$CH_3C_6H_4NH_2$	≈4.0	2.54	2.24
$BrC_6H_4NH_2$	≈4.1	2.64	2.32

a) Broad signal.

complexes by the iron(II) chelate were carried out under an atmosphere of nitrogen which had been purified by passing it through acidic chromium(II) ion solutions. Kinetic runs were made under pseudo-first-order conditions in which the concentration of the iron(II) calculate was at least twenty times that of cobalt(III). For relatively slow reactions, the rate was monitored by the measurement of the absorption change (≈500 nm) of the reaction mixture in a thermostated cell compartment of a Union Giken SM-101 spectrophotometer. The cobalt(III) and the iron(II) chelate solutions were mixed by means of a Union Giken MX-7 mixing apparatus. Reaction which were too rapid to be followed by the conventional technique were studied with a Yanagimoto SPS-1 stopped-flow spectrophotometer. The spectral change of the reaction mixture, shown in Fig. 2, was observed by means of a Union Giken RA-1300 rapid-scan spectrophotometer.

Results and Discussion

It was estimated from the known values of the formation constants of the iron(II) chelate species[20)] that the predominant species of the iron(II) chelate in the reaction mixture was the normal form of Fe(edta)$^{2-}$ under the conditions employed. The iron(III) chelate species produced in the reaction mixture by the oxidation of Fe(edta)$^{2-}$ could also be estimated to be the normal form of Fe(edta)$^-$.[20)] A gradual increase in the absorbance at about 510 nm due to the cobalt(II) chelate was observed upon the addition of a solution of the iron(II) chelate to that of the cobalt(III) chelate under a nitrogen atmosphere. In the wave-length region between 500 and 600 nm, the molar extinction coefficients of the cobalt(III), iron(II), and iron(III) in the reaction mixture were very small compared with that of the cobalt(II) chelate under the present conditions. An example of the spectral change for Co(dop)(HOC$_2$H$_4$NH$_2$)$_2^{2+}$ is presented in Fig. 2. It is considered that the reductions of cobalt(III) chelates by Fe(edta)$^{2-}$ all give a product of the cobalt(II) which has a square planar configuration. It has been reported that the cobalt(II)–macrocyclic Schiff-base complexes with a square planar configuration have one or two absorption peaks (log $\varepsilon = 10^3 - 10^4$) in the visible region.[22,23)]

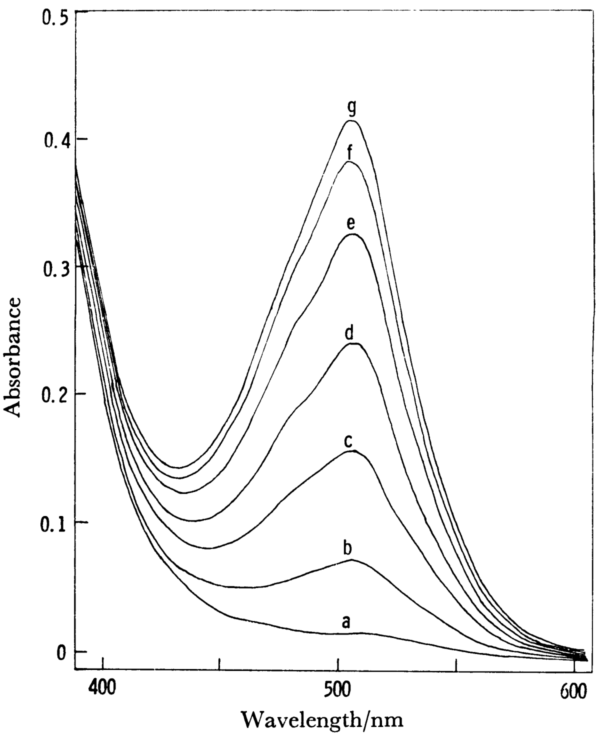

Fig. 2. Spectral change of the reaction mixture.
Initial concentrations: [Co(dop)L$_2^{2+}$]$_0$ = 1.0 × 10^{-4} M, L = 2-aminoethanol, [Fe(edta)$^{2-}$]$_0$ = 1.0 × 10^{-3} M, pH = 5.0, μ = 0.2, room temp, Scan time: 20 nm/s, a: initial stage, b: 110 s, c: 240 s, d: 420 s, e: 720 s, f: 1200 s, g: final stage.

TABLE 3. RATE CONSTANTS FOR THE Fe(edta)$^{2-}$-REDUCTIONS OF Co(dop)L$_2^{2+}$ AT μ=0.2 AND 25°C[a)]

L	k/M^{-1} s^{-1}
CH$_3$NH$_2$	$(6.8 \pm 0.5) \times 10^{-2}$
	7.1×10^{-2} [b)]
C$_2$H$_5$NH$_2$	$(1.4 \pm 0.06) \times 10^{-1}$
HOC$_2$H$_4$NH$_2$	1.9 ± 0.04
	1.9[c)]
	2.0[d)]
C$_6$H$_5$NH$_2$	$(3.4 \pm 0.05) \times 10^3$
	3.1×10^3 [e)]
	3.2×10^3 [f)]
CH$_3$C$_6$H$_4$NH$_2$	$(1.3 \pm 0.04) \times 10^3$
BrC$_6$H$_4$NH$_2$	$(5.3 \pm 0.5) \times 10^3$

a) Unless otherwise stated, the experimental conditions were [Co(dop)L$_2^{2+}$]$_0$ = 1.0 × 10^{-4}M, [Fe(II)]$_0$ = 2.0 × 10^{-3}M, [X]$_f$ = 0M ([X]$_f$ is the concentration of free amine), and pH = 5.0. b) [X]$_f$/[Co(III)]$_0$ = 100. c) pH = 4.5. d) pH = 5.4. e) [Fe(II)]$_0$/[Co(III)]$_0$ = 48. f) [Fe(II)]$_0$/[Co(III)]$_0$ = 98.

Plots of $\log(A_\infty - A_t)$ *vs.* time were linear for at least three half-lives for the saturated amine derivatives and two half-lives for the aromatic amine derivatives, where A_∞ is the absorbance when the reaction is completed and A_t, that at time t. The second-order rate constants can be calculated by means of this equation: $k = 2.303 \times m/[\mathrm{Fe(II)}]$, where m is the value of the slope of the straight line. The second-order rate constants for the primary amine derivatives are summarized in Table 3. The second-order rate constants were kept essentially constant by varying the initial concentration of the iron(II) chelate from 2.0 × 10^{-3} to 1.0 × 10^{-2} M; they were independent of the hydrogen-ion concentration in the pH region between 4.5 and 5.4. A rate law consistent with the experimental results is given by:

$$d[\mathrm{Co(II)}]/dt = k[\mathrm{Co(III)}][\mathrm{Fe(edta)}^{2-}] \qquad (1)$$

where k is the second-order rate constant.

It may safely be assumed that the rate constants obtained correspond to those of Reaction 2, because the reaction is first-order with respect to the concentration of the iron(II) chelate and the rate is not affected by the initial addition of the corresponding free amine to the reaction mixture:

$$\mathrm{Co(dop)L_2^{2+}} + \mathrm{Fe(edta)^{2-}} \rightleftharpoons \mathrm{Co(dop)L_2^{+}} + \mathrm{Fe(edta)^{-}} \qquad (2)$$

$$\mathrm{Co(dop)L_2^{+}} \rightleftharpoons \mathrm{Co(dop)^{+}} + 2\mathrm{L} \qquad (3)$$

That is, the rate-determining step of the reaction is Reaction 2, not the ligand-substitution process represented by 3.

The rate data summarized in Table 3 show that the rate is very sensitive to the nature of the axial ligands: the value of the rate constants vary from 6.8×10^{-2} M^{-1} s^{-1} for methylamine to 5.3×10^3 M^{-1} s^{-1} for bromoaniline. The reduction rate is enhanced by a decrease in the donor ability of the axial Lewis-base ligand. For a series of runs while varying the axial ligands, a linear relationship between the logarithmic rate constant and the pK_a of the amines was found to hold for the reactions investigated (Fig. 3).

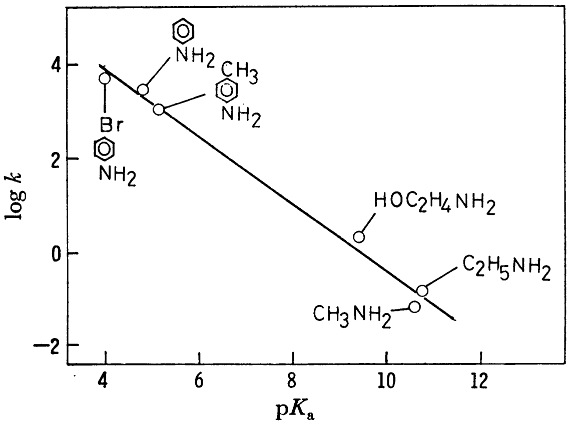

Fig. 3. Relationship between pK_a of axial amine ligand and logarithmic rate constant of the reduction of Co(dop)L_2^{2+} by Fe(edta)$^{2-}$.

Based on the Franck-Condon principle, for the reductions of the cobalt(III) complexes, the reorganization of the cobalt(III) complex would occur prior to the electron-transfer to lower the energy level of the acceptor orbital, which may be d_{z^2} one.[24–26] In the present case, the amounts of free energy for the reorganization may be considered to be dependent upon that for stretching the axial ligands, since the free energy for the reorganization of these ligands would be small as compared with that of the equatorial tetradentate ligand, which is tightly coordinated to the cobalt(III) ion. Such bond stretching energy may increase with an increase in the bond strength between the cobalt(III) ion and the donor atom of the primary amine. It is considered that the Co–N (axial ligand) bond is strengthened when the value of pK_a of the amine increases, since it has substantially the σ bonding nature. It might be concluded that the linear relationship shown in Fig. 3 holds in the electron-transfer reactions, since the predominant factor controlling the activation free energy is the free energy for the reorganization of the axial ligands.

Table 4. Activation parameters for the reduction of Co(dop)L_2^{2+}

L	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/e.u.
CH_3NH_2	22.9	8.6
$C_2H_5NH_2$	23.9	18.0
$HOC_2H_4NH_2$	18.4	13.2
$C_6H_5NH_2$	16.2	12.0
$CH_3C_6H_4NH_2$	17.5	13.7
$BrC_6H_4NH_2$	15.0	10.0

The activation parameters for the reactions obtained from the temperature dependence of the rate constant are presented in Table 4. The relatively small variation in the activation entropy as compared with that in the activation enthalpy seems to indicate that the large change in the rate constant upon the variation in the axial ligands is mostly attributable to the relatively large variation in the activation enthalpy.

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20) The pK values of EDTA are pK_1=1.99, pK_2=2.67, pK_3=6.16, and pK_4=10.26, while the formation constants are log $K_{Fe^{II}HL}$=2.8, log $K_{Fe^{II}L}$=14.3, log $K_{Fe^{II}HL}$=1.4, log-$K_{Fe^{III}L}$=25.1, and log $K_{Fe^{III}OHL}$=6.5.[21] The definitions used here are $K_{Fe^{II}L}$=[FeY^{2-}]/[Fe^{2+}][Y^{4-}](Y=edta), $K_{Fe^{II}LH}$=[FeHY$^-$]/[FeY^{2-}] [H$^+$], $K_{Fe^{III}L}$=[FeY$^-$]/[Fe^{3+}][Y^{4-}], $K_{Fe^{III}HL}$=[FeHY]/[FeY$^-$][H$^+$], and $K_{Fe^{III}OHL}$=[Fe(OH)Y^{2-}]/[FeY$^-$]-[OH$^-$].

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