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Electrode Kinetics of the Redox Couples of Co(III/II) Complexes with Ethylenediamine-*N*-acetate, Iminodiacetate, and Diethylenetriamine

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The electrochemical kinetic parameters of $\mathrm{Co(edma)_2^{1+/0}}$ (edma: ethylenediamine-*N*-acetate), $\mathrm{Co(ida)_2^{1-/2-}}$ iminodiacetate), $\mathrm{Co(dien)_2^{3+/2+}}$ (dien: diethylenetriamine), $\mathrm{Co(1,2\text{-}pn)_3^{3+/2+}}$ (1,2-pn: 1,2-propanediamine), and $\mathrm{Co(gly)_3^{0/1-}}$ (gly: glycinate) redox couples were determined by d.c. and normal pulse polarographic measurements as well as galvanostatic double pulse measurements. A difference in the evaluated kinetic parameters for the geometric isomers, *trans*(*O*)- and *cis*(*O*)-$\mathrm{Co(edma)_2^{1+/0}}$ and *trans*(*N*)- and *cis*(*N*)-$\mathrm{Co(ida)_2^{1-/2-}}$ couples, was recognized. The values of the standard rate constant for the bis forms with dien, edma, and ida were reduced with increase in the number of replacement of amino groups in dien by carboxyl groups. The standard rate constants of the redox couples of Co(III/II) complexes with a series of bi- and tridentate polyamines and aminocarboxylates increase in proportion to the number of nitrogen donor atoms involved in the ligands.

The relationship between the structure of metal complexes and their electrochemical reactivity has been the research subject of electrochemists for the past three decades.[1] Attempts were made to correlate the structure of Co(III) complexes with their polarographic half-wave potentials or to their reduction rates. The Co(III) complexes with a wide variety of unidentate ligands and their geometric isomers with mixed ligands were used for this purpose.

As regards Co(III) complexes with multidentate ligands, however, only a few papers have been reported. Bond *et al.*[2] found that the half-wave potentials for the reduction of three geometric isomers of $\mathrm{Co(dien)_2^{3+}}$ (dien=diethylenetriamine) in acetone solvent slightly differ from each other. Gouzerh[3] reported that the half-wave potentials of *cis*(*N*)- and *trans*(*N*)-$\mathrm{Co(ida)_2^{1-/2-}}$ (ida=iminodiacetate) redox couples are 0.16 and 0.05 V *vs.* SCE, respectively. Recently, Rader and Mcmillin[4] proposed that the electrolytic reductions of *cis*(*N*)- and *trans*(*N*)-$\mathrm{Co(ida)_2^-}$ isomers are reversible and irreversible, respectively, and that the *cis*(*N*) configuration is favored in the Co(II) system. However, no attempt has been made to evaluate the electrochemical kinetic parameters. Systematic examination of the redox behavior of a series of similar metal complexes containing multidentate ligands has not been reported so far.

We have attempted to measure the electrochemical kinetic parameters of $\mathrm{Co(dien)_2^{3+/2+}}$, $\mathrm{Co(edma)_2^{1+/0}}$ (edma=ethylenediamine-*N*-acetate) and $\mathrm{Co(ida)_2^{1-/2-}}$ redox couples. Discussion was made on the relative effects of amino and carboxyl groups on the electrode kinetics, where dien, edma, and ida are chosen as typical tridentate ligands, which make the five-membered chelate ring with metal ion and contain the amino, imino, and/or carboxyl groups as the donating groups. The difference in the redox behavior of the geometric isomers was also examined. In order to confirm the results obtained for tridentate ligands we have determined the kinetic parameters of $\mathrm{Co(1,2\text{-}pn)_3^{3+/2+}}$ (1,2-pn=1,2-propanediamine) and $\mathrm{Co(gly)_3^{0/1-}}$ (gly=glycinate) redox couples.

Experimental

Reagents. *trans*-(*O*)-$\mathrm{Co(edma)_2^+}$ and *cis*(*O*)-$\mathrm{Co(edma)_2^+}$ were prepared according to the method of Fujii *et al.*[5] *cis*-Complexes obtained, however, contained an appreciable amount of *trans*-form. A *trans*-form free product was obtained by the following procedure utilizing the fact that the *trans*-form is soluble in a concentrated sodium perchlorate solution but not the *cis*-form: the initial product was dissolved in a saturated $NaClO_4$ solution, and the *cis*-complex precipitated was filtered, decanted with cold water and methanol, and dried. *cis*(*N*)-$\mathrm{Co(ida)_2^-}$,[6] *trans*(*N*)-$\mathrm{Co(ida)_2^-}$,[6] $\mathrm{Co(dien)_2^{3+}}$,[7] $\mathrm{Co(1,2\text{-}pn)_3^{3+}}$,[8] *mer*-$\mathrm{Co(gly)_3^0}$,[9] and *fac*-$\mathrm{Co(gly)_3^0}$,[9] were synthesized by the standard procedures, where the following abbreviations were used: edma, $NH_2CH_2CH_2NHCH_2COO^-$; ida, $NH(CH_2COO^-)_2$; dien, $NH_2CH_2CH_2NHCH_2CH_2NH_2$; 1,2-pn, $NH_2CH_2CH(CH_3)NH_2$; gly, $NH_2CH_2COO^-$. Results of the elementary analysis for each species are as follows:

trans(*O*)-$\mathrm{[Co(edma)_2]Cl\cdot 2H_2O}$	Found (%)	H(6.27), C(26.39), N(15 35), Cl(9.96),
	Calcd (%)	H(6.08), C(26.32), N(15.36), Cl(9.72)
cis(*O*)-$\mathrm{[Co(edma)_2]ClO_4}$	Found	H(4.65), C(24.01), N(14.20), Cl(8.97),
	Calcd	H(4.62), C(24.47), N(14.26), Cl(9 02)
trans(*N*)-$\mathrm{K[Co(ida)_2]\cdot 2H_2O}$	Found	H(3.86), C(23.73), N(7.00)
	Calcd	H(3.56), C(24.24), N(7.06)
cis(*N*)-$\mathrm{K[Co(ida)_2]\cdot 5/2H_2O}$	Found	H(3.48), C(23.79), N(6.94)
	Calcd	H(3.73), C(23.71), N(6.91)
mer-$\mathrm{[Co(dien)_2]Cl_3\cdot 2H_2O}$	Found	H(7.41), C(24.32), N(21.30) Cl(24.40)
	Calcd	H(7.41), C(23.57), N(20.61) Cl(26.09)
$\mathrm{[Co(1,2\text{-}pn)_3]Cl_3\cdot 2H_2O}$	Found	H(7.70), C(23.12), N(20 97), Cl(26.22)
	Calcd	H(8 08), C(25.51), N(19.83), Cl(25.10)
mer-$\mathrm{[Co(gly)_3]\cdot 2H_2O}$	Found	H(5.11), C(23.30), N(13 60)
	Calcd	H(5 08), C(22.73), N(13.25)
fac-$\mathrm{[Co(gly)_3]\cdot H_2O}$	Found	H(4.77), C(23.88), N(13.98)
	Calcd	H(4.72), C(24.09), N(14.04)

Ethylenediamine-*N*-acetic acid dihydrochloride dihydrate (Hedma·2HCl·2H_2O), diethylenetriamine (dien), and iminodiacetic acid were prepared and/or purified by the methods described in the previous paper.[10] 1,2-Propanediamine diperchlorate was prepared from perchloric acid and 1,2-propanediamine and then purified by recrystallization three times from water. Other chemicals were of reagent grade. All solutions were prepared with triply distilled water.

Apparatus. An apparatus containing d.c. and pulse polarographic modes constructed in our laboratory was employed, the polarograms being recorded with a X-Y recorder (Riken Denshi Co., Model F-42Cp, Tokyo). The electrolytic cell was designed to measure pH values accurately.[10] A digital pH/mV meter (Orion Research, Model 801) and a glass electrode (Beckman, No. 40495) were used for pH measurements. The dropping mercury electrode (DME) with the following characteristics was used: flow rate of mercury $m=0.45$ mg s^{-1}, the drop time $\tau=4.5$ s at the height of mercury head $h=72.0$ cm in 1 M $NaClO_4$ solution (1 M= 1 mol dm^{-3}). The test solution was deaerated with argon gas before each measurement of the current-voltage curves. All measurements were performed in a paraffin oil thermostat at 25.0±0.1 °C. Potentials were measured and recorded with respect to a saturated calomel reference electrode (SCE).

Results

D.c. and Normal Pulse Polarographic Measurements of trans*(O)- and* cis*(O)-Co(edma)$_2^{+/0}$ Couples.* A solution in which the bis-form of Co(II) complexes with respect to edma is predominantly present was used for the sake of convenience. The mechanism of the electrode processes might be as follows:

$$\begin{tikzcd} cis(O)\text{-Co(edma)}_2^+ \arrow[r, shift left, "+e"] & cis(O)\text{-Co(edma)}_2^0 \arrow[l, shift left, "\alpha_c(cis),\ k_0(cis)"] \arrow[d, shift right] \\ trans(O)\text{-Co(edma)}_2^+ \arrow[r, shift left, "+e"] & trans(O)\text{-Co(edma)}_2^0, \arrow[l, shift left, "\alpha_c(trans),\ k_0(trans)"] \arrow[u, shift right] \end{tikzcd} \tag{1}$$

where α_c denotes the cathodic transfer coefficient and k_0 the standard rate constant of the charge transfer process.

D.c. polarographic current-potential curves of *cis*(*O*)- and *trans*(*O*)-Co(edma)$_2^+$ in 1.0 M NaCl solution were measured in the pH range 8.3—9.7 and the quasi-reversible one-electron reduction waves with diffusion-controlled limiting currents were observed for both species. The reversible half-wave potential $E_{1/2}^r$ was determined by means of extrapolation,[11] the values obtained being given in Table 1. The difference in the values of $E_{1/2}^r$ of the *cis*- and the *trans*-forms exceeds 10 mV, being independent of the drop time in the range 3—6 s. This suggests that within the d.c. polarographic time scale the Co(II) species produced by the reduction at the electrode remain in the same geometric form as the Co(III) species, although the Co(II) species are labile, and the standard potential of the *cis*-Co(III/II) couple is *ca.* 10 mV more negative than that of *trans*-Co(III/II) couple. Thus in the analysis of d.c. and pulse polarographic waves it is not necessary to consider any effects of geometric configuration changes at the state of Co(II) complex.

The electrochemical kinetic parameters were evaluated from the analysis of normal pulse polarograms.

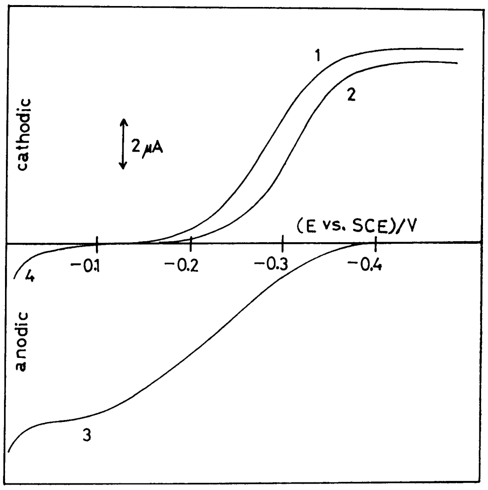

Fig. 1. Typical normal pulse polarograms of the Co(edma)$_2^{+/0}$ couple in 1.0 M NaCl solution.
(1): Reduction wave of 1.0 mM *trans* (*O*)-Co(edma)$_2^+$, (2): reduction wave of 1.0 mM *cis*(*O*)-Co(edma)$_2^+$, (3): oxidation wave of 1.0 mM Co(edma)$_2^0$, (4): residual current.
Concentration of Hedma=20 mM, pH=8.3 and sampling time $\tau_s=34.5$ ms.

Figure 1 shows typical normal pulse polarograms for the reduction of the *cis*(*O*)- and the *trans*(*O*)-Co(edma)$_2^+$ complexes as well as the oxidation of Co(edma)$_2^0$ complex. The half-wave potential of reduction waves shifted to cathodic direction with decreasing sampling time, τ_s, and their limiting current was diffusion-controlled, as proved from the fact that the product of the limiting current and $\tau_s^{1/2}$ is always constant.

The current-potential relationship for normal pulse polarograms of the simple electrode process, Ox+$ne\rightleftarrows$ Red, is given by[12]

$$E = E^* - \frac{2.303RT}{\alpha_c nF}\log\left\{x\left[\frac{1.75+x^2(1+\exp\zeta)^2}{1-x(1+\exp\zeta)}\right]^{1/2}\right\} \tag{2}$$

with

$$E^* = E_{1/2}^r + \frac{2.303RT}{\alpha_c nF}\log\left\{\frac{4}{\sqrt{3}}\,\frac{k_0\sqrt{\tau_s}}{\sqrt{D}}\right\}, \tag{3}$$

$$x = i/(i_d)_{\mathrm{Cott}}, \tag{4}$$

$$\zeta = (nF/RT)(E-E_{1/2}^r), \tag{5}$$

$$D = D_{\mathrm{Ox}}{}^{1-\alpha_c}D_{\mathrm{Red}}{}^{\alpha_c}, \tag{6}$$

where $(i_d)_{\mathrm{Cott}}$ denotes the diffusion current expressed by the Cottrel equation, i the normal pulse polarographic current, E the electrode potential, τ_s the sampling time, D_{Ox} and D_{Red} are the diffusion coefficients of Ox and Red, respectively, the other symbols having their usual meanings. The log-plots of the normal pulse polarograms, in which the log-term on r.h.s. of Eq. 2 is plotted against E, gave straight lines for the reduction of *cis*(*O*)- and *trans*(*O*)-Co(edma)$_2^+$ (Fig. 2). The straight lines have constant slopes for the *cis*(*O*)- and *trans*(*O*)-species, respectively, within experimental errors. The cathodic transfer coefficients were evaluated from their reciprocal slopes. The value of E^* was obtained from the intersects of these lines with the zero-line. The plots of E^* against log τ_s, shown in Fig. 3, give straight lines, their slopes also enabling us to evaluate the transfer

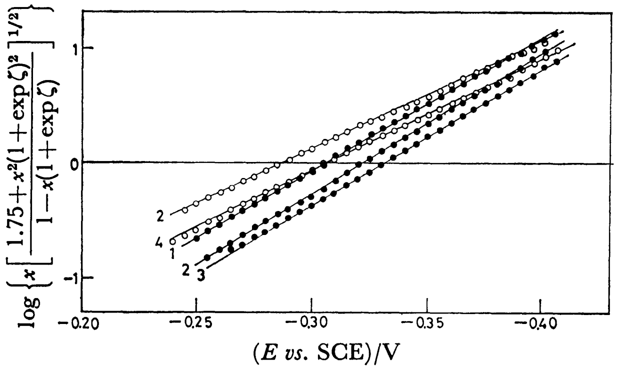

Fig. 2. Representative results for the plots of $\log\left[x\left\{\frac{1.75+x^2(1+\exp\zeta)^2}{1-x(1+\exp\zeta)}\right\}^{1/2}\right]$ vs. E for the reduction of 1.0 mM *cis*(*O*)- and *trans*(*O*)-Co(edma)$_2^+$.

(●): *cis*(*O*)-Species and (○): *trans*(*O*)-species. Sampling time τ_s = (1) 24.1 ms, (2) 8.7 ms, (3) 5.9 ms, and (4) 3.1 ms. Other conditions are same as in Fig. 1.

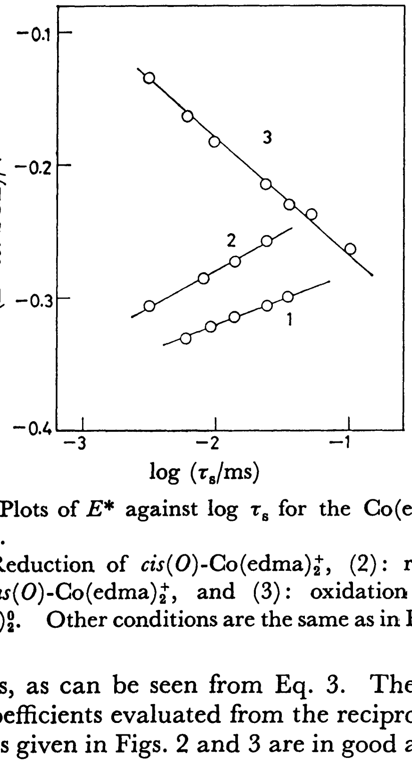

Fig. 3. Plots of E^* against log τ_s for the Co(edma)$_2^{+/0}$ couple.

(1): Reduction of *cis*(*O*)-Co(edma)$_2^+$, (2): reduction of *trans*(*O*)-Co(edma)$_2^+$, and (3): oxidation of Co(edma)$_2^0$. Other conditions are the same as in Fig. 1.

coefficients, as can be seen from Eq. 3. The cathodic transfer coefficients evaluated from the reciprocal slopes of the plots given in Figs. 2 and 3 are in good agreement with each other; they are 0.70 and 0.57 for the *cis*- and the *trans*-forms, respectively. The standard rate constants of charge transfer processes, k_0, were evaluated by means of Eq. 3. The values obtained are given in Table 1, where the values of diffusion coefficients used (6.2×10^{-6} and 7.3×10^{-6} cm^2 s^{-1} for the *cis*- and *trans*-forms, respectively) were obtained from the cathodic limiting currents of d.c. polarograms by using the Ilkovic equation or from those of normal pulse polarograms by using the Cottrell equation. We find that the standard rate constants for the reduction of the Co(III) complexes are in the order: *trans*(*O*)>*cis*(*O*).

The d.c. polarogram for the oxidation of the Co(edma)$_2^0$ complex shows the quasi-reversible nature (Fig. 4), its reversible half-wave potential being obtained as 0.281±0.001 V *vs.* SCE by means of extrapolation.[11]

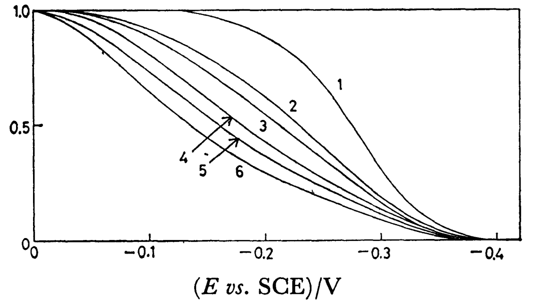

Fig. 4. Normalized d.c. and normal pulse polarograms for the oxidation of Co(edma)$_2^0$ in 1.0 M NaCl solution. (1) D. c. polarogram at the drop time τ=4.0 s, (2) normal pulse polarograms at the sampling time τ_s= 52.4 ms, (3) 24.1 ms, (4) 8.7 ms, (5) 5.9 ms, and (6) 3.1 ms. Other conditions are the same as in Fig. 1.

The half-wave potential of the normal pulse polarograms shifts to the anodic direction as the sampling time is reduced (Fig. 4), their limiting current being diffusion-controlled. At the sampling times below 30 ms the limiting currents of the oxidation wave start to overlap with the dissolution-wave of mercury. Thus, the current was measured as the difference between the total current and the residual current as measured in the solution containing no Co(II) ion at the same potential. The relevant electrochemical kinetic parameters for the oxidation of the Co(edma)$_2^0$ complex were evaluated according to the same procedure as mentioned for the reduction of Co(III) complex and are summarized in Table 1, where the value of diffusion coefficient used was 5.9×10^{-6} cm^2 s^{-1}.

At present we have no means to decide what form of the geometrical isomer of Co(edma)$_2^0$ complex is predominantly present in the bulk of solution. However, the following indicates that the predominant species at equilibrium is the *cis*(*O*)-form: (1) The value of the reversible half-wave potential obtained from the d.c. polarographic oxidation wave is in good agreement with that of the reduction wave of *cis*(*O*)-Co(edma)$_2^+$ complex, and (2) agreement between the standard rate constants determined from the oxidation wave of Co(II) complex and the reduction wave for the *cis*(*O*)-form of Co(III)

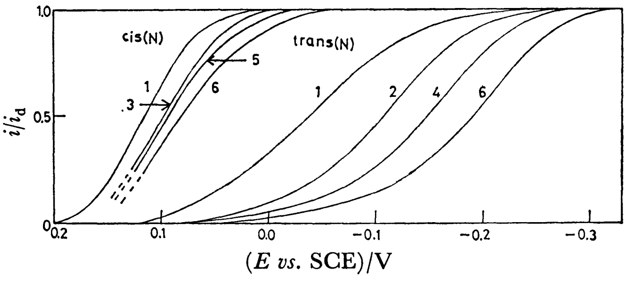

Fig. 5. Normalized d.c. and normal pulse polarograms for the reduction of 1.0 mM *cis*(*N*)-Co(ida)$_2^-$ in 1.0 M KNO$_3$ solution.

(1) D. c. polarogram at τ=4.2 s, (2) normal pulse polarograms at τ_s=75.0 ms, (3) 24.1 ms, (4) 14.0 ms, (5) 8.7 ms, and (6) 3.1 ms. Concentration of H$_2$ida= 10 mM and pH=8.3.

complex is quite good, the sum of their transfer coefficients being equal to unity.

D.c. and Normal Pulse Polarographic Measurements of trans-*(*N*)- and* cis*(*N*)-Co(ida)*$_2^{1-/2-}$ *Couples.* Figure 5 shows the d.c. and normal pulse polarograms for reduction of *trans*(*N*)- and *cis*(*N*)-Co(ida)$_2^-$ complexes under the conditions in which the bis-species exists predominantly in the state of Co(II). In the case of the *cis*-species the current was measured carefully as the difference between the total and residual currents since the reduction current of the complex at the foot of the wave overlapped with the dissolution current of mercury. The log-plot of d.c. polarogram for the *cis*-species give a straight line with the reciprocal slope of 58 mV, corresponding to the reversible wave, whereas the log-plot of the *trans*-species indicates that the electrode reaction is quasi-reversible (close to irreversible) (Fig. 6).

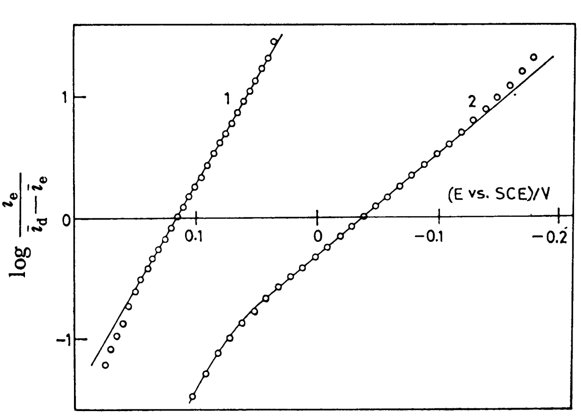

Fig. 6. D. c. polarographic log-plots for the reduction of *cis*(*N*)- and *trans*(*N*)-Co(ida)$_2^-$.
(1): *cis*(*N*) and (2) *trans*(*N*).

In order to evaluate the kinetic parameters of reduction for the Co(III) complex, it is necessary to know the isomer form of Co(II) complex produced by reduction. Rader and Mcmillin[4] proposed that the reduced product of *trans*(*N*)-Co(ida)$_2^-$ isomerizes to the corresponding *cis*-isomer and that *cis*(*N*)-Co(ida)$_2^-$ is formed at the electrode upon reoxidation, as judged from the assignment of UV-vis. absorption spectra of bulk electrolysis product. They also stated that the isomerization reaction may proceed rapidly. However, our detailed examination of the isomerization kinetics using the anodic normal pulse measurements with cathodic pre-electrolysis of the *cis*(*N*)- and *trans*(*N*)-Co(ida)$_2^-$ gave no support for the *rapid* isomerization. The overlap of the polarogram of anodic reaction for the Co(II) species with the dissolution current of mercury was a main obstacle against detailed analysis. That the formation of the *cis*-form does not proceed in a quantitative way within d.c. and pulse polarographic time-scales is suggested also by the disagreement between the reversible half-wave potentials for the reduction of the *cis*- and *trans*-Co(III) complexes (Table 1). At any rate, the *cis*(*N*)-configuration is favored at equilibrium for the state of Co(II).[4] Therefore, *cis*(*N*)-Co(ida)$_2^-$ keeps preferably the *cis*(*N*)-configuration after being reduced at the electrode, whereas the reduced product of *trans*(*N*)-Co(ida)$_2^-$ may gradually be isomerized to the *cis*(*N*)-form. Even if the isomerization process might proceed rapidly, the electrochemical kinetic parameters of *trans*(*N*)-Co(ida)$_2^-$ can be evaluated with sufficient accuracy, since the electrode reaction of *trans*(*N*)-form is d.c. polarographically quasi-reversibe (close to irreversible) and thus pulse-polarographically irreversible, so that the potential-shift due to the follow-up isomerization reaction may be negligibly small.

The kinetic parameters of the *cis*(*N*)- and *trans*(*N*)-Co(ida)$_2^-$ complexes were evaluated by means of the same method as described in the previous section. The reduction half-wave potentials for the *cis*- and *trans*-forms shifted to cathodic direction as the sampling time was reduced (Fig. 5) and their limiting currents were diffusion-controlled.

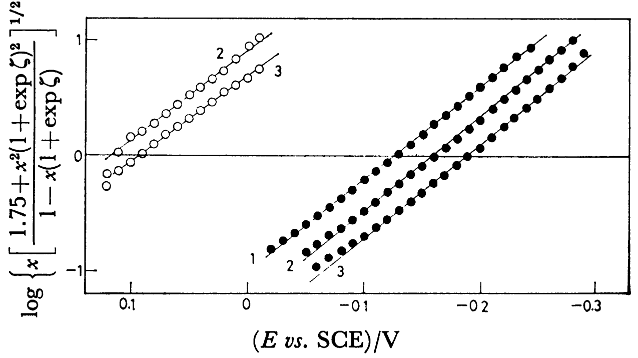

Fig. 7. Representative plots of
$\log\left[x\left\{\frac{1.75+x^2(1+\exp\zeta)^2}{1-x(1+\exp\zeta)}\right\}^{1/2}\right]$ *vs.* E for the reduction of 1.0 mM *cis*(*N*)- and *trans*(*N*)-Co(ida)$_2^-$.
(○): *cis*(*O*)-Species and (●): *trans*(*O*)-species.
τ_s=(1) 34.0 ms, (2) 8.7 ms, and (3) 3.1 ms. Other conditions are the same as in Fig. 5.

The log-plots afford a set of straight lines at the different sampling times (Fig. 7). The cathodic transfer coefficients were obtained from the reciprocal slopes of these lines as follows: $\alpha_c(trans)=0.47\pm0.02$ and $\alpha_c(cis)=0.46\pm0.04$. The standard rate constants evaluated from the values of E^* are summarized in Table 1. Magnitude difference in these two values amounts to several tens. The diffusion coefficients used to evaluate the kinetic parameters were 5.6×10^{-6} and 6.8×10^{-6} cm^2 s^{-1} for the *cis*- and *trans*-forms, respectively, as determined from cathodic limiting currents of normal pulse polarograms.

Galvanostatic Double Pulse Measurements of Co(dien)$_2^{3+/2+}$ *Couples.* Although the Co(dien)$_2^{3+}$ complex has three geometric isomers, meridional(*mer*), symmetrical facial(*s-fac*), and unsymmetrical facial(*u-fac*), the *mer*-Co(dien)$_2^{3+}$ species which can easily be synthesized was chosen as a typical species of the Co(III) complex with polyamine ligand. D.c. polarographic reduction wave showed a reversible nature and its half-wave potential was constant at −0.448 V *vs.* SCE in the presence of a large excess of dien at pH above 8.5. The rate of charge transfer processes for the Co(dien)$_2^{3+/2+}$ couple was very rapid, so that their kinetic parameters could not be evaluated even by the normal pulse polarographic technique. We therefore used the galvanostatic double pulse method with polarographic generation of reactant(g.d.p.p. method),[13] which has been recognized to be one of the most powerful techniques for very fast charge transfer processes. The analysis of experimental results was performed by using Eqs. 16 and 18 of Ref. 13. The experimental plots of the overpotential η_h *vs.* square root of the first pulse width $\sqrt{t_1}$ and of the exchange current density i_0 *vs.* applied d.c. potential E are shown in Figs. 8 and 9, respectively, in accordance with Eqs. 16 and 18 of Ref. 13, respectively. The theoretical slope was calculated by use of the diffusion coefficient of 4.4×10^{-6} cm^2 s^{-1} obtained from the d.c. polarographic limiting current (Fig. 8). The standard rate constant and the cathodic transfer coefficient obtained are given in Table 1.

Electrochemical Kinetic Parameters of Co(1,2-pn)$_3^{3+/2+}$ and mer-*Co(gly)$_3^{0/1-}$ Couples.* For the sake of comparison, the kinetic parameters for the reduction of the Co(1,2-pn)$_3^{3+}$ complex were also evaluated by the g.d.p.p. measurement (Table 1). The Co(1,2-pn)$_3^{3+}$ has two geometric isomers, *mer* and *fac*, with respect to methyl group but the product synthesized according to Ref. 8 may be a mixture of two isomers. However, d.c. polarogram of the reduction of the synthesized complex showed only a single reversible reduction wave at −0.465 V *vs.* SCE. We thus used the synthesized product recrystallized without separation of the isomers.

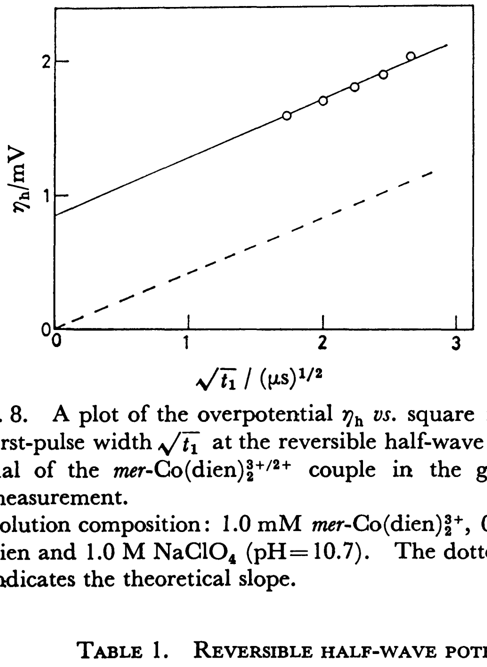

Fig. 8. A plot of the overpotential η_h *vs.* square root of first-pulse width $\sqrt{t_1}$ at the reversible half-wave potential of the *mer*-Co(dien)$_2^{3+/2+}$ couple in the g.d.p.p. measurement.
Solution composition: 1.0 mM *mer*-Co(dien)$_2^{3+}$, 0.10 M dien and 1.0 M NaClO$_4$ (pH=10.7). The dotted line indicates the theoretical slope.

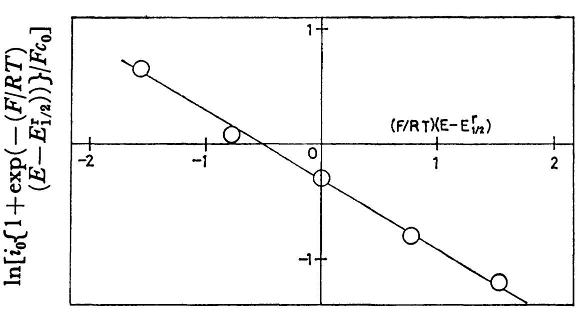

Fig. 9. A plot of ln $[i_0\{1+\exp(-(F/RT)(E-E^r_{1/2}))\}/Fc_0]$ *vs.* $(F/RT)(E-E^r_{1/2})$ for the Co(dien)$_2^{3+/2+}$ couple.

In contrast to the electrochemical behavior of the polyamine complexes, the rate of reduction of *mer*-Co(gly)$_3^0$ was very slow and the reduction wave was d.c. polarographically irreversible. Thus, the log-plot of normal pulse polarograms gave only the cathodic transfer coefficient and the cathodic rate constant at $E=0$, *i. e.*, at the potential of SCE. According to Hin-Fat and Higginson,[17] the standard potential of the Co(gly)$_3^{0/1-}$ couple is -0.06 ± 0.01 V *vs.* SCE. If we use this value, we can calculate the standard rate constant of this couple, which is also given in Table 1 together with the cathodic rate constant at $E=0$.

No electrochemical measurements for *fac*-Co(gly)$_3^{0/1-}$ couple were performed since the *fac*-Co(gly)$_3^0$ species is insoluble in aqueous solutions containing 1 M supporting electrolytes.

Discussion

On the basis of the kinetic parameters summarized in Table 1, we can find some correlation between the electrochemical reactivity of Co(III/II) complexes and their structure.

(1) For the reduction of Co(III) complexes, six coordination sites of which are occupied by amines of similar ligands, the standard rate constant, k_0, increases

Table 1. REVERSIBLE HALF-WAVE POTENTIALS AND KINETIC PARAMETERS OF THE ELECTRON TRANSFER REACTIONS OF Co(III/II) REDOX COUPLES IN 1.0 M SUPPORTING ELECTROLYTES AT 25 °C

Redox system	($E^r_{1/2}$ *vs.* SCE)/V	k_0/cm s^{-1}	α_c	Medium
mer-Co(dien)$_2^{3+/2+}$	−0.448	$(7.8\pm0.1)\times10^{-1}$ [a]	0.66 ± 0.05	0.1 M dien, NaClO$_4$
cis(*O*)-Co(edma)$_2^{1+/0}$	−0.279	$(3.4\pm0.1)\times10^{-3}$ [b]	0.70 ± 0.02	0.02 M Hedma, NaCl
trans(*O*)-Co(edma)$_2^{1+/0}$	−0.267	$(8.5\pm0.1)\times10^{-3}$ [b]	0.58 ± 0.02	0.02 M Hedma, NaCl
trans(*O*)-Co(edma)$_2^{1+/0}$	−0.263	$(8.5\pm0.1)\times10^{-3}$ [b]	0.59 ± 0.02	0.02 M Hedma, NaClO$_4$
Co(edma)$_2^{0/1+}$	−0.281	$(3.0\pm0.1)\times10^{-3}$ [b]	0.31 ± 0.02 [c]	0.02 M Hedma, NaCl
cis(*N*)-Co(ida)$_2^{1-/2-}$	0.115	$(1.1\pm0.2)\times10^{-2}$ [b]	0.46 ± 0.04	0.01 M H$_2$ida, KNO$_3$
trans(*N*)-Co(ida)$_2^{1-/2-}$	0.027	$(4.0\pm0.1)\times10^{-4}$ [b]	0.47 ± 0.02	0.01 M H$_2$ida, KNO$_3$
Co(1,2-pn)$_3^{3+/2+}$	−0.465	$(6.2\pm0.1)\times10^{-1}$ [a]	0.68 ± 0.05	0.1 M 1,2-pn, NaClO$_4$
mer-Co(gly)$_3^{0/1-}$	-0.06 ± 0.01 [e]	$(3.0\pm0.1)\times10^{-5}$ [b,d] $(9\pm2)\times10^{-5}$ [b]	0.51 ± 0.02	0.05 M gly, NaClO$_4$

a) Galvanostatic double pulse method. b) Normal pulse polarographic method. c) Anodic transfer coefficient (α_a). d) Cathodic rate constant at the potential of SCE($E=0$). e) Ref. 17.

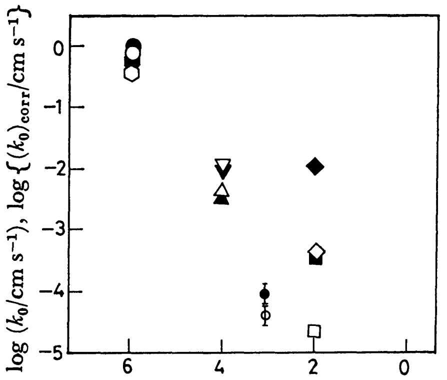

Fig. 10. Correlation between the standard rate constants and the number of bonded nitrogen donor atoms.
(●, ○): *mer*-Co(dien)$_2^{3+/2+}$, (⬢, ⬡): Co(1,2-pn)$_3^{3+/2+}$, (▼, ▽): *trans*(*O*)-Co(edma)$_2^{1+/0}$, (▲, △): *cis*(*O*)-Co-(edma)$_2^{1+/0}$, (◆, ◇): *cis*(*N*)-Co(ida)$_2^{1-/2-}$, (■, □): *trans*(*N*)-Co(ida)$_2^{1-/2-}$, and (ɸ, ɸ): *mer*-Co(gly)$_3^{0/1-}$.
The solid and open symbols denote the measured values, k_0, and the values corrected by the Frumkin theory, $(k_0)_{\mathrm{corr}}$, respectively.

in the order: Co(dien)$_2^{3+/2+}$>Co(1,2-pn)$_3^{3+/2+}$, Co-(en)$_3^{3+/2+}$ (en: ethylenediamine)[14]>Co(NH$_3$)$_6^{3+/2+}$.[15,16] This order is the same as that of the number of coordination sites involved in the ligand, *i. e.*, tridentate>bidentate>unidentate.

(2) Increase in the number of replacement of amino groups in dien by carboxyl groups reduces the values of k_0. The values of k_0 increase in the order: Co(dien)$_2^{3+/2+}$>Co(edma)$_2^{1+/0}$>Co(ida)$_2^{1-/2-}$ (Fig. 10). The complex species studied have a different number of charges, the difference between their reversible half-wave potentials amounting to *ca.* 500 mV, so that the ϕ_2-potential at the outer Helmholtz plane may affect the kinetics of electrode reactions concerned. The open symbols in Fig. 10 express the values of the standard rate constant corrected for the double layer effect by means of the Frumkin theory,[18] in which the values of ϕ_2 were taken from Russell's Tables.[19] We find that for the present series of the redox couples of Co(III/II) complexes with bi- and tridentate polyamines and aminocarboxylates the logarithms of the corrected values, $(k_0)_{\mathrm{corr}}$, increase in proportion to the number of nitrogen donor atoms involved in the ligand.

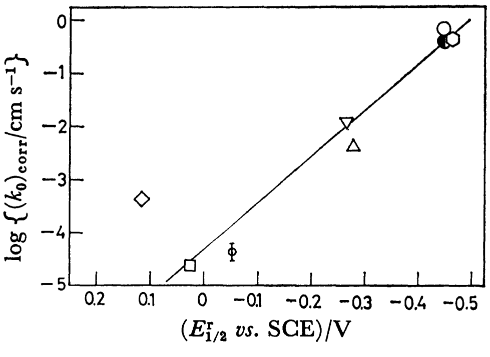

Fig. 11. Linear relationship between log$(k_0)_{\mathrm{corr}}$ and $E^{\mathrm{r}}_{1/2}$.
(◐): Co(en)$_3^{3+/2+}$. Other symbols are the same as in Fig. 10.

(3) Oyama *et al.*[20–22] showed that the linear relation between the logarithms of cathodic rate constants and the corresponding standard potentials holds for the Cd(II) and Pb(II) complexes with EDTA and related compounds. It is of interest to see if such a correlation prevails for the present series of Co(III/II) redox couples. Log $(k_0)_{\mathrm{corr}}$ is plotted against the reversible half-wave potential $E^{\mathrm{r}}_{1/2}$ in Fig. 11. We see linear correlation, except for the *cis*(*N*)-Co(ida)$_2^{1-/2-}$ couple whose reversible half-wave potential is unusually positive. As can be seen from Table 1, the values of $E^{\mathrm{r}}_{1/2}$ are also proportional to the number of the nitrogen donor atoms involved in the ligand, so that the linear correlation given in Fig. 11 could be attributed to that of Fig. 10.

(4) The difference of the kinetic parameters for the geometric isomers is obvious from the data in Table 1.

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