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Nonbridging Ligand Effects on the Reduction of Nitrilopolyaminocarboxylato-cobalt(III) Complexes by Iron(II)

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The effects of the nonbridging ligand on the rate of electron-transfer reactions between $Co(ox)N_4^+$-type complexes ($N_4=(NH_3)_4$, $(en)_2$, trien, $(phen)_2$, and $(dpy)_2$) and Fe^{2+} have been reported in a previous paper.[1] The results show that the variation in the rate is mainly due to the change in the enthalpy of activation. It is of interest to investigate systematically how the nonbridging ligands affect the enthalpy and entropy of activation in the Fe^{2+} reduction of the cobalt(III) complexes. The author wishes now to report on the nonbridging ligand effects on the reactivities of the nitrilotriacetato- and ethylenediamine-*N*,*N'*-diacetatocobalt(III) complexes with Fe^{2+}.

Experimental

Materials. The *cis*-α-$[Co(edda)(NH_3)_2]ClO_4$,[2,3] *cis*-α-$[Co(edda)(en)]ClO_4$,[2] $[Co(nta)(en)]$,[4,5] *trans*-(N)-$K[Co(nta)(am)]$,[6] (am=glycine, β-alanine, and γ-aminobutyric acid) were prepared by methods similar to those described in the references cited. The $Co(nta)(H_2O)(NH_2CH_2CH_3)$ solution was prepared by the dissolution of $K[Co(nta)(NH_2CH_2CH_3)(OH)]$, which has itself been prepared by modifying the method of the preparation of $[Co(nta)(en)]$[4] into a perchloric acid solution. The $Co(edda)(H_2O)_2^+$ and the $Co(nta)(H_2O)_2$ solutions were prepared by the equation of *cis*-α-$Na[Co(edda)Cl_2]$ and the dissolution of $K[Co(nta)(H_2O)(OH)]$ respectively into the perchloric acid solution.

The preparation of the iron(II) solution and the determinations of the concentrations of iron(II), the perchlorate ion, and the hydrogen ion were carried out by methods similar to those described in a previous paper.[7] Reagent-grade chemicals were used for the preparation of the reaction mixtures.

Kinetic Measurements. The reactions were followed spectrophotometrically by observing the decrease in the absorbance of the Co(III) complexes at a wavelength in the vicinity of the first absorption maximum. The determinations of the rate constants of *cis*-α-$Co(edda)(NH_3)_2^+$ and *cis*-α-$Co(edda)(en)^+$ were performed in the temperature range of 50—80 °C because of the very small solubility and reactivities of these complexes. The rate constants at 25 °C were obtained by the extrapolation of the Arrhenius plots. In the course of the reactions, the decompositions of none of the complexes were observed under the conditions adopted.

Results and Discussion

The rate constants and the activation parameters are listed in Tables 1 and 2. The reactions of *cis*-α-$Co(edda)(en)^+$ were followed under the conditions of $[H^+]=0.86$ M and $\sum[ClO_4^-]=2.45$ M; the rate constant at $\sum[ClO_4^-]=1.00$ M, $[H^+]=0.36$ M, and 25 °C should be slightly smaller than 1.65×10^{-8} $M^{-1}\cdot s^{-1}$.

The relationship between the second-order rate constant and the hydrogen ion concentration for Co(nta)(en) is shown in Fig. 1. Similar hydrogen ion effects were also observed for the *cis*-α-$Co(edda)(H_2O)_2^+$ and *cis*-α-$Co(edda)(NH_3)_2^+$. In the cases of the Fe^{2+} reduction of the positively-charged and noncharged Co(III) complexes, not such a large effect of the hydrogen ion is observed, though it has been found that the hydrogen

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[1] K. Ohashi, This Bulletin, **45**, 3093 (1972).

[2] K. Kuroda and K. Watanabe, *ibid.*, **44**, 1034 (1971).

[3] $edda^{2-}={}^-O_2CCH_2NHCH_2CH_2NHCH_2CO_2^-$.

[4] K. Watanabe, Presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, (1970); Proceedings, p. 543.

[5] $nta^{3-}=N(CH_2COO)_3^{3-}$.

[6] N. Koine, N. Sakota, J. Hidaka, and Y. Shimura, This Bulletin, **42**, 1583 (1969).

[7] Y. Kurimura, K. Ohashi, T. Otsuki, and K. Yamamoto, *ibid.*, **44**, 1293 (1971).

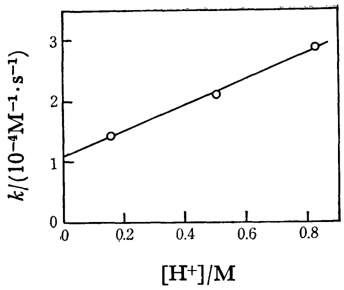

Fig. 1. The relation between the second-order rate constant *k* and hydrogen-ion concentration in the Fe^{2+} reduction of Co(nta)(en).
$\sum[ClO_4^-]=2.50$ M, 40.2 °C, $HClO_4$-$NaClO_4$ medium.

ion slightly accelerates the Fe^{2+} reduction rates of some negatively-charged Co(III) complexes.[8,8a] The mechanism of the hydrogen-ion dependence has not yet been made clear.

Though the electron-transfer mechanism could not be ascertained directly, it is reasonable to assume that these reactions occure *via* an inner-sphere mechanism, since the reductions of Co(HY)(H_2O), and Co(YOH)(H_2O) (Y^{4-}=the ethylenediaminetetraacetate ion and YOH^{3-}=the hydroxyethylenediaminetriacetate ion) with Fe^{2+} proceed *via* the carboxylato-bridged activated state.[8]

The experimental results presented above serve to establish how the enthalpy and entropy of the activation and reactivities change when the nonbridging ligands are varied (Table 1). The variations in the reactivities of *cis*-α-Co(edda)A_2^+ ($A_2=(H_2O)_2$, $(NH_3)_2$, and (en)), Co(nta)B_2 ($B_2=(H_2O)_2$, $(H_2O)(NH_2CH_2CH_3)$, and (en)), and Co(nta)(am)$^-$ (am=glycine, β-alanine, and γ-aminobutyric acid) are due primarily to the changes in the enthalpies of activation. The entropies of activation increase slightly with a decrease in the reactivities of the Co(III) complexes in the three series.

Table 1. The rate constants and the activation parameters for the Fe^{2+} reduction reactions of nitrilotriacetato- and ethylenediamine-*N*,*N′*-diacetato-cobalt(III) complexes

Complex ions	Rate constant $M^{-1}\cdot s^{-1}$	$\Delta H^{\ddagger}$ kcal·mol^{-1}	$\Delta S^{\ddagger}$ eu
Co(nta)$(H_2O)_2$	1.44[a]	7.1±1.0	−33.9±3.4
Co(nta)-$(H_2O)(HN_2CH_2CH_3)$	9.78×10^{-3} [a]	11.6±1.5	−28.8±5.0
Co(nta)(en)	4.98×10^{-5} [a]	15.9±1.1	−24.8±3.7
Co(nta)(gly)$^-$	4.65×10^{-4} [a]	13.7±1.3	−27.9±4.5
Co(nta)(β-ala)$^-$	2.51×10^{-3} [a]	12.3±0.7	−29.0±2.5
Co(nta)-(γ-aminobut)$^-$	1.13×10^{-2} [a]	11.5±1.4	−28.7±4.7
cis-α-Co-(edda)$(H_2O)_2^+$	2.94×10^{-3} [b]	13.2±0.8	−25.8±2.7
cis-α-Co-(edda)$(NH_3)_2^+$	1.20×10^{-6} [b]	18.5±1.3	−23.5±4.4
cis-α-Co-(edda)(en)$^+$	1.65×10^{-8} [c]	24.1±0.7	−12.9±2.3

a) $\sum[ClO_4^-]=1.00M$, $[H^+]=0.10M$, 25 °C.
b) $\sum[ClO_4^-]=1.00M$, $[H^+]=0.36M$, 25 °C.
c) $\sum[ClO_4^-]=2.45M$, $[H^+]=0.84M$, 25 °C.

The reactivities of the Co(nta)(am)$^-$ series decrease in this order: γ-aminobutyric acid>β-alanine>glycine. In a previous paper,[9] it was mentioned that the strain on the chelate ring of the nonbridging ligand accelerates the Fe^{2+} reduction rate. The decreasing order of reactivity is consistent with that of the strain on the chelate ring of the amino acid.

It is of interst to note here that the entropies of activation of the Co(nta)(am)$^-$ and Co(nta)B_2 complexes are almost the same, though the enthalpies of the activation decrease with the reactivities of the complexes.

Table 2. The rate constants and the activation parameters for the Fe^{2+} reduction reactions of nitrilopolyaminocarboxylato-cobalt(III) complexes

Complex ions	Rate constant M^{-1} sec^{-1}	$\Delta H^{\ddagger}$ kcal·mol^{-1}	$\Delta S^{\ddagger}$ eu
Co(nta)$(H_2O)_2$	1.44[a]	7.1±1.0	−33.9±3.4
Co(edda)$(H_2O)_2^+$	2.94×10^{-3} [a]	13.2±0.8	−25.8±2.7
Co(edtaOH)(H_2O)	4.61×10^{-3} [b]	13.6±0.4	−23.5±1.4
Co(edtaH)(H_2O)	8.50×10^{-3} [b]	10.5±0.9	−33±3
Co(edta)$^-$	6.00×10^{-4} [b]	11.2±1.4	−36±5

a) This work, $\sum[ClO_4^-]=1.00$ M, $[H^+]=0.36$ M, 25 °C.
b) From Ref. 8, 25 °C, Ionic strength=1.00.

The rate constants and the activation parameters for the reductions of nitrilopolycarboxylato-Co(III) complexes by Fe^{2+} are listed in Table 2. The reactivity of the Co(nta)$(H_2O)_2$ complex is much larger than those of the other complexes. In these complexes, the efficiency of the nitrilopolycarboxylato ligand as the mediator in the electron-transfer is of almost the same degree. Therefore, the large reactivity of the Co(nta)$(H_2O)_2$ complex must be due to the smaller reorganization energy of the nonbridging ligand before electron transfer occurs. The small enthalpy of activation for the Co(nta)$(H_2O)_2$ complex supports the above-mentioned interpretation.

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[8] P. B. Wood and W. C. F. Higginson, *J. Chem. Soc.*, **1965**, 2116.

[8a] Y. Kurimura, I. Meguro, and K. Ohashi, This Bulletin, **44**, 3367 (1971).

[9] K. Ohashi, K. Yamamoto, I. Hirako, and Y. Kurimura, *ibid.*, **45**, 1712 (1972).