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A Kinetic Study of the Reactions of Several Cobalt(III) Complexes with Ascorbic Acid

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The kinetics of the reactions of $[Co(phen)_3]^{3+}$, $[Co(bpy)_3]^{3+}$, and $[Co(en)(phen)_2]^{3+}$ (phen=1,10-phenanthroline, bpy=2,2′-bipyridine, and en=ethylenediamine) with ascorbic acid (H_2A) have been studied over the temperature range from 17.0 to 35.0 °C, at an ionic strength of 0.10 mol dm^{-3} ($LiClO_4$), and over the pH range from 3.60 to 5.04 (acetate buffer). The $[Co(phen)_3]^{3+}$ and $[Co(bpy)_3]^{3+}$ ions were reduced by both HA^- (k_1 path) and A^{2-} (k_2 path) ions: the second-order rate constants at 25.0 °C are (0.40 ± 0.07) dm^3 mol^{-1} s^{-1} and $(5.8 \pm 1.1) \times 10^6$ dm^3 mol^{-1} s^{-1} for the $[Co(phen)_3]^{3+}$ ion, and (0.13 ± 0.02) dm^3 mol^{-1} s^{-1} and $(2.1 \pm 0.5) \times 10^6$ dm^3 mol^{-1} s^{-1} for the $[Co(bpy)_3]^{3+}$ ion. The $[Co(en)(phen)_2]^{3+}$ ion was reduced only by the A^{2-} ion; $k_2 = (1.0 \pm 0.2) \times 10^6$ dm^3 mol^{-1} s^{-1} (25.0 °C). The $[Co(phen)_3]^{3+}$, $[Co(bpy)_3]^{3+}$, and $[Co(en)(phen)_2]^{3+}$ ions were not reduced by H_2A. The activation parameters (ΔH^* and ΔS^*) for the ascorbate reduction of the $[Co(phen)_3]^{3+}$ ion were larger than those of the $[Co(bpy)_3]^{3+}$ ion. This is in contrast to the results of the self-exchange reactions of the $[Co(phen)_3]^{3+/2+}$ and $[Co(bpy)_3]^{3+/2+}$ couples. The mechanisms will be discussed in terms of the activation parameters and the Marcus cross relationships.

The kinetics of the oxidation of ascorbic acid (H_2A) to dehydroascorbic acid (A) by a metal complex have been investigated extensively.[1–5] It has been shown that Cu^{2+} and $[Fe(H_2O)_6]^{3+}$ catalyze the autoxidation of ascorbic acid.[1] The kinetics of the inner-sphere oxidation of ascorbic acid by Cu^{2+} or $[Fe(H_2O)_6]^{3+}$ have been examined,[2,3] as have the outer-sphere oxidations by $[Co(H_2O)_6]^{3+}$,[4] and Fe(III), Ir(IV), and Mo(V).[5] The application of the Marcus theory allowed an estimate of the redox potential and the free energy of activation for the ascorbic acid/radical couple.[5]

Cobalt(III) complexes are very interesting in investigating the electron-transfer reactions because of the problems of the spin-multiplicity change and the ligand-reorganization energy.[6] However, the reactions of cobalt(III) complexes with ascorbic acid have rarely been investigated since Iwasaki[7] reported in 1942 that some cobalt(III) complexes catalyzed the autoxidation of ascorbic acid. As ascorbic acid is a π-donor, ascorbic acid can be expected to interact with cobalt(III) complexes with π-conjugated ligands. We have selected the cobalt(III) complexes ligating 1,10-phenanthroline or 2,2′-bipyridine in order to elucidate the mechanism of the reactions of cobalt(III) complexes with ascorbic acid.

Experimental

Reagents. The $[Co(phen)_3]Cl_3 \cdot 7H_2O$,[8] $[Co(bpy)_3]Cl_3 \cdot 3H_2O$,[8] and $[Co(en)_3]Cl_3$[9] complexes were prepared as has been described elsewhere. The perchlorate salts, $[Co(phen)_3](ClO_4)_3 \cdot 2H_2O$, $[Co(bpy)_3](ClO_4)_3 \cdot 3H_2O$, and $[Co(en)_3](ClO_4)_3$, were obtained by adding sodium perchlorate to solutions of the chloride complexes. $[Co(en)(phen)_2](ClO_4)_3 \cdot 2H_2O$,[10] $[Co(en)_2(phen)](ClO_4)_3$,[11] and $Na[Co(edta)] \cdot 4H_2O$†,[12] were prepared according to the published procedures. The L-ascorbic acid was supplied by Wako Pure Chemical Industries. The lithium perchlorate, $LiClO_4 \cdot 3H_2O$, was obtained according to the procedure reported previously.[13] All the solutions used for the measurements were prepared using water obtained by the distillation of alkaline permanganate solutions. A solution of ascorbic acid, partly neutralized with lithium carbonate, was freshly prepared under a nitrogen atmosphere. The acetate buffer solutions were prepared by adding acetic acid to lithium carbonate and purged once with nitrogen gas which had been scrubbed twice with alkaline potassium pyrogallate.

Kinetic Measurements. Solutions containing a cobalt(III) complex, $LiClO_4$, and an acetate buffer were added to an optical cell, which was then sealed with a serum cap. After the solution had been purged with a nitrogen atmosphere for 15 min, the reaction was initiated by the addition of the ascorbic-acid solution by means of a syringe. The change in absorbance with time was followed with a Hitachi 200-20 spectrophotometer. The wavelengths used for the measurements were 350 nm ($[Co(bpy)_3]^{3+}$ and $[Co(en)(phen)_2]^{3+}$), 352 nm ($[Co(en)_2(phen)]^{3+}$), 353 nm ($[Co(phen)_3]^{3+}$), 466 nm ($[Co(en)_3]^{3+}$), and 535 nm ($[Co(edta)]^-$). In order to ensure a pseudo-first order condition, ascorbic acid was in at least a tenfold excess over the cobalt(III) complexes: the initial concentrations of ascorbic acid and the cobalt(III) complexes were $(0.50—1.02) \times 10^{-2}$ mol dm^{-3} and $(1.64—5.16) \times 10^{-4}$ mol dm^{-3} respectively.

The temperature was kept constant within 0.1 °C at each desired temperature, while the ionic strength (I) was adjusted to 0.1 mol dm^{-3} with lithium perchlorate.

The pH of the solutions was measured by the use of a Hitachi-Horiba F-7 pH meter. The $[H^+]$ was computed from the pH using a value of 0.83 (at 25 °C and $I=0.10$ mol dm^{-3}) for the activity coefficients of H^+.[14]

Results

In the reactions of $[Co(phen)_3]^{3+}$ and $[Co(bpy)_3]^{3+}$ with ascorbic acid, the absorbance over the range from 300 nm to 400 nm decreased with the time during the course of the reaction. As the dissociations of $[Co(phen)_3]^{2+}$ and $[Co(bpy)_3]^{2+}$ are fast (the rate constants are 0.174 s^{-1} [15] and 0.32 s^{-1} [16] at 25 °C respectively), the reaction corresponds to the absorbance change for the slow steps in the following reactions:

$$[Co(phen)_3]^{3+} \xrightarrow[slow]{H_2A} [Co(phen)_3]^{2+} \xrightarrow[fast]{} [Co(phen)_2(H_2O)_2]^{2+} \qquad (1)$$

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† edta: Ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate anion.

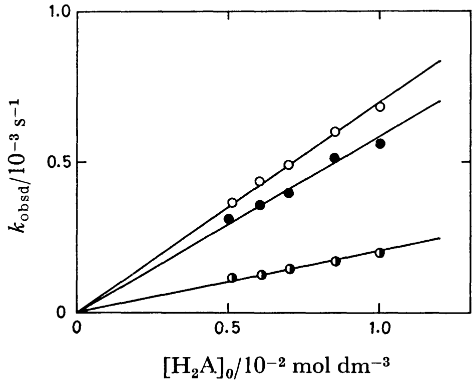

Fig. 1. Plots of k_{obsd} vs. $[H_2A]_0$ for the cobalt(III)–ascorbic acid system.
○: $[Co(phen)_3]^{3+}$ at pH 4.53, ●: $[Co(bpy)_3]^{3+}$ at pH 4.83, ◑: $[Co(en)(phen)_2]^{3+}$ at pH 4.83.

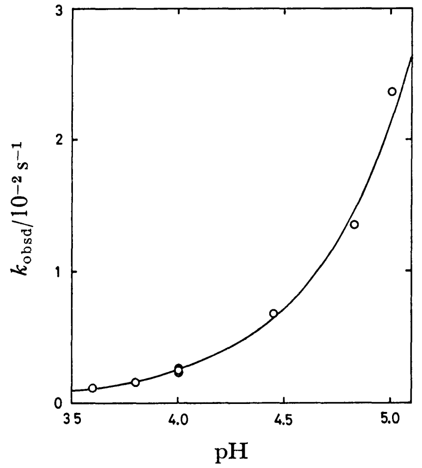

Fig. 2. Plots of k_{obsd} vs. pH for the $[Co(phen)_3]^{3+}$–ascorbic acid system.

$$[Co(bpy)_3]^{3+} \xrightarrow[\text{slow}]{H_2A} [Co(bpy)_3]^{2+} \xrightarrow[\text{fast}]{} [Co(bpy)_2(H_2O)_2]^{2+}. \tag{2}$$

Plots of $-\ln(A_t-A_\infty)$ vs. the time were linear for at least 85% completion (A_t and A_∞ represent the absorbance at time t and infinity respectively). The observed first-order rate constants (k_{obsd}) obtained from the slope of this straight line show also a linear dependence on the initial concentrations of ascorbic acid (Fig. 1). As the cobalt(III) complexes are one-electron oxidants, ascorbic acid radicals may be formed by the one-electron transfer from the ascorbic acid to the cobalt(III) complexes. Moreover, the dismutation of the ascorbic-acid radicals is very fast.[17] Thus, the rate law was described as follows:

$$-\frac{1}{2}d[Co(III)]/dt = k[Co(III)][H_2A]_0. \tag{3}$$

The second-order rate constants obtained from $k_{obsd}/[H_2A]_0$ increased with a decrease in the acidity (pH 3.60—5.04), as is shown in Fig. 2. The present reaction can, then, be described by this sequence:

$$H_2A \overset{K_1}{\rightleftharpoons} HA^- + H^+ \tag{4}$$

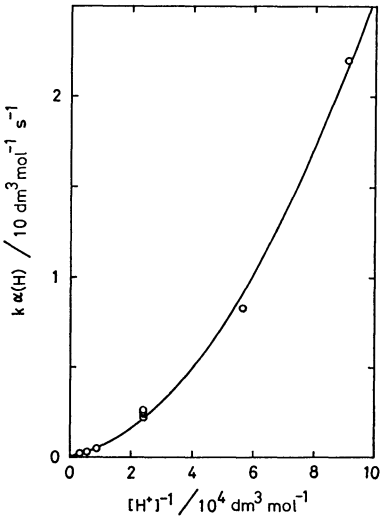

Fig. 3. Plots of $k\alpha(H)$ vs. $[H^+]^{-1}$ for the $[Co(phen)_3]^{3+}$–ascorbic acid system at 25.0 °C.

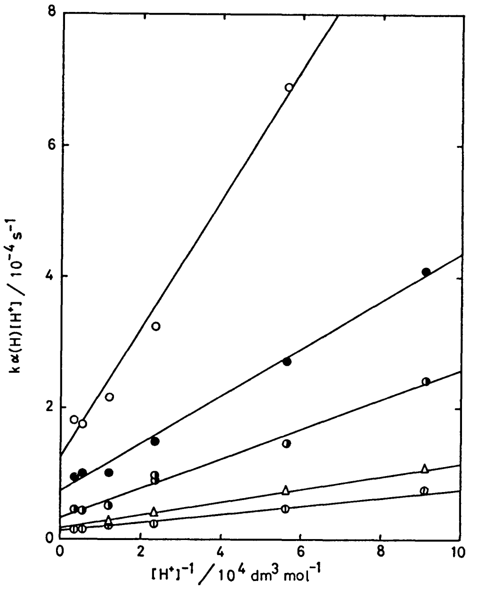

Fig. 4. Plots of $k\alpha(H)[H^+]$ vs. $[H^+]^{-1}$ for the $[Co(phen)_3]^{3+}$–ascorbic acid system.
⦶: 17.0 °C, △: 21.0 °C, ◑: 25.0 °C, ●: 30.0 °C, ○: 35.0 °C.

$$HA^- \overset{K_2}{\rightleftharpoons} A^{2-} + H^+ \tag{5}$$

$$Co(III) + H_2A \xrightarrow{k_0} \text{radical} + Co(II) \tag{6}$$

$$Co(III) + HA^- \xrightarrow{k_1} \text{radical} + Co(II) \tag{7}$$

$$Co(III) + A^{2-} \xrightarrow{k_2} \text{radical} + Co(II) \tag{8}$$

$$2\ \text{radical} \xrightarrow{\text{fast}} H_nA^{n-2} + A + nH^+, \tag{9}$$

where n is 1 or 2. The above mechanism leads to Eq. 10 for the second-order rate constant:

$$k = \frac{k_0+k_1K_1[H^+]^{-1}+k_2K_1K_2[H^+]^{-2}}{\alpha(H)}, \tag{10}$$

where $\alpha(H) = 1+K_1[H^+]^{-1}+K_1K_2[H^+]^{-2}$. As $K_1K_2[H^+]^{-2} \ll 1$ under the present experimental conditions,

TABLE 1. THE RATE CONSTANTS OF THE REACTIONS OF $[Co(phen)_3]^{3+}$, $[Co(bpy)_3]^{3+}$, AND $[Co(en)(phen)_2]^{3+}$ WITH ASCORBIC ACID AT $I=0.10$ mol dm^{-3} ($LiClO_4$)$^{a)}$

Oxidant	Temp °C	k_1 dm^3 mol^{-1} s^{-1}	$k_2K_1K_2$ 10^{-9} mol dm^{-3} s^{-1}	k_2 10^6 dm^3 mol^{-1} s^{-1}
$[Co(phen)_3]^{3+}$ $^{b)}$	17.0	0.22±0.05	0.77±0.35	—
	21.0	0.23±0.01	1.0±0.06	—
	25.0	0.40±0.07	2.4±0.5	5.8±1.1
	30.0	0.60±0.06	4.1±1.1	—
	35.0	0.62±0.09	11±3	—
$[Co(bpy)_3]^{3+}$ $^{c)}$	21.0	0.047±0.021	0.59±0.15	—
	25.0	0.13±0.02	0.88±0.23	2.1±0.5
	30.0	0.12±0.04	2.0±0.7	—
	35.0	0.12±0.03	4.2±0.7	—
$[Co(en)(phen)_2]^{3+}$	25.0	≈0	0.42±0.07	1.0±0.2

a) Data were obtained from at least five determinations. b) $\Delta H_1^{\ddagger}(k_1)=(46\pm4)$kJ mol^{-1}, $\Delta S_1^{\ddagger}(k_1)=(-92\pm4)$J K^{-1} mol^{-1}; $\Delta H_2^{\ddagger}(k_2K_1K_2)=(109\pm8)$kJ mol^{-1}, $\Delta S_2^{\ddagger}(k_2K_1K_2)=(-46\pm4)$J K^{-1} mol^{-1}. c) $\Delta H_1^{\ddagger}(k_1)=(38\pm4)$kJ mol^{-1}, $\Delta S_1^{\ddagger}(k_1)=(-140\pm8)$J K^{-1} mol^{-1}; $\Delta H_2^{\ddagger}(k_2K_1K_2)=(80\pm4)$kJ mol^{-1}, $\Delta S_2^{\ddagger}(k_2K_1K_2)=(-160\pm8)$J K^{-1} mol^{-1}.

α(H) can be simplified as $1+K_1[H^+]^{-1}$. The plots of the values of $k\alpha$(H) *vs.* $[H^+]^{-1}$ gave a quadratic curve (Fig. 3), and the intercept (k_0) was nearly zero. Therefore, the plots of the values of $k\alpha(H)[H^+]$ *vs.* $[H^+]^{-1}$ gave straight lines (Fig. 4). The values of k_1K_1 and $k_2K_1K_2$ are obtained from the intercept and the slope of this straight line respectively. The second-order rate constants, k_1 and k_2, calculated by the use of the values of K_1 and K_2 are listed in Table 1. The values of K_1 at each temperature were estimated from the values at 0.4, 25.0, and 40.0 °C given by Taqui Khan and Martell.[3)]

An acetate buffer had little effect on the rate of the reaction of $[Co(phen)_3]^{3+}$ with ascorbic acid (at pH 4.02 and 0.05—0.25 mol dm^{-3} acetate).

For the reaction of $[Co(en)_2(phen)]^{3+}$, $[Co(en)_3]^{3+}$, or $[Co(edta)]^-$, no significant spectral change was observed at 25.0 °C and pH 5.04.

Discussion

The rate constant for the A^{2-} reduction is 10^6 times larger than that for the HA^- reduction. The difference in this reactivity is similar to that in the reactions of cytochrome c-552,[18)] Horse Heart cytochrome c,[18)] $[Fe(CN)_6]^{3-}$,[19)] and Cu^{2+} [20)] with ascorbic acid. As the cobalt(III) complexes are substitution-inert, the electron-transfer reaction is considered to occur through an outer-sphere activated complex:

$$\mathrm{Co(III)} + \mathrm{HA^-}\ (\text{or } \mathrm{A^{2-}}) \overset{K_{os}}{\rightleftharpoons} [\mathrm{Co(III)^{3+}\cdot HA^-}]$$

$$(\text{or } [\mathrm{Co(III)^{3+}\cdot A^{2-}}]) \xrightarrow{k_{et}} \text{products}, \tag{11}$$

where K_{os} and k_{et} are the ion-pair formation constant and the rate constant of the intramolecular electron-transfer respectively. The values of K_{os} can be calculated from the Fuoss equation,[21)] where the distance of the closest approach of two ions is 5×10^{-8} cm for the $[Co(phen)_3]^{3+}$ and ascorbate couple; the values of 5.3 and 90 dm^3 mol^{-1} are obtained at 25 °C and $I=0.1$ mol dm^{-3} for the reactions of HA^- and A^{2-} respectively. The large difference in reactivity cannot be elucidated by this small difference in K_{os}. It may, then, be attributed to the intramoleular electron-transfer step if Reaction 11 occurs.

The $[Co(phen)_3]^{3+}$ and $[Co(bpy)_3]^{3+}$ ions were reduced by both HA^- and A^{2-} ions under the present experimental conditions. On the other hand, the $[Co(en)(phen)_2]^{3+}$ ion was reduced only by the A^{2-} ion, and neither the $[Co(en)_2(phen)]^{3+}$ nor the $[Co(en)_3]^{3+}$ ion was reduced by ascorbate ions. These cobalt(III) complexes were not reduced by H_2A. The difference in the reactivities of these reactions may correspond to that of the redox potentials of the complexes (0.391 V for $[Co(phen)_3]^{3+/2+}$, 0.316 V for $[Co(bpy)_3]^{3+/2+}$, and −0.214 V for $[Co(en)_3]^{3+/2+}$),[22)] but it cannot be explained why $[Co(edta)]^-$ is not reduced by ascorbic acid in spite of its higher redox potential (0.60 V).

Pelizzetti *et al.*[5)] reported on the application of the Marcus theory, which allowed an estimate of the formal reduction potential, $E_{11}^{\circ}(HA\cdot/HA^-)=0.88$ V, and the intrinsic parameter, $\Delta G_{11}^{\ddagger}(HA\cdot/HA^-)=17$ kJ mol^{-1}. Using these values, we calculated the rate constants of the reactions of $[Co(phen)_3]^{3+}$, $[Co(bpy)_3]^{3+}$, and $[Co(en)_3]^{3+}$ with HA^- from the Marcus cross relationships,[23)] neglecting the work terms, which are inferred to be small:[5,24)]

$$\Delta G_{12}^{\ddagger} = \lambda(1+\Delta G_{12}^{\circ}/\lambda)^2/4 \tag{12}$$

$$k = Z\exp(-\Delta G_{12}^{\ddagger}/RT) \tag{13}$$

$$\lambda = 2(\Delta G_{11}^{\ddagger}+\Delta G_{22}^{\ddagger}), \tag{14}$$

where Z is the collision frequency in a solution (10^{11} dm^3 mol^{-1} s^{-1}), where $\Delta G_{11}^{\ddagger}$ and $\Delta G_{22}^{\ddagger}$ refer to the self-exchange reactions of the reagents, and where ΔG_{12}° is the free-energy change of the reactions. The values calculated at 25 °C are in accord with the observed ones for the reactions of $[Co(phen)_3]^{3+}$ and $[Co(bpy)_3]^{3+}$ (Table 2).

The activation parameters of the reactions of $[Co(phen)_3]^{3+}$ with HA^- and A^{2-} are larger than those of the reactions of $[Co(bpy)_3]^{3+}$: $\Delta\Delta H_1^{\ddagger}=\Delta H_1^{\ddagger}([Co(phen)_3]^{3+})-\Delta H_1^{\ddagger}([Co(bpy)_3]^{3+})=8$ kJ mol^{-1} and $\Delta\Delta S_1^{\ddagger}=\Delta S_1^{\ddagger}([Co(phen)_3]^{3+})-\Delta S_1^{\ddagger}([Co(bpy)_3]^{3+})=48$

TABLE 2. COMPARISON BETWEEN THE OBSERVED RATE CONSTANTS AND THE CALCULATED ONES FROM THE MARCUS CROSS RELATIONSHIPS^a)

Oxidant	k_{22} b) $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$	ΔG^{*}_{22} $\mathrm{kJ\,mol^{-1}}$	E° c) V	ΔG°_{12} $\mathrm{kJ\,mol^{-1}}$	k_1(calcd) $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$	k_1(obsd) $\mathrm{dm^3\,mol^{-1}\,s^{-1}}$
$[\mathrm{Co(phen)_3}]^{3+}$	4.5×10 d)	53	0.391	47	1.4	0.40
$[\mathrm{Co(bpy)_3}]^{3+}$	1.8×10 d)	56	0.316	54	0.12	0.13
$[\mathrm{Co(en)_3}]^{3+}$	7.7×10^{-5} e)	86	-0.214	105	3×10^{-10}	—

a) Calculated at 25 °C and $I=0.1\ \mathrm{mol\,dm^{-3}}$; $E^\circ_{11}(\mathrm{HA\cdot/HA^-})=0.88$ V and $\Delta G^{*}_{11}(\mathrm{HA\cdot/HA^-})=17\ \mathrm{kJ\,mol^{-1}}$. b) The rate constant of the self-exchange of the cobalt(III) complex. c) Ref. 22. d) Ref. 25. e) F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, **65**, 1892 (1961).

$\mathrm{J\,K^{-1}\,mol^{-1}}$ for the $\mathrm{HA^-}$ path; $\Delta\Delta H^{*}_{2}=\Delta H^{*}_{2}([\mathrm{Co(phen)_3}]^{3+}) - \Delta H^{*}_{2}([\mathrm{Co(bpy)_3}]^{3+}) = 29\ \mathrm{kJ\,mol^{-1}}$ and $\Delta\Delta S^{*}_{2}=\Delta S^{*}_{2}([\mathrm{Co(phen)_3}]^{3+})-\Delta S^{*}_{2}([\mathrm{Co(bpy)_3}]^{3+}) = 110\ \mathrm{J\,K^{-1}\,mol^{-1}}$ for the $\mathrm{A^{2-}}$ path. This is in contrast to the result of the self-exchange reactions of the $[\mathrm{Co(phen)_3}]^{3+/2+}$ and $[\mathrm{Co(bpy)_3}]^{3+/2+}$ couples, that is, $\Delta\Delta H^{*} = \Delta H^{*}([\mathrm{Co(phen)_3}]^{3+}) - \Delta H^{*}([\mathrm{Co(bpy)_3}]^{3+}) = -11\ \mathrm{kJ\,mol^{-1}}$ and $\Delta\Delta S^{*}=\Delta S^{*}([\mathrm{Co(phen)_3}]^{3+})-\Delta S^{*}([\mathrm{Co(bpy)_3}]^{3+}) = -30\ \mathrm{J\,K^{-1}\,mol^{-1}}$.25) This suggests that the mechanism of the reactions of the cobalt(III) complexes with ascorbic acid is different from that of the self-exchange reactions of the complexes, which does not involve a π^*-π^* interaction between ligands of cobalt(II) and cobalt(III).26) The self-exchange of $[\mathrm{Co(edta)}]^{-/2-}$, which has a higher redox potential than these complexes, is very slow;27) the reaction of $[\mathrm{Co(edta)}]^{-}$ with ascorbic acid is also slow. Extended Hückel π-MO calculations28) have shown that the lowest π^* orbital energy for phen is higher than that of bpy by about $8\ \mathrm{kJ\,mol^{-1}}$.

On the basis of the above discussions, it can be thought that the reaction of the cobalt(III) complex with π-accepting ligands with π-donating ascorbic acid is much faster than that of the cobalt(III) complex without π-accepting ligands.

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