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Redox Potentials and Related Parameters of Cobalt(III/II) Complexes Containing Aminopolycarboxylates

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The formal potentials, reaction entropies, and other thermodynamic parameters have been determined for 12 (aminopolycarboxylato)cobalt(III/II) redox couples in aqueous solutions. It has been shown that the magnitudes of free energies derived from formal potentials are determined primarily by the entropies rather than enthalpies. The entropy differences of the redox couples are dependent mainly on the charges of the complex ions: -25 ± 4 J K^{-1} mol^{-1} for [complex]$^{-/2-}$ (six complexes), $+15 \pm 5$ J K^{-1} mol^{-1} for [complex]$^{0/-}$ (four complexes), and $+54 \pm 16$ J K^{-1} mol^{-1} for [complex]$^{2+/+}$ (one complex) at $I = 0.1$ M and 25 °C. The stability constants of several (aminopolycarboxylato)cobalt(III) complexes have also been obtained.

Introduction

The kinetics of redox reactions of metal complexes have been investigated extensively, and the importance of thermodynamic parameters in elucidating the mechanisms of the redox reactions has been well recognized.[1] Though there have been numerous studies of the kinetics of homogeneous redox reactions involving Co(III/II) complexes, the redox potentials of Co(III/II) couples have been reported for only a few complexes. This is mainly because of the irreversibility of the electrode processes and the lability of Co(II) complexes. In this work, however, a number of (aminopolycarboxylato)cobalt(III) complexes are found to be reduced reversibly at the mercury electrode and allow the determination of the formal redox potentials ($E^{\circ\prime}$) of the half-cell reactions

$$\mathrm{Co^{III}L + e^- \rightleftharpoons Co^{II}L} \qquad (1)$$

The entropy differences of the redox couples

$$\Delta S_{\mathrm{rc}}^\circ = S^\circ(\mathrm{Co^{II}L}) - S^\circ(\mathrm{Co^{III}L}) \qquad (2)$$

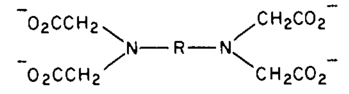
are also determined by measuring the temperature coefficients of nonisothermal electrochemical cells.[2] The factors that control the thermodynamic quantities—formal potentials, entropies, and enthalpies—of the (aminopolycarboxylato)cobalt(III/II) redox couples are examined by changing the nature of the coordinated ligands systematically.

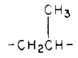
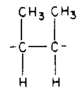
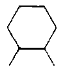
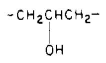
Experimental Section

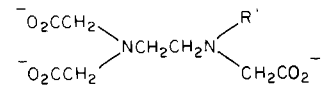
Materials. The solutions of sodium perchlorate and lithium perchlorate were prepared by treating the corresponding carbonate with an equivalent amount of 70% perchloric acid.

Two types of aminopolycarboxylates were used as ligands. One is tetraacetates and the other triacetates. The ligands and their abbreviations are given in Table I. The cobalt(III) complexes of these ligands were synthesized in the following procedures, were characterized by elemental analyses, and gave satisfactory results.

Table I. Structures and Abbreviations of Aminopolycarboxylates

Tetraacetates 

-R-	abbrevn	name
$-(\mathrm{CH_2})_2-$	edta	1,2-diaminoethane-*N,N,N',N'*-tetraacetate
$-(\mathrm{CH_2})_3-$	trdta	1,3-diaminopropane-*N,N,N',N'*-tetraacetate
$-(\mathrm{CH_2})_4-$	tdta	1,4-diaminobutane-*N,N,N',N'*-tetraacetate
 $-\mathrm{CH_2CH(CH_3)}-$	pdta	1,2-diaminopropane-*N,N,N',N'*-tetraacetate
 $-\mathrm{CH(CH_3)CH(CH_3)}-$	*ms*-bdta	*meso*-2,3-diaminobutane-*N,N,N',N'*-tetraacetate
	cydta	*trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate
 $-\mathrm{CH_2CH(OH)CH_2}-$	dpot	1,3-diamino-2-propanol-*N,N,N',N'*-tetraacetate

Triacetates 

-R'	abbrevn	name
-H	edtra	1,2-diaminoethane-*N,N,N'*-triacetate
$-\mathrm{CH_3}$	medtra	1,2-diaminoethane-*N*-methyl-*N,N',N'*-triacetate
$-(\mathrm{CH_2})_2\mathrm{OH}$	hedtra	1,2-diaminoethane-*N*-hydroxyethyl-*N,N',N'*-triacetate
$-(\mathrm{CH_2})_3\mathrm{OH}$	hpedtra	1,2-diaminoethane-*N*-hydroxypropyl-*N,N',N'*-triacetate

The following compounds were obtained by published procedures: $\mathrm{K[Co(trdta)]\cdot 2H_2O}$,[3] $\mathrm{K[Co(tdta)]\cdot 3H_2O}$,[4] $\mathrm{K[Co(pdta)]\cdot H_2O}$,[5]

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$K[Co(cydta)]\cdot 3H_2O$,[6] $[Co(edtra)(H_2O)]\cdot 1.5H_2O$,[7] $[Co(medtra)(H_2O)]\cdot 3H_2O$,[8] $[Co(hedtra)(H_2O)]$,[9] and $[(NH_3)_5Co\{(edta)Co(H_2O)\}](ClO_4)_2$.[10]

Preparation of $Na[Co(edta)]\cdot 4H_2O$. $Na_2H_2edta\cdot 2H_2O$ (37 g), sodium acetate trihydrate (20 g), cobalt(II) acetate tetrahydrate (25 g), and 5 g of active charcoal were added to 400 mL of water, to which 30 mL of 15% hydrogen peroxide was added. Air was passed through the mixture overnight at room temperature. Then, the solution was filtered and the filtrate evaporated to a small volume on a boiling water bath. The reddish violet crystals of $Na[Co(edta)]\cdot 4H_2O$ deposited upon cooling the solution in an ice bath. The compound was recrystallized from water by the addition of ethanol; yield 40.8 g.

Preparation of K[Co(dpot)]. H_4dpot (0.97 g), potassium acetate (1.8 g), and cobalt(II) acetate tetrahydrate (0.75 g) were dissolved in 40 mL of water, to which 1.4 g of lead dioxide was added. The solution was stirred for 20 min and then filtered. The filtrate was evaporated to a small volume. Reddish violet crystals of K[Co(dpot)] deposited upon the addition of ethanol. The complex was recrystallized from water by the addition of ethanol; yield 1.2 g.

Preparation of Na[Co(*ms*-bdta)]·$3H_2O$. H_4-*ms*-bdta was prepared by the procedure described in the previous paper.[11] The cobalt(III) complex was prepared by a method similar to that for K[Co(pdta)]·H_2O reported by Dwyer and Garvan.[5]

Preparation of [Co(hpedtra)(H_2O)]·$0.5H_2O$. Na_3hpedtra was prepared from *N*-(hydroxypropyl)ethylenediamine by a method similar to that for Na_3 medtra by Van Saun and Douglas.[8] The reaction mixture was used directly for the preparation of the cobalt(III) complex without isolation of the ligand. The cobalt(III) complex [Co(hpedtra)(H_2O)]·$0.5H_2O$, was prepared by a method similar to that for [Co(edtra)(H_2O)]·$0.5H_2O$ by Blackmer et al.[7]

Measurements. Cyclic voltammetry was performed by using solutions of (aminopolycarboxylato)coblat(III) at an appropriate pH and ionic strength with a three-electrode system consisting of a hanging-mercury-drop electrode, a platinum-wire auxiliary electrode, and a saturated calomel electrode (SCE). The SCE was thermostated at 25 °C and was connected to the cell solution by a 3.5 M KCl salt bridge, which was separated from the cell solution with a 0.25 M Na_2SO_4 agar bridge to prevent the precipitation of $KClO_4$. Therefore, the entire cell assembly can be expressed as

$$\underbrace{\mathrm{SCE}\;\Bigg|\;\begin{matrix}3.5\ \mathrm{M}\\ \mathrm{KCl}\end{matrix}}_{25^\circ\ \mathrm{C}}\;\Bigg|\;\underbrace{\begin{matrix}0.25\ \mathrm{M}\\ \mathrm{Na_2SO_4\ agar}\end{matrix}\;\Bigg|\;\begin{matrix}\mathrm{NaClO_4\ (or\ LiClO_4),}\\ \mathrm{Co(III/II)}\end{matrix}\;\Bigg|\;\mathrm{Hg}}_{\text{temp varied}}$$

The temperature of the cell solution was varied from 0 to 50 °C. The temperature coefficient of the overall potential of the nonisothermal cell can be approximated to be equal to that of the Galvani metal solution potential difference at the working electrode, which can be related to the entropy difference of the oxidized and the reduced species by eq 3., where F denotes the Faraday constant. The temperature

$$F(\mathrm{d}E^\circ/\mathrm{d}T) = \Delta S_{\mathrm{rc}}{}^\circ \tag{3}$$

coefficient of the potential difference across the thermal liquid junction within the salt bridge and that of the thermocouple potential difference between the hot and cold regions of the mercury electrode are negligible as compared with the experimental uncertainties in the present experiments.[2,12-14]

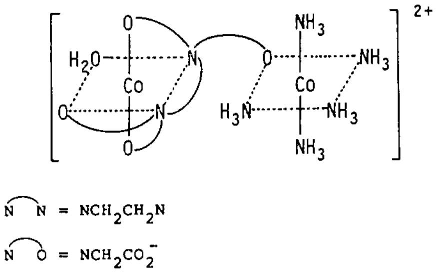
The pHs of the solutions were adjusted to be 4–6 where no pH dependence of the potentials was observed.

Cyclic voltammograms were obtained with a Yanaco P-1000 voltammetric analyzer at sweep of 0.025–1 V s^{-1}; most voltammograms were obtained at 0.05 V s^{-1}.

Results and Discussion

The X-ray analyses and the infrared and NMR spectra have indicated that aminopolycaraboxylates of the tetraacetate type used in this work act as hexadentate ligands for cobalt(III) ions.[3-5,15-18] Higginson and Samuel reported that, from equilibrium studies, cobalt(II)–edta, –pdta, and –cydta complexes are mixtures of hexadentate species and pentadentate species, respectively.[19] As will be shown below, these cobalt(III/II) couples show reversible electrochemical behavior and the structural changes accompanied by the redox processes, if present, do not interfere with the electrode reactions.

It is known that the in-plane acetate arms in $[Co(edta)]^-$ are more strained than the out-of-plane acetate arms.[15] A structural feature similar to this was also found for $[Co(trdta)]^-$.[16] Therefore, in the cobalt(III) complexes containing the aminopolycarboxylates of the triacetate type ([CoL(H_2O)]), the water ligand may occupy an in-plane or equatorial site. In fact, the NMR spectra indicate that [Co(edtra)(H_2O)], [Co(medtra)(H_2O)], and [Co(hedtra)(H_2O)] are the equatorial isomers.[20] It is also confirmed by X-ray analysis that $K[Co(NO_2)(edtra)]\cdot 1.5H_2O$ takes the equatorial form.[21] From a consideration similar to this, it was suggested that $[(NH_3)_5Co\{(edta)Co(H_2O)\}]^{2+}$ has the structure shown by I, in which the water ligand again occupies the equatorial site.[10]



I

Electrochemical data determined by cyclic voltammetry for (aminopolycarboxylato)cobalt(III/II) are summarized in Table II. All the complexes included in the table show both cathodic and anodic peaks at the hanging-mercury-drop electrode at 0–0.4 V vs. SCE, and the peak height ratios are approximately unity. The separations of the two peaks are 60–78 mV at 25 °C for all the complexes except the dimer, $[(NH_3)_5Co\{(edta)Co(H_2O)\}]^{2+}$, implying reversible one-electron electrode processes.[22] The data for the dinuclear complex are for the redox process of the cobalt atom surrounded by edta:

$$[(NH_3)_5Co^{III}\{(edta)Co^{III}(H_2O)\}]^{2+} + e^- \rightleftharpoons [(NH_3)_5Co^{III}\{(edta)Co^{II}(H_2O)\}]^{+} \tag{4}$$

The separation between cathodic and anodic peaks is 150 mV, implying a quasi-reversible one-electron electrode process. The reduction of the pentaamminecobalt(III) moiety in this complex takes place at −0.15 V vs. SCE irreversibly.

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(1) For example: Marcus, R. A.; Sutin, N. *Inorg. Chem.* **1975**, *14*, 212. Weaver, M. J.; Yee, E. L. *Ibid.* **1980**, *19*, 1936.

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(22) In a previous paper,[23] it was found that the polarographic waves of $[Co(edta)]^{-/2-}$, $[Co(trdta)]^{-/2-}$, and $[Co(pdta)]^{-/2-}$ were reversible.

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Table II. Electrochemical Data and Thermodynamic Parameters of (Aminopolycarboxylato)cobalt(III/II) Complexes at 25 °C

complex	electrolyte	$E^{\circ\prime}$/mV vs. SCE	ΔE^a/ mV	ΔS_{rc}°/ J K^{-1} mol^{-1}	ΔG° [b]/ kJ mol^{-1}	ΔH° [b]/ kJ mol^{-1}	ΔS° [b]/ J K^{-1} mol^{-1}
$[Co(edta)]^{-/2-}$	0.1 M $NaClO_4$	128 ± 4	68	−30 ± 4	−35.6 ± 0.4	−70 ± 2	−114 ± 4
	1.0 M $NaClO_4$	129 ± 3	60	−7 ± 6	−35.7 ± 0.3	−63 ± 2	−91 ± 6
$[Co(trdta)]^{-/2-}$	0.1 M $NaClO_4$	49 ± 4	67	−28 ± 7	−28.0 ± 0.4	−61 ± 3	−112 ± 7
	1.0 M $NaClO_4$	52 ± 3	64	−5 ± 5	−28.3 ± 0.3	−55 ± 2	−89 ± 7
$[Co(tdta)]^{-/2-}$	1.0 M $NaClO_4$	301 ± 15	75		−52.3 ± 1.5		
$[Co(pdta)]^{-/2-}$	0.1 M $NaClO_4$	121 ± 3	64	−24 ± 5	−34.9 ± 0.3	−67 ± 2	−108 ± 5
	1.0 M $NaClO_4$	122 ± 3	64	−10 ± 5	−35.0 ± 0.3	−63 ± 2	−94 ± 5
$[Co(\textit{ms}\text{-}bdta)]^{-/2-}$	0.1 M $NaClO_4$	93 ± 3	65	−28 ± 5	−32.2 ± 0.3	−66 ± 2	−112 ± 5
$[Co(cydta)]^{-/2-}$	0.1 M $NaClO_4$	110 ± 2	68	−23 ± 3	−33.9 ± 0.2	−66 ± 1	−107 ± 3
	1.0 M $NaClO_4$	117 ± 3	63	−16 ± 7	−34.6 ± 0.3	−64 ± 2	−100 ± 7
$[Co(dpot)]^{-/2-}$	0.1 M $LiClO_4$	101 ± 8	65	−14 ± 5	−33.0 ± 0.8	−62 ± 2	−98 ± 5
$[Co(edtra)(H_2O)]^{0/-}$	0.1 M $NaClO_4$	222 ± 5	78	13 ± 9	−44.7 ± 0.5	−66 ± 3	−71 ± 9
$[Co(medtra)(H_2O)]^{0/-}$	0.1 M $NaClO_4$	238 ± 4	71	22 ± 7	−46.2 ± 0.4	−65 ± 3	−62 ± 7
	1.0 M $NaClO_4$	236 ± 2	73	31 ± 3	−46.0 ± 0.2	−62 ± 1	−53 ± 3
$[Co(hedtra)(H_2O)]^{0/-}$	0.1 M $NaClO_4$	261 ± 4	78	8 ± 7	−48.5 ± 0.4	−71 ± 3	−76 ± 7
$[Co(hpedtra)(H_2O)]^{0/-}$	0.1 M $LiClO_4$	217 ± 4	72	18 ± 6	−44.2 ± 0.4	−64 ± 2	−66 ± 6
$[(NH_3)_5Co\{(edta)Co(H_2O)\}]^{2+/+}$	0.1 M $LiClO_4$	287 ± 8	150	54 ± 16	−51.0 ± 0.8	−60 ± 6	−30 ± 16

[a] The separation between cathodic and anodic peaks determined at a sweep rate of 50 mV s^{-1}. [b] The values are hybrid constants (see ref 27).

The half-wave potentials were obtained by averaging the peak potentials and were approximated to be equal to $E^{\circ\prime}$ (differences in diffusion and activity coefficients between the oxidized and reduced species were assumed to be small).

A. ΔG° Values. From the $E^{\circ\prime}$ values of the complexes, the free energies of the reactions

$$Co^{III}L + {}^1/{}_2H_2 \rightleftharpoons Co^{II}L + H^+ \qquad (5)$$

were calculated and are given in Table II. The ΔG° values are insensitive to the ionic strength. Among the tetraacetato complexes with five-membered chelate rings involving two nitrogen atoms, those with electron-releasing substituents, i.e., pdta, *ms*-bdta, and cydta complexes, have less negative ΔG° values than the edta complex. The ΔG° values for the trdta and the dpot complexes, which have six-membered chelate rings involving two nigrogen atoms, are less negative than that for the edta complex, suggesting that the six-membered chelate ring is relatively less favorable than the five-membered chelate ring for the reduction of Co(III) complexes. The trdta complex has a less negative ΔG° value than the dpot complex, which has an electron-withdrawing hydroxyl group. These suggest that the stronger basicity of the nitrogen atoms[24] makes the value of ΔG° less negative. Though there are some variations among the ΔG° values of tetraacetato complexes in Table II as mentioned above, all of them are in a narrow range of −32 ± 4 kJ mol^{-1} except the tdta complex.

The values of the triacetato complexes are also close to each other but are much more negative than those for the tetraacetato complexes except the tdta complex. The ΔG° value of the dinuclear complex is the most negative compared with the two groups of the mononuclear complexes.

B. ΔS_{rc}° Values. The entropy differences of the redox couples, ΔS_{rc}° were obtained by using eq 3 and are also given in Table II. The value for the tdta complex could not be determined because the cyclic voltammogram was not well-defined at higher temperature. The ΔS_{rc}° values are less negative at higher ionic strengths, which is consistent with the decrease of the charge effects with increasing ionic strength as has been observed for some copper(III/II) redox couples.[25] It is seen from Table II that the ΔS_{rc}° values can be classified into three groups according to their charges. For tetraacetato complexes of charge 1−/2−, the ΔS_{rc}° values are in a narrow range of −14 to −30 J K^{-1} mol^{-1}, for triacetato complexes of charge 0/1−, they are +8 to +22 J K^{-1} mol^{-1}, and ΔS_{rc}° for the complex of charge 2+/1+ is as large as +54 J K^{-1} mol^{-1} at $I = 0.1$: The values of ΔS_{rc}° increase with the increase of the charge of the complex ions. An estimation of the effect of charge and ionic radius is made by using the classic Born equation; the values obtained by the Born equation are −40 J K^{-1} mol^{-1} for the redox couple of charge 1−/2− and radius of 3 Å, −10 J K^{-1} mol^{-1} for the couple of charge 0/1− and radius of 3 Å, and +24 J K^{-1} mol^{-1} for the couple of charge 2+/1+ and radius of 4 Å. Although this trend is in a good agreement with that observed experimentally, the experimental values are always more positive than the calculated values by 20–30 J K^{-1} mol^{-1}. Much more pronounced differences between the experimental and calculated (Born) values were observed in many other redox couples of complex ions, which have been attributed to structure-making effects of complex ions due to hydrogen bonding or other specific solute–solvent interactions[2] and structural effects.[25] The rather small differences observed in the (aminopolycarboxylato)cobalt(III/II) couples indicate that their ΔS_{rc}° values depend primarily on the electrostatic effects, and other effects such as specific solute–solvent interactions and structural factors are minor. A part of the difference between the experimental and calculated values may be attributable to the increase of bond lability accompanying reduction.

C. ΔH° Values. The use of ΔS_{rc}° of 84.0 J K^{-1} mol^{-1} for the standard hydrogen couple $H^+/{}^1/{}_2H_2$[26] makes it possible to calculate the values of ΔS° and hence ΔH° of reaction 5. These thermodynamic parameters are also included in Table II.[27]

The most striking feature of the results is that the ΔH° values for all the complexes in Table II are in a narrow range of −61 to −72 kJ mol^{-1} ($I = 0.1$), though the ΔG° values are classified into three groups as has been mentioned earlier. It is surprising that $[(NH_3)_5Co\{(edta)Co(H_2O)\}]^{2+}$ also shows an enthalpy value close to those of the other complexes.

The results indicate that the differences in ΔG° values among the tetraacetato complexes, the triacetato complexes, and the dinuclear complex are attributable to the differences in ΔS° values; i.e., the most important factor determining the

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Table III. Stability Constants of Co(III) Complexes at $I = 0.1$, 25 °C

Co(III) complex	log ($K_{\mathrm{Co}^{\mathrm{III}}\mathrm{L}}$/ $K_{\mathrm{Co}^{\mathrm{II}}\mathrm{L}}$)	log $K_{\mathrm{Co}^{\mathrm{II}}\mathrm{L}}$	log $K_{\mathrm{Co}^{\mathrm{III}}\mathrm{L}}$
[Co(edta)]$^-$	24.89	16.03[a-c]	40.92
[Co(trdta)]$^-$	26.31	15.39[a,c,d]	41.70
[Co(tdta)]$^-$	22.0	15.58[a,c,d]	37.6
[Co(pdta)]$^-$	25.01	17.40[e]	42.41
[Co(*ms*-bdta)]$^-$	25.49	16.9[f]	42.4
[Co(cydta)]$^-$	25.20	18.73[a,b,g]	43.93
[Co(dpot)]$^-$	25.35	13.92[h]	39.27
[Co(hedtra)(H_2O)]	22.65	14.8[i]	37.5

[a] Calculated from the value of $K_{\mathrm{Co}^{\mathrm{II}}\mathrm{L}}$ at 20 °C, $I = 0.1$ by use of the $\Delta H°$ value. [b] Schwarzenbach, G.; Gut, R.; Anderegg, G. *Helv. Chim. Acta* 1954, *37*, 937. [c] Anderegg, G. *Ibid.* 1964, *47*, 1801. [d] L'Eplattenier, F.; Anderegg, G. *Ibid.* 1964, *47*, 1792. [e] Ogino, H. *Bull. Chem. Soc. Jpn.* 1965, *38*, 771. [f] Calculated from the value of $K_{\mathrm{Co}^{\mathrm{II}}\mathrm{L}}$ at 20 °C, $I = 0.1$ (Majer, J.; Novak, V.; Svicekowa, M. *Chem. Zvesti* 1964, *18*, 481). The $\Delta H°$ value was estimated by the present authors. [g] Anderegg, G. *Helv. Chim. Acta* 1963, *46*, 1833. [h] Thompson, L. C.; Kundra, S. K. *J. Inorg. Nucl. Chem.* 1966, *28*, 2945. [i] Calculated from the value of $K_{\mathrm{Co}^{\mathrm{II}}\mathrm{L}}$ at 30 °C, $I = 0.1$ (Chaberek, S., Jr.; Martell, A. E. *J. Am. Chem. Soc.* 1955, *77*, 1477). The $\Delta H°$ value was estimated by the present authors.

magnitude of free energies of (aminopolycarboxylato)cobalt(III/II) couples is the entropies, which in turn are dependent primarily on the charge of the complexes.

Quite recently, the enthalpy of the oxidation reaction of $[\mathrm{Co^{II}(edta)}]^{2-}$ by MnO_4^- was determined by a direct thermometric titration to be -101.4 kJ mol^{-1} by Doi.[28] The thermodynamic parameters of reaction 5 were also calculated by combining the $\Delta H°$ value of the oxidation reaction of $[\mathrm{Co(edta)}]^{2-}$ by MnO_4^- with those of related reactions, the results obtained by the nonelectrochemical method being $\Delta G° = -37.1$ kJ mol^{-1}, $\Delta H° = -69.9$ kJ mol^{-1}, and $\Delta S° = -110$ J K^{-1} mol^{-1} at $I = 0.1$, 25 °C. These are in a reasonably good agreement with those in Table II, supporting the validity of the experimental procedure employed in this work.

D. Stability Constants of Co(III) Complexes. The number of stability constants reported for cobalt(III) complexes is limited because of the experimental difficulty due to the inertness of the cobalt(III) complexes. As the formal potentials of (aminopolycarboxylato)cobalt(III/II) couples were determined (Table II), the stability constants of the cobalt(III) complexes, $K_{\mathrm{Co^{III}L}}$, can be caluclated by using the redox potential of $\mathrm{Co(aq)}^{3+}/\mathrm{Co(aq)}^{2+}$[29] and the stability constants of the cobalt(II) complexes, $K_{\mathrm{Co^{II}L}}$. The results are summarized in Table III. It is seen that the stability order is almost parallel for Co(III) and Co(II) complexes of tetraacetate, though the order is reversed for the edta and the trdta complexes.[23] The $K_{\mathrm{Co^{III}L}}$ values of triacetato complexes were not obtained except for that of the hedtra complex because of the absence of the $K_{\mathrm{Co^{II}L}}$ data. The stability constant of $[\mathrm{Co^{III}(hedtra)(H_2O)}]$ is much smaller than that of $[\mathrm{Co^{III}(edta)}]^-$ as compared with the stability constants of the cobalt(II) complexes. The relative destabilization of the Co(III) complex of the triacetate is manifested in its more negative $\Delta G°$ value. As has been stated in the previous section, the magnitude of $\Delta G°$ is governed by the entropy term; that is to say, the relative destabilization of the (triacetato)cobalt(III) complex compared with (tetraacetato)cobaltate(III) complexes is attributable to the effect of the entropy, which is governed mainly by the charge of the complexes.

Registry No. Na[Co(edta)], 14025-11-7; K[Co(trdta)], 26527-97-9; K[Co(tdta)], 25640-45-3; K[Co(pdta)], 15137-60-7; Na[Co(*ms*-bdta)], 85977-11-3; K[Co(cydta)], 22476-11-5; K[Co(dpot)], 85977-12-4; Co(edtra)(H_2O), 26599-29-1; Co(medtra)(H_2O), 33972-19-9; Co(hedtra)(H_2O), 33972-21-3; Co(hpedtra)(H_2O), 85977-13-5; $[(\mathrm{NH_3})_5\mathrm{Co}\{(\mathrm{edta})\mathrm{Co}(\mathrm{H_2O})\}](\mathrm{ClO_4})_2$, 61813-11-4; $\mathrm{Co(edta)}^{2-}$, 14931-83-0; $\mathrm{Co(trdta)}^{2-}$, 16904-03-3; $\mathrm{Co(tdta)}^{2-}$, 42912-34-5; $\mathrm{Co(pdta)}^{2-}$, 52582-07-7; Co(*ms*-bdta)$^{2-}$, 26425-14-9; $\mathrm{Co(cydta)}^{2-}$, 28161-91-3; $\mathrm{Co(dpot)}^{2-}$, 14930-81-5; $\mathrm{Co(edtra)(H_2O)}^-$, 85977-14-6; $\mathrm{Co(medtra)(H_2O)}^-$, 85977-15-7; $\mathrm{Co(hedtra)(H_2O)}^-$, 28161-92-4; $\mathrm{Co(hpedtra)(H_2O)}^-$, 85977-16-8; $(\mathrm{NH_3})_5\mathrm{Co}\{(\mathrm{edta})\mathrm{Co}(\mathrm{H_2O})\}^+$, 85977-17-9.

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Rates of Decarboxylation of the Bis(carbonato)(ethylenediamine)cobaltate(III) Ion in Phosphoric Acid Buffer Solutions and Aqueous Perchloric Acid

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The kinetics of the complete decarboxylation of the bis(carbonato) complexes $\mathrm{K[Co(en)(CO_3)_2]\cdot H_2O}$ and $\mathrm{Na[Co(en)(CO_3)_2]\cdot H_2O}$ in aqueous acidic solutions have been investigated. The interpretation of the data is that only the second decarboxylation has been studied at the experimental conditions. The rate data for the ring-opening step that is related to the loss of the second CO_2 from the title complex are described by a pseudo-first-order rate constant of the form $k_{\mathrm{obsd}} = k_{\mathrm{a}} + k_{\mathrm{b}}[\mathrm{H_3O^+}]$. Rate parameters at 5 °C and $I = 1.0$ M ($NaClO_4$) are $k_{\mathrm{a}} = (5.7 \pm 1.0) \times 10^{-4}$ s^{-1} and $k_{\mathrm{b}} = (4.37 \pm 0.12) \times 10^{-2}$ M^{-1} s^{-1} with activation parameters for the acid-catalyzed pathway of $\Delta H_{\mathrm{b}}^{*} = 12 \pm 2$ kcal mol^{-1} and $\Delta S_{\mathrm{b}}^{*} = -21$ ● 8 cal deg^{-1} mol^{-1}. An induction period noted during the decarboxylation reaction is ascribed to the formation of the ring-opened monodentate carbonato aquo species $\mathrm{Co(en)(CO_3)(HCO_3)(H_2O)}$ or $\mathrm{Co(en)(HCO_3)(H_2O)_3}^{2+}$. We have been unable to isolate a stable bidentate $\mathrm{Co(en)(CO_3)(H_2O)_2}^+$ intermediate as has been found for the analogous pyridine complex. The kinetic results are compared with those for the decarboxylation of other mono(carbonato)cobalt(III) and bis(carbonato)cobaltate(III) complexes.

Introduction

Bidentate carbonato complexes decarboxylate at rates that are quite sensitive to the nature of the "nonparticipating" ligands, metal center, and charge on the complex itself.[1,2] Indeed, reported rate constants for the acid-catalyzed ring-opening step vary over approximately 7 orders of magnitude,

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(1) There have been numerous studies. Reference 2 is a recent investigation and cites much of the previous work.

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