

# The Probable Structures of Cobalt(II)-EDTA Type Complexes in Aqueous Solution from Oxidation Experiments

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**Abstract:** The rate constants and the immediate products are determined for the outer-sphere oxidation of a series of cobalt(II)-EDTA type compounds by iron(III) and ruthenium(III) complexes. The results indicate that at pH  $\geq 4.5$  the cobalt(II) complexes should be represented largely as  $\geq 80\%$   $\text{Co(EDTA)}^{2-}$  and  $\text{Co(CyDTA)}^{2-}$ , in which all donor atoms in the ligand are coordinated; and  $\geq 95\%$   $\text{Co(HyDTA)(H}_2\text{O)}^-$ , in which the ligand is five-coordinated. Some unusual properties of  $\text{Co(CyDTA)(H}_2\text{O)}^-$  are revealed.

Increasing attention is being paid to the question of the nature and number of bonding sites in multidentate ligands, using a variety of approaches: nmr, infrared, and consideration of values of formation and rate constants for behavior in solution, and X-ray crystallography for the solid state. The investigations of the structures of solid metal-EDTA complexes by Hoard and his colleagues have led to several interesting surprises.<sup>1</sup> Much less is known, however, about these structures in solution, particularly of the labile complexes, such as those of the bivalent transition metals. The situation for the latter has been summarized by Higginson,<sup>2</sup> who concluded that many contained quinque-dentate ligands, *i.e.*, the complex should be represented as  $\text{M(EDTA)(H}_2\text{O)}^{2-}$ , with one uncoordinated carboxylate group, rather than as the structure  $\text{M(EDTA)}^{2-}$ , in which all donor sites are coordinated.<sup>3</sup>

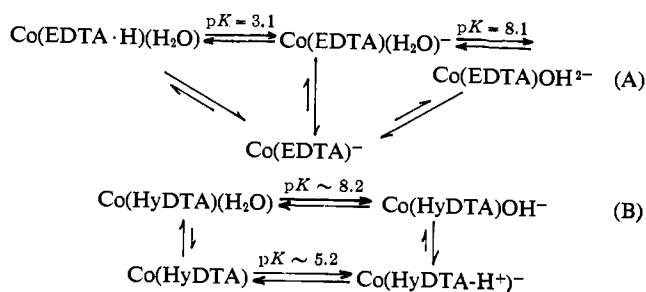
There is one approach to the solution of this problem, admittedly limited to the easily oxidizable metal complexes. This is to treat that complex with a series of rapidly reacting outer-sphere oxidants at different pH's, and to identify the resultant product soon after it is formed. If, in addition, the oxidation rate constants are also measured, then it will be shown that it is possible to make reasonable deductions as to the structure of the original reactant in solution. In the case of two of the three species which have been examined, namely cobalt(II)-EDTA and -HyDTA complexes,<sup>4</sup> the cobalt(III) products have been characterized spec-

trally, and they are relatively stable to interconversion.<sup>5,6</sup> Schemes A and B show the known species and their appropriate pK values. It was necessary for us however to study the corresponding cobalt(III)-CyDTA<sup>4</sup> complexes, to determine their spectra and interconversion rate constants.

## Experimental Section

**Materials.** The ligands were commercial products. Their purity was checked by titration and found to be  $\geq 98\%$ . 2,2'-Bipyridine was a gift from Imperial Chemical Industries Ltd., and was purified by heating *in vacuo* at 130°. The solid complexes used were prepared by literature methods and characterized by their spectra. These included  $\text{KCo(EDTA)} \cdot 3\text{H}_2\text{O}$ ,<sup>7</sup>  $\text{Na}_2\text{Co(EDTA)OH} \cdot 3\text{H}_2\text{O}$ ,<sup>8</sup>  $\text{KMn(CyDTA)} \cdot 2.5\text{H}_2\text{O}$ ,<sup>9</sup>  $\text{KMn(CyDTA)} \cdot 2.5\text{H}_2\text{O}$ ,<sup>10</sup> *trans*- $[\text{Co(py)}_4\text{Cl}_2] \cdot 6\text{H}_2\text{O}$ ,<sup>11</sup> and  $\text{Fe(bipy)}_3(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ .<sup>12</sup> The species  $\text{Fe(phen)}_3^{3+}$  and  $\text{Fe(phen-5-SO}_3)_3$  were prepared *in situ* from Fe(II), ligand ( $\sim 1:3$ ), and Ce(IV) in  $\text{H}_2\text{SO}_4$  in slight deficiency. The ion  $\text{Ru(bipy)}_3^{3+}$  was formed by oxidation of  $\text{Ru(bipy)}_3^{2+}$  (G. F. Smith Co., Columbus, Ohio) with  $\text{PbO}_2$  in acid solution. The spectrum obtained of the solution after filtering was in good agreement with that reported.<sup>13</sup> The ion is stable only in acid (pH  $< 2.5$ ) medium.

**Examination of Oxidation Product.** Cobalt(II) ion and ligand (10% excess of 1:1 mole ratio) was treated with oxidant (10% excess of Fe(III), or 5% deficiency of Mn(III)) at the appropriate pH. In the concentrations used ( $\sim 10^{-2}$  M) the oxidation was complete within seconds, after which time the solution was adjusted to pH 9.5-10.0. This converts the complexes to  $\text{Co(EDTA)OH}^{2-}$  or  $\text{Co(HyDTA)OH}^-$ , which only slowly change to  $\text{Co(EDTA)}^-$  or  $\text{Co(HyDTA-H}^+)^-$ . The adjustment was unnecessary with the CyDTA complex, which only slowly converts even in the  $\text{Co(CyDTA)(H}_2\text{O)}^-$  form. With iron(III) oxidations, the solution was then rapidly passed through an ion-exchange column (Dowex 50 WX8,  $\text{Na}^+$  form). The effluent, free of any cationic reactant and product, could be examined within 90 sec after oxidation. This separation was unnecessary when Mn(III) complexes or  $\text{Co(py)}_4\text{Cl}_2^+$  were used as oxidants, since the Mn(II) and Co(II) products, unlike the Fe(II) species, are colorless in the pertinent spectral region. One can accurately estimate the per cent of six-coordinated species from the spectra, using a number of wavelengths, or alternatively show the absence of five-coordinated species from the lack of further spectral change. The results are shown in Table I.



(1) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964), and previous references.

(2) W. C. E. Higginson, *J. Chem. Soc.*, 2761 (1962).

(3) These will be referred to as five-coordinated and six-coordinated complexes, respectively, although in the former case octahedral coordination is envisaged.

(4) EDTA = ethylenediamine-N,N,N',N'-tetraacetate; HyDTA = N-(2-hydroxyethyl)ethylenediamine-N,N',N'-triacetate; CyDTA = *trans*-1,2-cyclohexanediaminetetraacetate.

(5) I. A. W. Shimi and W. C. E. Higginson, *J. Chem. Soc.*, 260 (1958); R. Dyke and W. C. E. Higginson, *ibid.*, 1998 (1960).

(6) S. P. Tanner and W. C. E. Higginson, *ibid.*, A, 537 (1966).

(7) F. P. Dwyer, F. C. Gyrfas, and D. P. Mellor, *J. Phys. Chem.*, **59**, 296 (1955).

(8) F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **83**, 2610 (1961).

(9) Y. Yoshino, A. Ouchi, Y. Tsunoda, and M. Kojima, *Can. J. Chem.*, **40**, 775 (1962).

(10) R. E. Hamm and M. A. Suwyn, *Inorg. Chem.*, **6**, 137 (1967).

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(12) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952).

(13) R. R. Meller, W. W. Brandt, and Sr. M. Pike, *J. Amer. Chem. Soc.*, **77**, 3179 (1955).

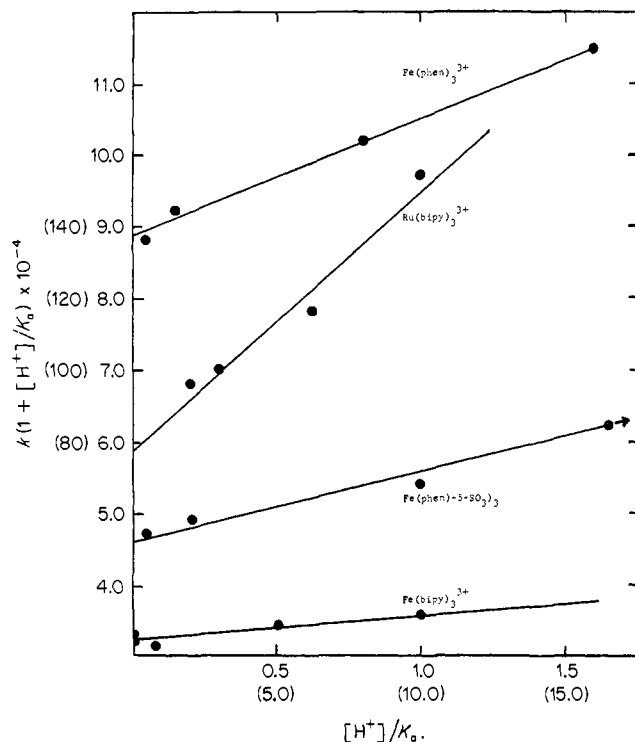


Figure 1. Plots of  $k(1 + [H^+]/K_a) \times 10^{-4}$  vs.  $[H^+]/K_a$  for oxidation of Co(II)-EDTA complex. Data for  $\text{Ru}(\text{bipy})_3^{3+}$  at  $5^\circ$  and  $I = 1.0$  M. All others at  $25^\circ$  and  $I = 0.5$  M. Ordinates in parentheses refer to  $\text{Ru}(\text{bipy})_3^{3+}$  system.

**Kinetic Procedure.**  $\text{Fe}(\text{phen})_3^{3+}$  and  $\text{Fe}(\text{bipy})_3^{3+}$  ions are slowly reduced in acid and rapidly reduced in alkaline solution;  $\text{Ru}(\text{bipy})_3^{3+}$  ions are only stable at pH's lower than 2.7. These oxidants were therefore used in deficiency (0.005–0.020 mM) in the kinetic studies and their actual concentrations were unimportant.

Table I. Products of Oxidation of Cobalt(II) Complexes at  $25^\circ$  ( $I = 0.5$  M)

Reductant	Oxidant	pH	% ( $\pm 5\%$ ) product of six-dentated complex <sup>a</sup>
Co(II)-EDTA	$\text{Fe}(\text{bipy})_3^{3+}$	5.0	$\geq 95$
		2.5	86
Co(II)-EDTA	$\text{Fe}(\text{phen})_3^{3+}$	4.4	$\geq 97$
Co(II)-EDTA	$\text{Ru}(\text{bipy})_3^{3+}$	2.5	73
Co(II)-EDTA	$\text{Mn}(\text{EDTA})(\text{H}_2\text{O})^-$	5.0	17
		4.3	37
Co(II)-EDTA	$\text{Mn}(\text{CyDTA})(\text{H}_2\text{O})^-$	5.5	62
		4.5	80
Co(II)-EDTA	$\text{Co}(\text{py})_4\text{Cl}_2^+$	5.0	$\text{Co}(\text{EDTA})\text{Cl}_2^-$ ,
		2.7	$\text{Co}(\text{EDTA})^-$
Co(II)-EDTA	$\text{IrCl}_6^{2-}$	3.9–5.4	89 <sup>b</sup>
		2.7	34 <sup>b</sup>
Co(II)-CyDTA	$\text{Fe}(\text{bipy})_3^{3+}$	4.7	$\geq 95$
Co(II)-CyDTA	$\text{Mn}(\text{CyDTA})(\text{H}_2\text{O})^-$	4.5	$\sim 70^c$
		4.1	$\sim 50^c$
Co(II)-CyDTA	$\text{Co}(\text{py})_4\text{Cl}_2^+$	5.0	$\text{Co}(\text{CyDTA})\text{Cl}_2^-$ ,
			$\text{Co}(\text{CyDTA})^-$
Co(II)-HyDTA	$\text{Fe}(\text{bipy})_3^{3+}$	7.0	–0

<sup>a</sup> For example,  $\text{Co}(\text{EDTA})^-$ ,  $\text{Co}(\text{CyDTA})^-$ , or  $\text{Co}(\text{HyDTA}-\text{H}^+)$ .  
<sup>b</sup> Reference 17. <sup>c</sup> Approximate values, since the spectrum of  $\text{Co}(\text{CyDTA})(\text{H}_2\text{O})^-$  is not accurately known.

The Co(II) complex concentrations were varied from 0.20 to 1.0 mM. Good first-order plots were obtained ( $k_{\text{obsd}}$ ) from which the apparent second-order rate constant ( $k = k_{\text{obsd}}/[\text{Co}^{11}]_{\text{T}}$ ) could be calculated. This was a constant at a particular pH. The value

of  $k$  is related to the second-order rate constant for reaction of the unprotonated cobalt(II) form ( $k_1$ ), the protonated form ( $k_2$ ), and the pH, by

$$k = \frac{k_1 K_a + k_2 [H^+]}{K_a + [H^+]} \quad (1)$$

where  $K_a = [\text{unprotonated form}][H^+]/[\text{protonated form}]^{-1}$ . The plots of  $k(1 + [H^+]/K_a)$  against  $[H^+]/K_a$  are shown in Figure 1, and are linear as expected. The intercept equals  $k_1$  and the slope value is  $k_2$ . The gain of  $\text{Fe}(\text{bipy})_3^{3+}$  and  $\text{Fe}(\text{phen})_3^{3+}$  was monitored at 520–550 m $\mu$ , and that of  $\text{Ru}(\text{bipy})_3^{3+}$  at 480 m $\mu$ , using a stopped-flow apparatus of the Dulz and Sutin design.<sup>14</sup> A similar expression to (1) holds for the pH dependence of the observed first-order ring closure rate constant ( $k_{\text{obsd}}$ ) for the CyDTA complex in terms of  $\text{Co}(\text{CyDTA})(\text{H}_2\text{O})^-$ , rate constant  $k_1$ , and  $\text{Co}(\text{CyDTA} \cdot \text{H})(\text{H}_2\text{O})$ ,  $k_2$ . These changes were followed at 340 m $\mu$ .

At pH 5.0, there is a mixture of  $\text{Co}(\text{EDTA})^{2-}$  and  $\text{Co}(\text{EDTA})(\text{H}_2\text{O})^{2-}$ . If these are oxidized by  $\text{Fe}(\text{phen})_3^{3+}$  with rate constants  $k_{\text{Co}(\text{EDTA})^{2-}}$  and  $k_{\text{Co}(\text{EDTA})(\text{H}_2\text{O})^{2-}}$ , respectively, then since there is  $\geq 97\%$   $\text{Co}(\text{EDTA})^{2-}$  in the product

$$k_{\text{Co}(\text{EDTA})^{2-}}[\text{Co}(\text{EDTA})^{2-}] \geq 33k_{\text{Co}(\text{EDTA})(\text{H}_2\text{O})^{2-}}[\text{Co}(\text{EDTA})(\text{H}_2\text{O})^{2-}] \quad (2)$$

The observed rate constant  $k_1$  ( $9.1 \times 10^4$  M<sup>-1</sup> sec<sup>-1</sup> at pH 5) is related to these rate constants by the expression

$$k_1[\text{Co}(\text{EDTA})^{2-} + \text{Co}(\text{EDTA})(\text{H}_2\text{O})^{2-}] = k_{\text{Co}(\text{EDTA})^{2-}}[\text{Co}(\text{EDTA})^{2-}] + k_{\text{Co}(\text{EDTA})(\text{H}_2\text{O})^{2-}}[\text{Co}(\text{EDTA})(\text{H}_2\text{O})^{2-}] \quad (3)$$

The reasonable assumption is made that  $k_{\text{Co}(\text{EDTA})(\text{H}_2\text{O})^{2-}} \approx k_{\text{Co}(\text{EDTA} \cdot \text{H})(\text{H}_2\text{O})^-}$ , which is the rate constant for oxidation of the protonated Co-EDTA species by  $\text{Fe}(\text{phen})_3^{3+}$  ( $1.6 \times 10^4$ ). Combining (2) and (3) leads to (4).

$$[\text{Co}(\text{EDTA})^{2-}] \geq 5[\text{Co}(\text{EDTA})(\text{H}_2\text{O})^{2-}] \quad (4)$$

The kinetic data are shown in Table II. The second-order rate constant  $k$  is usually the mean of several determinations, independent of the concentration of reactants over a fivefold change. The final values are collected in Table III with Arrhenius parameters

Table II. Kinetic Data for Oxidation of Cobalt(II) Complexes ( $I = 0.5$  M)

Reactants	Temp, °C	pH	$k \times 10^{-3}$ , M <sup>-1</sup> sec <sup>-1</sup>	
$\text{Fe}(\text{bipy})_3^{3+} + \text{Co}(\text{II})\text{-EDTA}$	25.0	1.9	2.7	
	25.0	3.0	18	
	25.0	3.3	23	
	25.0	4.1	29	
	25.0	5.1	33	
	25.0	5.4	32	
	14.3	5.4	21	
$\text{Fe}(\text{phen})_3^{3+} + \text{Co}(\text{II})\text{-EDTA}$	5.5	5.1	14	
	5.5	1.9	0.85	
	25.0	2.8	44	
	25.0	3.1	57	
	25.0	3.8	80	
$\text{Fe}(\text{phen-5-SO}_3)_3 + \text{Co}(\text{II})\text{-EDTA}$	25.0	4.4	88	
	25.0	2.5	18	
	25.0	3.0	27	
	25.0	3.7	41	
	25.0	4.4	47	
$\text{Ru}(\text{bipy})_3^{3+} + \text{Co}(\text{II})\text{-EDTA}$	5.0	2.0	140	
	5.0	2.2	160	
	5.0	2.5	250	
	5.0	2.7	320	
	$\text{Fe}(\text{bipy})_3^{3+} + \text{Co}(\text{II})\text{-CyDTA}$	25.0	2.2	17
25.0		2.5	22	
25.0		2.7	32	
25.0		3.1	45	
25.0		4.6	60	
$\text{Fe}(\text{bipy})_3^{3+} + \text{Co}(\text{II})\text{-HyDTA}$		25.0	6.5	17
		15.0	6.5	13
		5.0	6.5	10

(14) G. Dulz and N. Sutin, *Inorg. Chem.*, 2, 917 (1963).

**Table III.** Rate Constants for Oxidation of Cobalt(II) Complexes at 25° ( $I = 0.5 M$ )

Reductant	Oxidant	$k_1, M^{-1} \text{ sec}^{-1}$	$\Delta H_1^*$	$\Delta S_1^*$	$k_2, M^{-1} \text{ sec}^{-1}$	$\Delta H_2^*$	$\Delta S_2^*$
Co(II)-EDTA	Fe(bipy) <sub>3</sub> <sup>3+</sup>	$3.3 \times 10^4$	7	-15	$2.8 \times 10^8$	11	-6
	Fe(phen) <sub>3</sub> <sup>3+</sup>	$9.1 \times 10^4$			$1.6 \times 10^4$		
	Fe(phen-5-SO <sub>3</sub> ) <sub>3</sub>	$4.6 \times 10^4$			$1.0 \times 10^4$		
	Ru(bipy) <sub>3</sub> <sup>3+</sup>	$7.9 \times 10^6$ <sup>a</sup>			$7.3 \times 10^4$ <sup>a</sup>		
Co(II)-CyDTA	Fe(bipy) <sub>3</sub> <sup>3+</sup>	$6.7 \times 10^4$	5	-19	$7.0 \times 10^8$		
Co(II)-HyDTA	Fe(bipy) <sub>3</sub> <sup>3+</sup>	$1.7 \times 10^4$	4	-26			

<sup>a</sup> At 5.0° and  $I = 1.0 M$ .

determined for three of the systems. Errors in  $k_1$  and  $k_2$  are approximately  $\pm 8\%$  and in  $\Delta H_1^*$  and  $\Delta H_2^* \pm 1 \text{ kcal mol}^{-1}$ .

## Results

The products of oxidation of cobalt(II) complexes, determined by spectral analysis, are shown in Table I. The rate constants and Arrhenius parameters for oxidation of the protonated (e.g., Co(EDTA·H)(H<sub>2</sub>O)<sup>-</sup>) and nonprotonated forms are contained in Table III.

It was not possible to isolate a solid complex containing the Co(CyDTA)(OH)<sup>2-</sup> ion using an analogous method to the corresponding EDTA species.<sup>5</sup> The five-coordinated species was consequently generated *in situ* by oxidizing the Co(II)-CyDTA species with Mn(CyDTA)(H<sub>2</sub>O)<sup>-</sup> at pH 2.2. At this pH there is about 80% protonated cobalt(II) complex, and since the oxidation rate constant is pH-invariant (2.1–4.8,  $0.45 M^{-1} \text{ sec}^{-1}$  at 25°,  $I = 0.5 M$ ), this means that about 80% Co(CyDTA)(H<sub>2</sub>O)<sup>-</sup> plus Co(CyDTA·H)(H<sub>2</sub>O) is produced in solution by this means. The spectrum of such solutions changed to that of Co(CyDTA)<sup>-</sup> slowly and the first-order rate constant was measured over a pH range (0.5–4.5). From these measurements, rate constant values were obtained for the unprotonated species and protonated species of  $7.0 \times 10^{-4} \text{ sec}^{-1}$  and  $\sim 1.6 \times 10^{-2} \text{ sec}^{-1}$  (25°,  $I = 0.7 M$ ), respectively. It was thus apparent that the  $5 \leftrightarrow 6$  interconversions, as in the case with EDTA complexes, were sufficiently slow to pose no problems in the identification of the immediate outer-sphere oxidation product of cobalt(II)-CyDTA solutions.

The  $pK_a$  value for the Co(CyDTA·H)(H<sub>2</sub>O)  $\rightleftharpoons$  Co(CyDTA)<sup>-</sup> + H<sub>3</sub>O<sup>+</sup> process is  $\sim 1.0$  and much lower than that for EDTA complexes ( $\sim 3.0$ ). This lower value was confirmed qualitatively by oxidizing ( $5 \times 10^{-3} M$ ) Co(CyDTA·H)(H<sub>2</sub>O)<sup>-</sup> or Co(EDTA·H)(H<sub>2</sub>O)<sup>-</sup>, separately, with Fe(bipy)<sub>3</sub><sup>3+</sup> at pH 1.8, and then adjusting the solutions to pH 3.0. Ring closure occurred with the release of H<sup>+</sup> ions only in the EDTA case.

## Discussion

The bulk of the work and discussion is concerned with the cobalt(II)-EDTA system. Higginson concluded from evidence then available<sup>2</sup> that a substantial number of EDTA complexes of bivalent metals contained quinquedentate ligands, *i.e.*, could be represented by M(EDTA)(H<sub>2</sub>O)<sup>2-</sup> with one free carboxylate group. The observation of definite visible spectral changes accompanying the protonation of the Cu(II) and Co(II) complexes,<sup>15</sup> which has been confirmed in the present study, does however suggest that there is at least some six-coordinated EDTA present in the nonprotonated

form. Protonation of an uncoordinated carboxylate group is not expected to lead to spectral changes associated with the ligand field.

The iron(III) and ruthenium(III) complexes shown in the tables are inert, and also it is difficult to see how the ligands can act as bridges, so that these oxidants almost certainly will react by an outer-sphere mechanism. The major product is Co(EDTA)<sup>-</sup>, and were the rate constants for oxidation of five- and six-coordinated EDTA-cobalt(II) complexes identical, this would show that Co(EDTA)<sup>2-</sup> is present to the extent of 97% or more at pH >4. The behavior of the five-coordinated species is simulated by the protonated species Co(EDTA·H)(H<sub>2</sub>O)<sup>-</sup>, which predominates at pH <3, and this, in fact, reacts by a factor of 5–12 slower than the unprotonated complex (Table III). This is not merely an electrostatic effect since the difference persists even when the noncharged oxidant Fe(phen-5-SO<sub>3</sub>)<sub>3</sub> is used. It appears reasonable, therefore, to assume that Co(EDTA)(H<sub>2</sub>O)<sup>2-</sup> will react slightly more slowly than Co(EDTA)<sup>2-</sup>, and this must be allowed for in the analysis of the product distribution (see the Experimental Section). When this allowance is made, one still concludes from the experiments with the three different oxidants that  $\geq 80\%$  of the cobalt(II) complex is present as Co(EDTA)<sup>2-</sup> in weakly acid solution.

Inner-sphere oxidation can occur with either form of the cobalt(II)-EDTA complex since the carboxylate is easily ruptured from the metal. Naturally, the product from such oxidations is less diagnostic of the reactant configuration. An inner-sphere reaction must occur in the oxidation by Fe(CN)<sub>6</sub><sup>3-</sup>, since the bridged intermediate is observed,<sup>16</sup> and in the oxidation by Co(py)<sub>4</sub>Cl<sub>2</sub><sup>2+</sup> from the nature of the product (Table I). Dyke and Higginson<sup>17</sup> have concluded that oxidation by IrCl<sub>6</sub><sup>2-</sup> also proceeds through a bridged transition state [Cl<sub>2</sub>IrCl·Co(EDTA)<sup>4-</sup>]<sup>‡</sup>, which on breaking up allows an unbound carboxylate group to move into coordination giving a six-coordinated product. The increase in proportion of five-coordinated product (Table I) as the pH decreased was ascribed to protonation of the free carboxylate group, which is less likely to interact with the cobalt to form Co(EDTA)<sup>-</sup> ion.<sup>17</sup> These results, based on a five-coordinated cobalt(II) reactant, could also be explained as an inner-sphere oxidation of Co(EDTA)<sup>2-</sup>, in which a carboxylate group is severed during the oxidation, or even as an outer-sphere oxidation, in which the product at pH 3.9–5.4 reflects a  $\sim 90\%$  Co(EDTA)<sup>2-</sup> starting reactant. The latter idea is strengthened by consideration of the rate constant for the Co(II)-EDTA, IrCl<sub>6</sub><sup>2-</sup> reaction. The value  $1.4 \times 10^4 M^{-1} \text{ sec}^{-1}$  at 25° can be calculated

(16) A. W. Adamson and E. Gonick, *Inorg. Chem.*, 2, 129 (1963); D. H. Huchital and R. G. Wilkins, *ibid.*, 6, 1022 (1967).

(17) R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 2802 (1963).

(15) T. R. Bhat and M. Krishnamurty, *J. Inorg. Nucl. Chem.*, 25, 1147 (1963).

from the Marcus relation,<sup>18</sup> which applies to outer-sphere reactions.<sup>19</sup> It is in excellent agreement with the experimentally determined value<sup>17</sup> of  $4 \times 10^3 M^{-1} \text{sec}^{-1}$  at 22°.

The reactions with the strong oxidants  $\text{Mn}(\text{EDTA})(\text{H}_2\text{O})^-$  and  $\text{Mn}(\text{CyDTA})(\text{H}_2\text{O})^-$  are best understood in terms of an inner-sphere process. The large amount of five-coordinated product from oxidation by  $\text{Mn}(\text{EDTA})(\text{H}_2\text{O})^-$  arises because an effective hydroxo-bridged path can operate with the substantial amount of  $\text{Mn}(\text{EDTA})\text{OH}^{2-}$ ,  $\text{p}K = 5.1$ ,<sup>9</sup> present in the oxidant solution. A five-coordinate product then results by addition of a proton to the cobalt(III) hydroxo species formed after collapse of the bridge. This viewpoint is supported by the facts that increasing amounts of six-coordinate product arise (a) as the acidity increases and (b) when  $\text{Mn}(\text{CyDTA})(\text{H}_2\text{O})^-$ , with a much higher  $\text{p}K$  value (8.1),<sup>10</sup> is used as oxidant.

Examination of models shows that CyDTA is even more likely, because of the rigid stereochemistry of the cyclohexane ring, to coordinate at all donor centers; and this imposition of six-coordination is shown in the relatively rapid conversion<sup>8</sup> of  $\text{Co}(\text{CyDTA})\text{Cl}^{2-}$  to  $\text{Co}(\text{CyDTA})^-$ , *vide infra*, and, in a more extreme form, in the inability of metal ions to interact directly with  $\text{M}^{\text{II}}-\text{CyDTA}$  complexes in exchange reactions.<sup>20</sup> The ligand is apparently prevented from undergoing a process of simultaneous unwrapping and transfer of its coordinated groups from one metal ion to another, as is observed with EDTA. It is not surprising then that oxidation of  $\text{Co}(\text{II})-\text{CyDTA}$  by  $\text{Fe}(\text{bipy})_3^{3+}$  indicates  $\geq 80\%$  six-coordinated,  $\text{Co}(\text{CyDTA})^{2-}$ , in the former solutions. As with the EDTA analog, protonation of  $\text{Co}(\text{II})-\text{CyDTA}$  solutions shows marked spectral changes, with an isosbestic point at 465  $\text{m}\mu$ , also indicating substantial six-coordination in the unprotonated species. From a series of spectra, at differing pH, a  $\text{p}K_a$  of 2.9 can be determined,<sup>21</sup> identical with the value obtained potentiometrically.<sup>22</sup> Once again oxidation by the  $\text{Mn}(\text{III})$  species almost certainly occurs by an inner-sphere mechanism, and oxidation by  $\text{Co}(\text{py})_4\text{Cl}_2^+$  produces some  $\text{Co}(\text{CyDTA})\text{Cl}^{2-}$ , which converts quite quickly to  $\text{Co}(\text{CyDTA})^-$ .

The lower formation constant (by 1.7  $\text{p}K$  units)<sup>23</sup> and heat of reaction (2.4  $\text{kcal mol}^{-1}$ )<sup>24</sup> of cobalt(III)-HyDTA complexes compared with those of EDTA are thermodynamic indications of five-coordinated structures for the HyDTA complex. Oxidation of  $\text{Co}(\text{II})-\text{HyEDTA}$  with  $\text{Fe}(\text{bipy})_3^{3+}$  at  $\text{pH} \sim 7$ , rapid removal of iron complexes by ion exchange, adjustment to  $\text{pH} \sim 9.5$ , and spectral examination of the resultant solution indicate exclusive production of  $\text{Co}(\text{HyDTA})\text{OH}^-$ , which slowly changes to the stable product  $\text{Co}(\text{Hy}$

$\text{DTA}-\text{H}^+)^-$ , in which the hydroxyethyl grouping has lost a proton and become coordinated.<sup>6</sup> The similar rate constant for oxidation of  $\text{Co}(\text{II})-\text{HyDTA}$  and EDTA by  $\text{Fe}(\text{bipy})_3^{3+}$  suggests that there is nothing unusual in the oxidation of the former causing the observed results, and it is concluded from these oxidation experiments that in solution ( $\text{pH} \geq 4.5$ ) the cobalt(II)-EDTA and -CyDTA complexes are mainly present ( $>80\%$ ) as the six-coordinated structures, whereas the HyDTA complex is predominantly  $\text{Co}(\text{HyDTA})(\text{H}_2\text{O})^-$ . Further results on EDTA complexes which are in agreement with these general findings with the  $\text{Co}(\text{II})$  complexes are now available. First, consideration of association constants of the protonated and non-protonated cobalt(II)-EDTA forms, with a variety of unidentate ligands, suggests the predominance of six-coordinated ligand in the nonprotonated species.<sup>25</sup> Then recently<sup>26</sup> the enthalpy changes accompanying the protonation of divalent metal-EDTA complexes in a reaction of the type  $\text{M}(\text{EDTA})^{2-} + \text{H}^+ \rightleftharpoons \text{M}(\text{EDTA} \cdot \text{H})(\text{H}_2\text{O})^-$  have been measured and are best interpreted also in terms of the predominance of the six-coordinated form. The enthalpy changes for protonation of EDTA complexes of Co, Ni, Cu, and Zn are all similar and appreciably more exothermic than would be expected if the carboxylate group was free. The oxidation of the  $\text{Cr}(\text{II})-\text{EDTA}$  complex in solution by a variety of oxidants shows only the production of the quinquevalent  $\text{Cr}(\text{III})-\text{EDTA}$  complex, suggesting that this type of coordination is favored by the  $\text{Cr}(\text{II})$  complex.<sup>27</sup>

Finally, although incidental with the main theme of the research, a comparison of the behavior of the cobalt(III)-CyDTA with the EDTA system is worthwhile. The  $\text{Co}(\text{III})-\text{CyDTA}$  complex has been made in only one form, a purple compound, aprotic in solution and with a spectrum which only changes in concentrated perchloric acid. It therefore contains the fully coordinated  $\text{Co}(\text{CyDTA})^-$  ion.<sup>8</sup> Examination of models shows that with the quinquevalent ligand, the free equatorial acetate group is more constrained and presumably nearer the coordinated sixth group (*e.g.*,  $\text{H}_2\text{O}$ ) in the CyDTA complex because of the cyclohexane ring. Interactions of methylene hydrogens of axial acetate group with cyclohexane ring hydrogens have been inferred from nmr studies.<sup>28</sup> This constraint apparently shows up in the substantially lower  $\text{p}K$  ( $\sim 1.0$ ), also previously noted<sup>28</sup> for  $\text{Co}(\text{CyDTA})(\text{H}_2\text{O})^- \rightarrow \text{Co}(\text{CyDTA} \cdot \text{H})(\text{H}_2\text{O})$ , compared with EDTA system ( $\text{p}K \sim 3.0$ ). In addition, the ring closure process  $\text{Co}(\text{CyDTA})\text{Cl}^{2-} \rightarrow \text{Co}(\text{CyDTA})^-$  and  $\text{Co}(\text{CyDTA})(\text{H}_2\text{O})^- \rightarrow \text{Co}(\text{CyDTA})^-$  have substantially lower  $\Delta H^*$  values than those for the EDTA analog.<sup>29</sup>

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