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The Kinetics of Ring Closure and Hydrolysis of a Number of Halo–Cobalt(III) Complexes of Diaminopolycarboxylate Ligands

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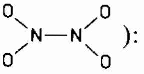
The kinetics of ring closure of $Co(EDTA)Br^{2-}$, $Co(CyDTA)(H_2O)^-$, $Co(CyDTA)Cl^{2-}$ and the hydrolysis of $Co(MEDTA)Cl^-$, $Co(MEDTA)Br^-$ and α-cis-$Co(EDDA)Cl_2^-$ have been studied.[a] *The results suggest that an aqua intermediate does not occur in the ring closure reactions. Biphasic rates have been detected in the first-order reactions of the bromo complexes and this is ascribed to the presence of two isomers. One of these has been prepared and its structure is discussed. Oxidation of $Co(EDDA)(H_2O)_2$ by $Copy_4Cl_2^+$ yields an isomeric mixture of $Co(EDDA)(H_2O)Cl$.*

Introduction

Cobalt(III) diaminopolycarboxylate complexes have been extensively studied from a number of viewpoints, including structural, spectral, NMR, thermodynamics and kinetic behavior.

Complexes of the type $Co(EDTA)X^{n-}$ (X = Cl, Br, OH, H_2O), in which EDTA[a] is acting as a quinquedentate ligand can exist in two isomeric forms (Ia, b). These slowly change in solution to $Co(EDTA)^-$, II, in which all six donor atoms of the ligand are coordinated (EDTA is represented by



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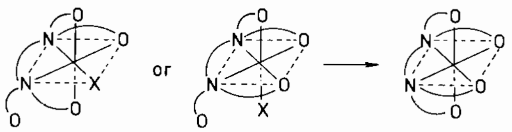

(1)

Ia Ib II

The study of ring closures of this type affords an opportunity to examine the group neighboring effect.[1a] There have been a number of kinetic investigations of this type of reaction involving EDTA and related ligands.[2–5] Ring closure may take place directly, and in this process a CH_2COO^- or CH_2COOH free arm either displaces the X group (S_N2 internal) or attacks a 5-coordinated intermediate produced by loss of X (represented by k_1 below). Alternatively, the ring closure may proceed through the intermediate formation of the aqua complex (X = H_2O), steps k_2, k_3, *e.g.*

$$\begin{tikzcd}
Co(EDTA)X^{2-} \arrow[r, "k_1"] \arrow[dr, "k_2"'] & Co(EDTA)^- \\
 & Co(EDTA)H_2O^- \arrow[u, dashed, "k_3"']
\end{tikzcd} \qquad (2)$$

Since the loss of water from $Co(EDTA \cdot H)H_2O$ or $Co(EDTA)H_2O^-$ is 10^2–10^3 faster than ring closure of $Co(EDTA)X^{2-}$, X = Cl at 25° C, it is not possible to differentiate between the possibilities from kinetics alone.

The ligand MEDTA forms analogous complexes to EDTA, $Co(MEDTA)X^{2-}$, X = Br, Cl, NO_2, in which the free acetate ring is replaced by a methyl group.[6] Since a ring closure is not now possible, examination of the hydrolysis reaction

$$Co(MEDTA)X^{2-} \longrightarrow Co(MEDTA)H_2O^- + X^- \qquad (3)$$

allows us to isolate the k_2 step in (2) and thus aids us in the delineation of the correct path for (2). If, for example, the rate constant for hydrolysis of Co(MEDTA)Cl^- was much slower than that for ring closure of $Co(EDTA \cdot H)Cl^-$, then a direct step for the latter, not involving an aqua intermediate, would be strongly supported.

Furthermore, a kinetic study of (3) might disclose the existence of two isomers, analogous to Ia and Ib, which have been deduced for $Co(EDTA)Br^{2-}$, from the biphasic nature of the ring closure reaction.[3]

The cobalt(III) complexes of CyDTA have been less examined than their EDTA counterparts. Since the rate constants for the ring closure of Co(CyDTA)H_2O^- and the loss of chloride from $Co(CyDTA)Cl^{2-}$ were determined to be comparable, in preliminary

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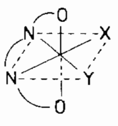
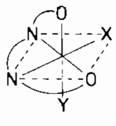
[a] Abbreviations used as follows: EDTA = ethylenediamine-N,N,N′,N′-tetraacetate; PDTA = propylenediamine-N,N,N′,N′-tetraacetate; CyDTA = *trans*-1,2-cyclohexanediamine-N,N,N′,N′-tetraacetate; HyDTA = N-(2-hydroxyethyl)ethylenediamine-N,N′,N′-triacetate; MEDTA = N-Methylethylenediamine-N,N′,N′-triacetate; EDDA = ethylenediamine-N,N′-diacetate. The protonated form of these ligands is denoted thus: EDTA · H.

experiments,[7] this system may allow us to detect any aqua intermediate in the ring closure reaction.

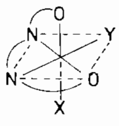
The dicarboxylate EDDA can coordinate in a number of ways around a octahedral framework.[8] The configuration in which it spans the plane, leaving *trans*-positions free, appears to be too strained to form, but three *cis*-isomers of Co(EDDA)XY are possible, IIIa, *α-cis* and IIIb and c, *β-cis:*



IIIa



IIIb



IIIc

The kinetics of hydrolysis of the *α-cis*- and *β-cis* isomers of $Co(EDDA)Cl_2^-$ and $Co(EDDA)Cl(H_2O)$ were reported after our work was completed.[9] Our rate studies were less extensive but agree generally with the results of Garrett and Watts. These were required for comparative purposes, with the other systems, as well as to help determine the nature of the product of the inner sphere redox reaction between CoEDDA $(H_2O)_2$ and $Copy_4Cl_2^+$ ions. We have found that the latter is an inner sphere oxidant towards a number of cobalt(II) complexes[7] and this aspect is pursued further in the study reported here.

Experimental

Preparation of Complexes

Most of the ligands were commercially available and purified by recrystallization from water. MEDTA was prepared as described by Van Saun and Douglas,[6] and EDDA was purified by recrystallization from a water–2-propanol mixture.[10] The purity of these ligands was checked by potentiometric titrations.

The complexes $K[Co(EDTA \cdot H)Cl] \cdot H_2O$,[11] Na[Co (EDTA·H)Br]·$3H_2O$ (isomeric mixture),[12] K[Co (MEDTA)Cl]·H_2O,[6] Na[Co(MEDA)Br] (isomeric mixture),[6] K[Co(CyDTA)]·$2H_2O$,[13] K[*α-cis*-Co(EDDA)CO_3]·$4H_2O$,[14] and $[Copy_4Cl_2]Cl \cdot 6H_2O$[15] were prepared by published methods. Materials were usually recrystallized from water. Their spectra agreed closely with literature reports. The following new compounds were prepared: K[Co(EDTA·H)Br]·H_2O (monoisomeric) resulted from heating K[Co(EDTA)]·$2H_2O$ in conc HBr, and evaporating the solution to a pasty blue–green mass. The work-up and recrystallization of the product was as described for the chloro complex.[11] Na[Co(MEDTA)Br], monoisomeric, was prepared from the isomer mixture (2.9 g) by heating on a steam bath for 15 min with 1.2 g silver acetate in 30 ml of water. Silver bromide was filtered and silver ions in the filtrate removed by dropwise addition of saturated KBr solution, until no more precipitate formed. The filtrate, after removing silver bromide, was evaporated to a thick paste. Addition of 2 ml 48% HBr and evaporation to dryness yielded the blue bromo complex which was dissolved in 15 ml H_2O and reprecipitated with 150 ml methanol. The product was filtered, washed with methanol and recrystallized twice from water–ethanol. K[Co(CyDTA·H)Cl]·2.5 HCl was prepared by dissolving K[Co(CyDTA)]·$2H_2O$ in conc HCl and evaporating to dryness. The solid residue was recrystallized from water–ethanol and the resultant purple–blue solid was dissolved in water. Methanol and acetone were added and the solution was filtered from solid impurities. About 1 ml conc HCl was added dropwise to the filtrate and warmed until the solution was blue. This solution was evaporated to dryness at room temperature with a stream of air. A blue solid could be removed from the residue. It was probably the same material as described by Dwyer and Garvan,[13] who had difficulty removing all HCl from it without reversion to the purple K[Co(CyTDA)]·$2H_2O$. The solid, dissolved in conc HCl, had spectral peaks at 403 nm and 585 nm. K[*α-cis*-Co(EDDA)Cl_2] resulted when K[*α-cis*-Co(EDDA)CO_3]·$4H_2O$ was dissolved in conc HCl and heated on a steam bath until the solution had turned bright blue. Evaporation of this solution almost to dryness and filtering gave a blue solid. For all these materials, the calculated amount of halide ion was liberated after hydrolysis.

A number of solutions of complex ions were prepared for the kinetic studies, as follows: Co(CyDTA·H) Cl^- by dissolving K[Co(CyDTA)]·$2H_2O$ in 1 ml conc HCl and warming on a steam bath until the blue color was completely formed ($\varepsilon_{585} = 229$, $\varepsilon_{404} = 188$). Co (CyDTA)Cl^{2-} was prepared in solution from *trans*-$Copy_4Cl_2^+$ and $Co(CyDTA)^{2-}$ (each 2 m*M*) at pH ~4.5. Reaction is complete within 5 mins at room temperature. [*α-cis*-Co(EDDA)(H_2O)Cl] from hydrolysis of *α-cis*-Co(EDDA)Cl_2^-. After removal of the first chlorine, the solution was stored in a freezer until used. Co(CyDTA)$(H_2O)^-$ by adding 0.072 g K[Mn (CyDTA)(H_2O)]·$2.5H_2O$[16] to 50 ml of $5 \times 10^{-2} M$ $Co(CyDTA)^{2-}$ in $HClO_4$ at pH = 2. The mixture was left for 2 min and then adjusted to pH = 4 for kinetic studies ($\varepsilon_{545} = 300$, $\varepsilon_{380} = 240$, in good agreement with previous studies).[7]

Characterization of Reaction Between Co(II)–EDDA and $Copy_4Cl_2^+$ Ions

A solution containing about $10^{-2} M$ EDDA·H_2 and $Co(NO_3)_2$, in 10% excess, was adjusted to pH = 4.5 and a freshly prepared solution of $Copy_4Cl_2^+$ in slight excess was added. The $Copy_4Cl_2^+$ and Co^{2+} ions were removed by elution through a Bio-Rad 50 W-X8 cation exchange resin. The solution was used for the kinetic measurements and analyzed as follows: for chloride analysis, the solution was further eluted through an anion exchange column (Dowex 21K, Cl^- form which

TABLE I. Kinetic Data for Hydrolysis, Ring Closure and Redox Reactions.

Ionic Strength *M*	pH	Temp. °C	$10^4 \times k$, sec^{-1}
$Co(EDTA)Br^{2-}$			
1.0	2.7	39.1	0.93[a]
			1.1[b]
			0.19[c]
		49.4	3.4[a]
			3.7[b]
			0.62[c]
		59.6	10.7[a]
			12.0[b]
			2.3[c]
			k, sec^{-1}
0.5[d]	0.5 *M* HNO_3	15.0	9.5×10^{3}[b]
			41[c]
		25.0	1.7×10^{4}[a]
			2.0×10^{4}[b]
			82[c]
		35.0	1.3×10^{4}[b]
			1.8×10^{2}[c]
3.0[e]	2.0 *M* $HClO_4$	15.0	1.5
		25.0	2.1
		35.0	2.8
$Co(MEDTA)Cl^-$			$10^4 \times k$, sec^{-1}
1.0	1.2	60.0	0.28
0.1	2.4		0.31
1.0	2.4		0.35
0.1[f]	4.7[f]		0.30
0.1	2.6	70.2	1.1
0.1	2.4	78.5	2.5
$Co(MEDTA)Br^-$			
0.1	2.4	65.1	0.28[a]
	2.2		0.28[b]
	2.2		0.06[c]
	2.5	70.0	0.43[a]
	2.4		0.42[b]
	2.4		0.12[c]
	2.8		0.42[b]
	2.8		0.10[c]
	2.6	78.5	1.1[a]
	2.4	78.8	1.2[b]
			0.23[c]
$Co(CyDTA)Cl^{2-}$			
$[Na^+]$, *M*			
~0	0.7	25.0	0.72[g]
~0	0.6	25.2	0.71
1.0	0.6	30.0	2.6
1.0	4.4	30.0	1.3
1.0	4.5	30.0	1.4[h]
~0	0.7	40.5	3.3
0.5	0.6	40.5	4.9
1.0	0.5	40.7	7.0
1.0	1.3	40.6	6.6
1.0	2.2	40.3	5.9[i]
1.0	3.2	40.4	4.9[j]
1.0	4.4	40.7	3.8
1.0	5.0	40.3	4.0[j]
1.0	5.1	40.7	3.7
1.0	6.1	40.6	4.7
0.7	4.2	40.6	3.2
0.4	4.0	40.6	2.6
1.0	4.4	51.5	11.7
1.0	0.7	50.7	19
$Co(CyDTA)(H_2O)^-$			
1.0	4.0	15.5	2.6
		24.5	7.2
		34.1	19
α-cis-$Co(EDDA)Cl_2^-$			
0.1	2.3	15.7	0.55
0.2	0.8	20.5	1.3
0.1	2.2	20.2	1.1
1.0	2.2	20.3	1.1
0.1	2.3	30.6	3.9
α-cis-$Co(EDDA)(H_2O)Cl$			
0.2	0.8	20.0	0.038
0.2	0.8	43.0	1.0
0.1	2.2	42.9	0.99
1.0	2.2	42.5	1.1
0.1	2.3	51.4	3.5
$Co(EDDA)(H_2O)Cl$[k]			
0.1	1.0	25.0	0.020[b]
			0.0056[c]
0.1	1.4	25.0	0.029[b,l]
			0.0051[c,m]
0.1	2.3	25.0	0.029[b]
			0.0059[c]
	3.5	25.0	0.077[b]
			0.0068[c]
1.0	1.4	25.0	0.027[b]
			0.0052[c]
0.1	3.1	60.0	4.2[b]
			0.61[c]
0.1	2.2	70.0	23[b]
			2.5[c]
1.0	2.0		21[b]
			2.4[c]

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[a] Pure isomer. [b] Isomeric mixture, fast component. [c] Isomeric mixture, slow component. [d] Reactions with Hg(II) solutions (~10 m*M*). [e] Reactions with Fe(II) ion (~2 *M*). [f] Sodium acetate–acetic acid buffer. [g] Using product of $Co(CyDTA)^{2-}$, $Copy_4Cl_2^+$ reaction. [h] Using solid $K[Co(CyDTA \cdot H)Cl] \cdot 2.5\,HCl$. [i] 0.3 *M* sodium tartrate buffer + 0.7 *M* $NaClO_4$. [j] 1.0 *M* citrate buffer, other runs at pH 4–5.1 contained 1.0 *M* acetate buffer. [k] Product of reaction (10). [l] Mean of four separate runs, ranging from 3.6×10^{-6} to 2.3×10^{-6} sec^{-1}. [m] Mean of four separate runs, ranging from 5.5×10^{-7} to 4.8×10^{-7} sec^{-1}.

TABLE II. Spectral (Maxima) and pK Characteristics.

Complex	λ_1	ε_1	λ_2	ε_2	pK	Ref.
$Co(EDTA \cdot H)Br$[b]	595	218	410	230		a
$Co(EDTA \cdot H)Br$[c]	580	240	410	240		a
$Co(EDTA \cdot H)H_2O$					3.1	2
$Co(CyDTA \cdot H)Cl^{2-}$	585	229	404	188	2.8	a
$Co(CyDTA \cdot H)H_2O$					~1	7
$Co(CyDTA)H_2O^-$	545	300	380	240		a
$Co(MEDTA)H_2O$	548	217	383	180	8.0	a
$Co(MEDTA)OH^-$	568	202	390	156		a
$Co(MEDTA)Cl^-$	578	210	403	188		6
	578	211	403	191		a
$Co(MEDTA)Br^-$[b]	588	206	400(inf)	228		a
$Co(MEDTA)Br^-$[c]	588	212	400(inf)	223		a
α-*cis*-$Co(EDDA)Cl_2^-$	597	162	418	120		a
	602	176	421	133		f
	588	184	416	134		9
α-*cis*-$Co(EDDA)(H_2O)Cl$	570	139	402	94		a
	576	145	405	97		f
	564	150	402	100		9
β-*cis*-$Co(EDDA)(H_2O)Cl$	542	157	400	165		9
$Co(EDDA)(H_2O)Cl$[d]	533	131	390	152		a
α-*cis*-$Co(EDDA)(H_2O)_2^+$	544	134	387	84	6.9, 10.2	a
	549	136	389	76		f
	537	136	387	75		9
β-*cis*-$Co(EDDA)(H_2O)_2^+$	515	180	383	137		9
$Co(EDDA)(H_2O)_2^+$[e]	523	153	375	117	7.3	a

[a] This work. [b] Pure isomer. [c] Mixed isomer. [d] Product from Reaction (7). [e] Product from hydrolysis of $Co(EDDA)(H_2O)Cl$. [f] K. Kuroda and K. Watanabe, *Bull. Chem. Soc. Japan, 44,* 1034 (1971).

had been soaked in $0.5M$ HNO_3 and then thoroughly washed with $0.5M$ HNO_3 and 4×10^{-4} $HClO_4$). The eluent was aquated to release the coordinated chloride by heating on a steam bath overnight, and this titrated with standard $Hg(NO_3)_2$ solution; for cobalt analysis, the solution was reduced with an excess of Cr^{2+} solution, and the Co^{2+} produced analyzed as $CoCl_4^{2-}$ spectrally ($\varepsilon_{662} = 521$, $\varepsilon_{690} = 550$).[17] A resultant ratio of Co : Cl = 1.05 : 1.0 was determined.

Kinetic Runs

In the hydrolysis and ring closure studies, either the solid complexes were added to the reaction medium (final concentration of complex 1–5 mM) at the appropriate pH and ionic strength, which had equilibrated at the temperature of the run. Usually aliquots were withdrawn at various times, quenched in ice and the absorbance measured at the appropriate wavelength in a Cary 14 equipped with a thermostated holder. Occasionally the reaction could be studied *in situ* in the Cary compartment. The redox reaction and the Hg(II) catalyzed hydrolysis were studied on a stopped-flow apparatus. For the examination of the Co(II) chelate, $Copy_4Cl_2^+$ interaction, the Co(II)–ligand ratio was adjusted to insure ≥ 95% complexing at pH 4 (usually 1 : 1). Several preparations of the pyridine complex were necessary during the study, because of its ready decomposition. Cobalt(II) solutions were standardized by diluting with conc HCl (2 ml solution to 10 ml acid) and measuring the absorbance of the resultant $CoCl_4^{2-}$ spectrum.[17] Standard $NaClO_4$ solutions were prepared by dissolving weighed amounts of Na_2CO_3 (A. R. Baker) in perchloric acid solution. Solutions of $Hg(NO_3)_2$ were analyzed by titration with standard chloride solutions.

Good first-order rate plots were obtained for at least 3 $t_{1/2}$'s except for the reactions of mixed isomers. In the latter cases two rate constants from the $A-A_\infty$ vs time semi-log plot were extracted in the usual way.[1b] In the study of the hydrolysis of $Co(EDDA)Cl_2^-$, since the second stage commenced before the first was completed, the first step was treated by the Guggenheim and Mangelsdorf methods.[18] The kinetic data are contained in Table I.

The pK values were determined by conventional spectral and potentiometric methods for a number of complexes in the course of the studies here. The values and spectral data are included in Table II. Since the ring closure of $Co(CyDTA \cdot H)Cl^-$ and $Co(CyDTA)Cl^{2-}$ had proceeded slightly before spectra of the species could be measured, the simultaneous equations (1 cm cell):

$$A_{585} = 229[\mathrm{Co(CyDTA){-}Cl}] + 202[\mathrm{Co(CyDTA)^-}] \quad (4)$$

$$A_{540} = 142[\mathrm{Co(CyDTA){-}Cl}] + 305[\mathrm{Co(CyDTA)^-}] \quad (5)$$

were used to calculate the concentrations of Co(CyDTA)$^-$ and Co(CyDTA)–Cl complexes at any pH. This was possible because the unprotonated and protonated chloro complexes (total concentration = [Co(CyDTA)–Cl]) had virtually identical absorption coefficients at 540 nm and 585 nm. Then at 370 nm where they differ,

$$A_{370} = A[\mathrm{Co(CyDTA){-}Cl}] + 184[\mathrm{Co(CyDTA)^-}] \quad (6)$$

so that A can be plotted against pH to obtain the pK (Figure 1).

Results

Kinetic data are collected in Tables III and IV.

EDTA Complexes

The ion Co(EDTA)Cl^{2-}, prepared from chlorination of the Co(II)–EDTA complex, or Co(EDTA·H)Cl$^-$, by treatment of Co(EDTA)$^-$ with conc HCl, gave identical uniphasic ring closure kinetics (see also ref. 5).

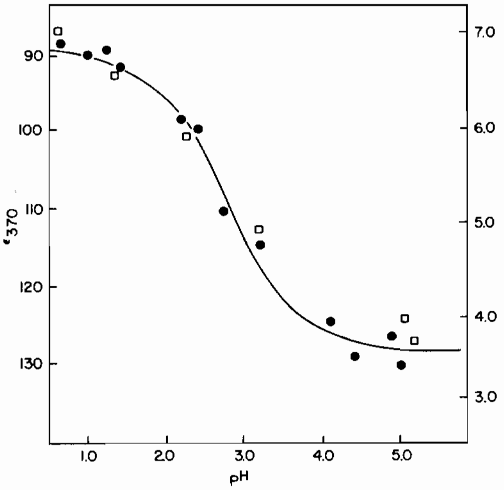


Figure 1. Molar absorption coefficient at 370 nm (●) and ring closure rate constant (○) for Co(III)–CyDTA–Cl complex *vs.* pH. The solid curve represents the theoretical for equation (9).

The rate constant, 1.2×10^{-4} sec^{-1} at 35° C and I = 1.0*M*, is in excellent agreement with that reported (1.0×10^{-4} sec^{-1}).[2]

Bromination of Co(II)–EDTA produces a sample of Co(EDTA)Br^{2-} which shows two rates on conver-

TABLE III. Activation Parameters for Ring Closure of Co(III) Diaminopolycarboxylate Complexes at 25° C.

Complex	$10^4\times k$, sec^{-1}	ΔH^{+} Kcal mol^{-1}	ΔS^{+} eu	Ref.
Co(EDTA·H)H$_2$O	2.3	25.0	+9	2
Co(EDTA)H$_2$O$^-$	19	24.6	+12	2
Co(EDTA·H)Cl$^-$	0.01	23.5	−5	3
	0.03	22.9	−7	2
Co(EDTA)Cl^{2-}	0.03	22.9	−7	2
Co(EDTA)Br^{2-}	0.17	19.4	−14	3
	0.20	21.8	−7	ab
	0.20	23.2	−2	ac
	0.018	21.9	−10	3
	0.030	24.6	+2	ac
Co(EDTA·H)Br	$\sim2\times10^{8}$ [d]			abc
	82×10^{4} [d]	10.7	−14	ac
Co(CyDTA·H)H$_2$O	160			7
Co(CyDTA)H$_2$O$^-$	7.0	18.8	−10	a
Co(CyDTA·H)Cl$^-$	1.5	17.8	−3	a
Co(CyDTA)Cl^{2-}	0.70	19.9	+4	a
Co(PDTA·H)H$_2$O	2.7	25.4	+10	4
Co(PDTA)H$_2$O$^-$	20	23.4	+7	4
Co(PDTA·H)Cl$^-$	0.04	20.3	−10	4
Co(PDTA·H)Br$^-$	0.12	16.6	−26	4
Co(HyDTA)H$_2$O	0.19	27.6	+13	2
Co(HyDTA)Cl$^-$	0.01	20.8	−16	3
Co(HyDTA)Br$^-$	0.05	20.6	−13	3

[a] This work. [b] Pure isomer. [c] From isomer mixture. [d] Hg(II) catalyzed rate constant, M^{-1} sec^{-1}, in 0.5*M* HNO$_3$.

TABLE IV. Activation Parameters for Hydrolysis Reactions of Co(III) Diaminopolycarboxylate Complexes at 25° C.

Complex	$10^4 \times k$, sec^{-1}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	Ref.
$Co(MEDTA)Cl^-$	0.0028	25.7	−2	a
$Co(MEDTA)Br^-$	0.021	23.5	−6	ab
$Co(MEDTA)Br^-$	0.0056	22.7	−11	ac
α-*cis*-$Co(EDDA)Cl_2^-$	2.0	23.3	+3	a
	2.3	23.0	−1	9
α-*cis*-$Co(EDDA)(H_2O)Cl$	0.080	25.9	+8	a
	0.10	22.6	−6	9
$Co(EDDA)(H_2O)Cl$	0.040	26.3	+5	ad
	0.005	25.8	−1	ad
α-*cis*-$Co(trien)Cl_2^+$	1.6	20.9	−6	e
β-*cis*-$Co(trien)Cl_2^+$	14.5	20.5	−3	e

[a] This work. [b] Pure isomer. [c] Slower portion from isomer mixture. [d] Product from reaction (10) with two rates.
[e] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, *6*, 2172 (1967).

sion to $Co(EDTA)^-$ and this has been ascribed to the existence of isomers Ia and Ib with different ring-closure rate constants.[3] We have confirmed this biphasic rate behavior and obtained associated activation parameters in only fair agreement with those of Morris and Busch (Table III).[3] We have studied the Hg(II)-catalyzed ring closure of the material by stopped-flow, and also observed two rates (Table III). On the other hand the Fe(II) reduction of $Co(EDTA)Br^{2-}$ shows a single rate constant over 3–4 $t_{1/2}$'s (k = 2.1 M^{-1} sec^{-1}, $\Delta H^{\neq}$ = 5.1 kcal mol^{-1} and $\Delta S^{\neq}$ = −38 eu at 25° C in 2*M* $HClO_4$.)

However, a sample of $Co(EDTA)Br^{2-}$ prepared from K[Co(EDTA)] and HBr gave uniphasic spontaneous, as well as Hg(II) catalyzed, ring closure rate behavior with rate constants which corresponded closely to those of the "fast-reacting" isomer of the mixture (Table III).

MEDTA Complexes

The hydrolysis of $Co(MEDTA)Cl^-$ was attended by sharp isosbestic points, and data from a number of wavelengths (*e.g.* 550 nm or 580 nm) gave identical excellent first-order plots for at least four half-lives. The rate constant was independent of (a) concentration of cobalt(III) complex (b) pH from 1.2 to 4.7 and (c) ionic strength change from 0.1 to 1.0*M*.

Although two isosbestic points at 465 nm and 571 nm were observed in the hydrolysis of $Co(MEDTA)Br^-$ prepared according to the literature,[6] the first-order kinetic plots could be separated into two components the faster reacting of which constituted 68±5% (Figure 2). The preparation of the ion from Co(MEDTA) H_2O and HBr led to a product which on hydrolysis gave the same isosbestic points, but additionally yielded a uniphasic first-order rate constant (using a number of wavelengths from 350 nm to 590 nm), which corresponded very well to the "fast" component of the mixture (Figure 2 and Table I). The rate constants are independent of ionic strength and pH from 1–6. Spectra of the single and mixed isomers are almost identical except below 400 nm (Figure 3); absorbance can therefore be used as a measure of concentrations even with the mixture. The behavior also explains the observation of isosbestic points with the mixture.

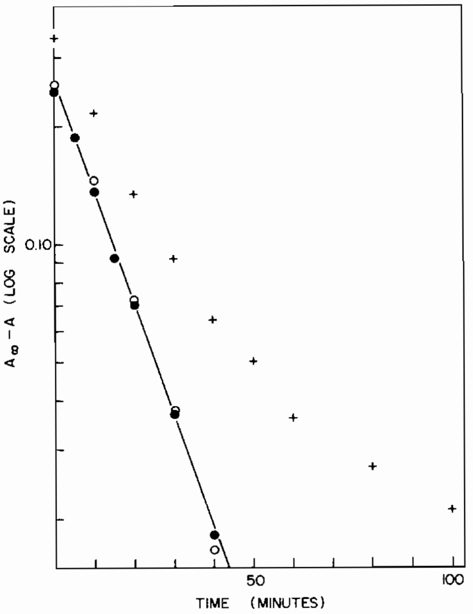


Figure 2. Rate plot for hydrolysis of $Co(MEDTA)Br^-$ at 78.8° C, pH = 2.6, I = 0.1. + = mixture of isomers (followed at 540 nm); ○ = fast-rate derived from mixture by subtraction of slow rate; ● = experimental points for fast isomer (550 nm).

The products from the hydrolysis of the chloro, "mixed" bromo and "pure" bromo species had identical spectra. A series of spectra between pH = 6 and pH = 9.6 gave isosbestic points at 396, 467 and 565 nm and

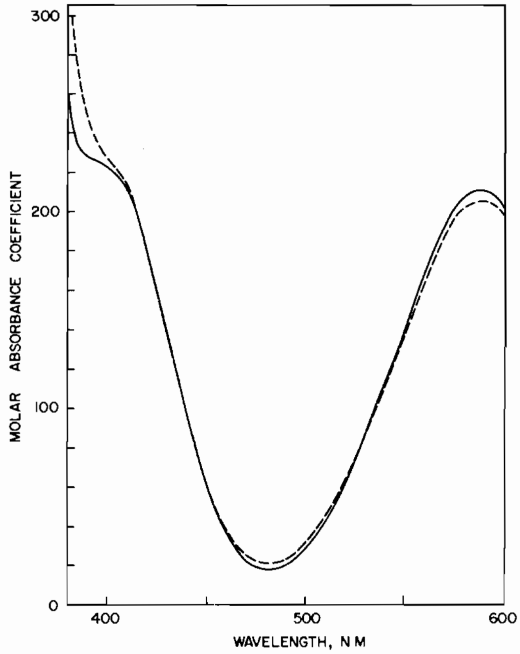


Figure 3. Absorption spectrum of Co(MEDTA)Br$^-$. —— represents mixed isomers; ---- faster reacting pure isomer.

a spectral pK value of 8.0 was determined, which agreed well with a potentiometric value of 7.95 (25°C, I = 0.1M). These values were also independent of the source of the aqua complex.

CyDTA Complexes

The Co(CyDTA)Cl^{2-} or Co(CyDTA·H)Cl$^-$ ion was usually prepared *in situ* by warming K[Co(CyDTA)]·2H$_2$O in conc HCl until blue and then adjusting to the appropriate pH and ionic strength. The chloro species obtained in this way gave on ring closure the same series of isosbestic points (at 353, 395, 455 and 575 nm) and reaction rate constant as did the solutions obtained from solid compounds, prepared by oxidation of Co(II)–CyDTA with Copy$_4$Cl$_2$$^+$ and from reaction of Co(CyDTA)$^-$ with HCl (Table I).

In contrast to the behavior of the EDTA and MEDTA complexes, Na$^+$ ion (from NaCl or NaClO$_4$) was found to accelerate the ring closure for both unprotonated and protonated forms:

$$V = k_{\mathrm{obsd}}[\mathrm{Co(III)}] = \{k_1 + k_2[\mathrm{Na^+}]\}[\mathrm{Co(III)}] \qquad (7)$$

For the unprotonated species, $k_1 = 1.8 \times 10^{-4}$ sec^{-1} and $k_2 = 2.1 \times 10^{-4} M^{-1}$ sec^{-1} and for the protonated form, $k_1 = 3.3 \times 10^{-4}$ sec^{-1} and $k_2 = 3.5 \times 10^{-4} M^{-1}$ sec^{-1} at 40.5° C. This indicates about equal contributions from the two paths at [Na$^+$] = 1.0M. The dependence of the rate on [H$^+$] was determined at [Na$^+$] = 1.0M. With the following scheme

$$\begin{tikzcd}
\mathrm{Co(CyDTA\cdot H)Cl^-} \arrow[rr, leftrightharpoons, "K"] \arrow[dr, "-\mathrm{HCl}", "k_{\mathrm{HX}}"'] & & \mathrm{Co(CyDTA)Cl^{2-}} + \mathrm{H^+} \arrow[dl, "-\mathrm{Cl^-}"', "k_{\mathrm{X}}"] \\
& \mathrm{Co(CyDTA)^-} &
\end{tikzcd} \qquad (8)$$

$$(1 + [\mathrm{H^+}]\mathrm{K}^{-1})k_{\mathrm{obsd}} = k_{\mathrm{HX}}[\mathrm{H^+}]\mathrm{K}^{-1} + k_{\mathrm{X}} \qquad (9)$$

and the experimental data (Figure 1) is best reproduced (solid line) with the values $k_{\mathrm{HX}} = 6.8 \times 10^{-4}$ sec^{-1}, $k_{\mathrm{X}} = 3.9 \times 10^{-4}$ sec^{-1}, and K = $2 \times 10^{-3} M$ (40.5° C). In the wavelength range 350–370 nm, the unprotonated and protonated species differ sufficiently for this to be a basis for a spectral determination of K (Figure 1). The value 1.6×10^{-3} is in good agreement with the kinetics results.

Previously, the rate constants for ring closure of Co (CyDTA)H$_2$O$^-$ and Co(CyDTA·H)H$_2$O have been determined at 25° C and I = 0.7M. The K value analogous to that in (8) was determined kinetically ($8 \times 10^{-2} M$).[7] In the present study activation parameters were determined for reaction of the unprotonated species. The results are shown in Table III.

EDDA Complexes

Hydrolysis of α-*cis*-Co(EDDA)Cl$_2$$^-$ gave α-*cis*-Co (EDDA)(H$_2$O)$_2$$^+$. Removal of the first chloride gave isosbestic points at 376, 399, 479 and 570 nm for 2–3 $t_{1/2}$'s, after which time some deviation occurred due to the intrusion of the second chloride loss. Isosbestic points at 355, 388 and 547 nm were observed for the hydrolysis of the second chloride. Consistent data for both stages were obtained at a number of wavelengths, 610 nm being usually employed. Rate constants were independent of ionic strength and pH 0.8–2.2 (Table I). Garnett and Watts[9] reported an [H$^+$]$^{-1}$ dependence for the hydrolysis of α- and β-*cis*-Co(EDDA)(H$_2$O)Cl ions, but for the α-isomer, this becomes apparent only at pH below 2.

These data were required to help characterize the product of reaction (10)

$$\mathrm{Co(EDDA)(H_2O)_2} + \mathrm{Copy_4Cl_2^+} \rightarrow \mathrm{Co(EDDA)(H_2O)Cl} + \mathrm{Co^{2+}} + 4\mathrm{py} + \mathrm{Cl^-} \qquad (10)$$

The stoichiometry of the reaction was established by showing a 1.05:1.0 ratio for Co;Cl in the Co(III)–EDDA product, which represented all the cobalt(III) present. An inner sphere reaction was thus confirmed for (10). That the product was an isomeric mixture was evidenced by (i) its spectra, as well as that of the diaqua hydrolysis product, (Table II) not agreeing with either α-*cis* or β-*cis* (obtained subsequent to the conclusion of our work[9]). Spectral analysis of the product of (10) indicated 70 ± 10% β-*cis*, and of the hydrolysis product 65 ± 15% β-*cis*; (ii) lack of isosbestic points in the hydrolysis of Co(EDDA)(H$_2$O)Cl at pH = 3; (iii) multiphasic rate plot in connection with hydrolysis studies. Analysis at 610–620 nm, where ε for the *α-cis* and reaction product are the same showed two rates, the fast portion of which could not be accurately determined. It approximated that of the *α-cis* (4×10^{-6} compared with 8.3×10^{-6} at 25° C) and represented only 17% of the complex present. There were occasional indications of the presence of a very small amount of a third fast reacting isomer.

Discussion

Detection of Isomers

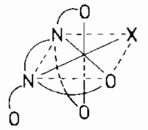
The presence of two isomers each of $Co(EDTA)Br^{2-}$ and $Co(MEDTA)Br^-$ ions prepared as described in the literature[6, 12] was strongly suggested by the biphasic kinetic plots obtained for ring closure[3] and hydrolysis respectively. Isomerism was further supported by the preparation of samples of the two complex ions which gave one reaction rate constant only. This corresponded very well with the appropriate "faster" reacting component of the mixture. For the EDTA complex, the Hg(II) catalyzed ring closure was also examined, and biphasic and uniphasic kinetics were observed, respectively, for the two samples of complex.

No evidence for mixed isomers has emerged from optical rotation measurements on these materials,[6, 11, 13] However the resolution of the ions may very well have led to preferential production of one of the isomers. Moreover, the electronic spectra of the single isomer differs significantly from the mixture only at wavelengths below 400 nm (Figure 3). Only one rate was observed in the Br_2 catalyzed ring closure of Co $(EDTA)Br^{2-}$ ion.[19] However, the difference in the mixture obtained by us (44% faster reacting component) and previous workers[3] (28%) shows that the composition of the product is very sensitive to the experimental conditions.

Conclusive evidence for the nature of the species has resulted from ^{13}C NMR examination of Co(EDTA) Cl^{2-} (a single isomer) and $Co(EDTA)Br^{2-}$ (both the isomeric mixture and the single isomer).[20] The data strongly support a Ia (X = Cl) configuration for the chloro complex and a Ib (X = Br) structure for the single isomeric $Co(EDTA)Br^{2-}$ ion. The sample of $Co(EDTA)Br^{2-}$ which gives biphasic kinetics is a mixture of Ia and Ib.

It is surprising that the single isomers of Co(EDTA) Cl^{2-} and $Co(EDTA)Br^{2-}$ have different configurations, especially since the equatorial arm is more strained than the axial, when coordinated.[21] Since no free arm is involved with MEDTA, we would expect Co $(MEDTA)Br^-$ to have a Ib type configuration also, although examination of models suggest that there is less interaction between the N-CH_3 and Br when the latter is in the equatorial position (Ia) and two structural isomers of $Co(R)$-(–)-$PD3A)(NO_2)^-$, PD3A = 1,2-propanediaminetriacetate, have equatorial NO_2 groups.[22] NMR studies should decide.

An alternative interpretation has been offered for the biphasic kinetics of ring closure of $Co(EDTA)Br^{2-}$ ion.[5] Consecutive (rather than concurrent) reactions are suggested. An unstable form in which the two acetates on the tertiary nitrogen are coordinated *trans* to one another (*e.g.* IV) rearranges ("slow" portion) to the isomer in which free acetate arm can span to the halide (*e.g.* Ia) and which reacts rapidly ("fast" portion). Such *trans*-equatorial and *cis*-equatorial isomer of $Co(ED3A)NO_2^-$, (ED3A = 1,2-ethanediaminetriacetate) have been recently characterized,[22] but it seems unlikely that a *trans* form will exist with –CH_2COO substitution (rather than H) on the N.



IV

The cobalt(III) product of the inner-sphere redox reaction (10) was shown to be an isomeric mixture by a number of observations (see Results Section). Kinetic plots and spectral results indicated about 20% *α-cis* in the mixture. The remaining isomer or isomers, which made up the bulk of the material, reacted about five times slower. Its associated rate constant, which is quite accurately defined, does not correspond at all well with that of *β-cis*,[9] although it is slower reacting than the *α-cis* isomer, as expected. Our spectral data either are not entirely consistent with an *α-cis* and a pure *β-cis* mixture and there may be amounts of both *β-cis* isomers (IIIb, c; X = Cl, Y = H_2O) present.

Mechanism for Ring Closure

The rate constant for ring closure of Co(EDTA · H) Cl^- is about ten-fold faster than aquation of the very similar ion $Co(MEDTA)Cl^-$, and is attended by a substantially lower $\Delta H^{\ddagger}$ value. This *suggests* that in the former process there is an important path involving direct ring closure (k_1 path), although the group neighboring effect does not enhance the rate markedly. There is evidence for the absence of an aqua intermediate in the ring closure of the CyDTA complex also. For the path

$$\mathrm{Co(CyDTA)Cl^{2-}} \xrightarrow{k_2} \mathrm{Co(CyDTA)(H_2O)^-} \xrightarrow{k_3} \mathrm{Co(CyDTA)^-} \qquad (11)$$

$k_2 = 10^{-3}$, $k_3 = 10^{-2}$ sec^{-1} at 52° C. The concentration of the aqua intermediate will reach a maximum[23]

$$\frac{[\mathrm{Co(CyDTA)(H_2O)^-}]_{\mathrm{max}}}{[\mathrm{Co(CyDTA)Cl^{2-}}]_{t=0}} = 10^{\frac{10^{-2}}{-(10^{-2}-10^{-3})}} \qquad (12)$$

$$\text{at a time, } t_{max} \text{ (in seconds)} = \frac{2.3 \log(10^{-2}/10^{-3})}{10^{-2}-10^{-3}} \quad (13)$$

This should lead to a maximum amount of 8% of the total cobalt as the aqua intermediate at about 45 minutes after the start of the reaction. At 354 nm, which is an isosbestic point for $Co(CyDTA)Cl^{2-}$ and $Co(CyDTA)^-$, Figure 4, and where a maximum difference occurs between the absorption coefficients of these and the aqua species,[7] an 0.014 absorption unit change should be observed. This was not detected suggesting that no intermediate is produced.

Some participation by the free carboxylate or carboxylic acid arm in the transition state (S_N2, internal) for ring closure of $Co(EDTA)H_2O^-$ and $Co(EDTA \cdot H)H_2O$ has been suggested,[2] while for the corresponding reactions of $Co(EDTA)X^{2-}$ and $Co(EDTA \cdot H)X^-$ (X = halides) either an S_N1 (5-coordinated intermediate) or S_N2 (solv) with an aqua intermediate were considered likely. Our results suggest that the latter is probably ruled out.

Hydrolysis and Ring Closure Rate Constants

The negative values for ΔS^{+} for reaction of chloro and, particularly bromo, derivatives of MEDTA complexes as well as in ring closure reactions agrees with a dissociative mechanism since in the formation of incipient halide in the transition state, increased solvation will lead to a lowering of entropy. Garnett and Watts[9] have characterized a number of cobalt(III) complexes of EDDA and studied the hydrolysis of *α-cis* and *β-cis*-$Co(EDDA)Cl_2^-$ and $Co(EDDA)(H_2O)Cl^-$ ions.[9] Our rate constants with the *α-cis* series are in good agreement with theirs (Table IV). In comparing with cationic polyamine cobalt(III) complexes, it is seen that the sign of the charge on the Co(III) complex has little influence on rates. This surprising result and other aspects of the hydrolysis data have been fully discussed.[9]

The substitution of a methyl group on the ethylenediamine backbone of EDTA has little effect on the ring closure rate constant. But the cyclohexane group crowds the methylene H of the free acetate arm which is thereby constrained to be close to chloride or H_2O in the five-coordinated species. This helps to force off the unidentate ligand, the higher rate constant (over that of EDTA) residing in a much lowered ΔH^{+} value. The enhanced rate of ring closure for the protonated form, $Co(CyDTA \cdot H)X$, over $Co(CyDTA)X$ may result from the proton of the constrained carboxylic acid group partially associating with the departing X group (X = Cl or $H_2\dot{O}$). Even Na^+ ion can help with this ring closure, an effect not observed with the other polycarboxylates. The marked stability of the six-coordinated CyDTA complex and the reluctance of one of the acetate arms to sever because of the juxtapositioning of the cyclohexane ring is shown in the reduced formation constant (compared with EDTA) for reaction of $Co(CyDTA)^{2-}$ with $Fe(CN)_6^{3-}$ to form the adduct $(CyDTA)Co^{III}{-}CN{-}Fe^{II}(CN)_5^{5-}$ and reduced rate constant for inner-sphere oxidation of $Co(CyDTA)^{2-}$ with $Copy_4Cl_2^+$ ion.[25] These differences cannot reside in thermodynamic drive for the reactions, since the standard redox potentials of Co (II)–EDTA and CyDTA complexes are virtually identical.[26]

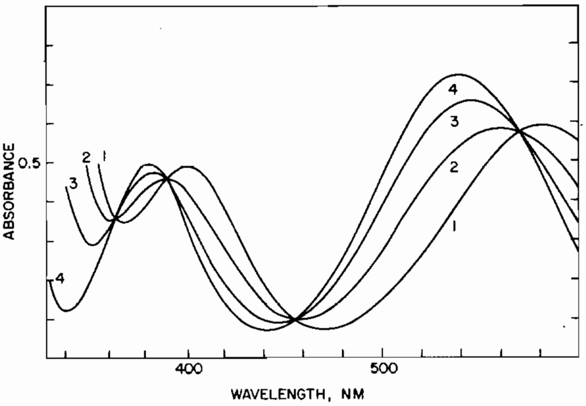


Figure 4. Absorption spectra at various times during ring closure of $Co(CyDTA)Cl^{2-}$. 2.3 m*M* complex at 51.7° C, pH = 4.4, I = 1.0*M* NaAc. 0 min (1); 8 min (2); 20 min (3) and 96 min (4).

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