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Reactions of Ethylenediamine-*N*,*N'*-diacetatodiaquo Complexes of Cobalt(III). 3. A Kinetic Study of the β-*cis*-$Co(EDDA)(OH_2)_2^+ \rightleftharpoons$ α-*cis*-$Co(EDDA)(OH_2)_2^+$ Isomerization Reaction

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In earlier papers we have described the oxalate anation of α-*cis*-$Co(EDDA)(OH_2)_2^+$ in both highly[1] and slightly[2] acidic aqueous media. Recently, the preparation of the β-*cis*-$Co(EDDA)(OH_2)_2^+$ isomer[3] has been reported.[4] In studying the reaction between oxalate species and the β-*cis*-diaquo isomer it soon became apparent that the β-*cis*-$Co(EDDA)(OH_2)_2^+ \rightleftharpoons$ α-*cis*-$Co(EDDA)(OH_2)_2^+$ isomerization reaction was very important in the chosen pH and temperature ranges. We wish to report here our characterization of the above isomerization reaction in the ranges $40 \leq T \leq 60$ °C and $1.47 \times 10^{-4} \leq [H^+] \leq 5.00 \times 10^{-2}$ M.

Experimental Section

Ethylenediamine-*N*,*N'*-diacetic acid was used as received from Pfaltz and Bauer, Inc. All other chemicals were reagent quality. Distilled water was used throughout.

α-*cis*-$[Co(EDDA)(OH_2)_2]ClO_4$ was prepared as previously described.[2] β-*cis*-$[Co(EDDA)(OH_2)_2]ClO_4$ was prepared by a method similar to that of Garnett and Watts.[4] Elution of the β-cis isomer was accomplished in a cooled (3 °C) column using 0.40 M $HClO_4$. Further, to be sure that the β-*cis*-$[Co(EDDA)(OH_2)_2]ClO_4$ complex was as free of any contamination as possible, it was recycled through the ion exchange and crystallization procedures before being used in characterization or kinetic studies. After filtration of the solid, washing with acetone yielded a nicely crystalline product. Elemental analysis was performed by Galbraith Laboratories, Inc. Anal. Calcd for β-*cis*-$[Co(EDDA)(OH_2)_2]ClO_4$ ($CoC_6H_{14}O_{10}N_2Cl$): C, 19.55; H, 3.83; N, 7.60. Found: C, 19.56; H, 3.94; N, 7.50.

Kinetic studies were made using a Coleman Perkin-Elmer Model 46 spectrophotometer equipped as previously described.[2] Rate constants were determined at 383 nm. This corresponds closely to a peak position as well as a large molar absorptivity difference position for α- and β-*cis*-$Co(EDDA)(OH_2)_2^+$. "Infinite" absorbance measurements were made after 9–12 half-lives and were checked intermittently for constancy. The complex concentration was 5.00×10^{-3} M in all of the experiments reported.

The procedure for a typical kinetic run is outlined as follows. Aliquots of stock solutions containing the proper amounts of HNO_3 (by dilution of standardized HNO_3) and $NaNO_3$ (by weight, $\mu = 0.50$) were brought to the desired temperature in a water bath. The reaction was initiated by adding solid complex (β-cis isomer) to the solution with rapid stirring. A portion of the solution was then transferred to a dry, equilibrated 1-cm cell and the absorbance followed as a function of time. The reference cell contained H_2O.

The equilibrium constant for the isomerization reaction was determined from the equilibrium spectrum at 387 nm after 10 half-lives.

Results and Discussion

Peak positions and molar absorptivities for our samples of β-*cis*-$[Co(EDDA)(OH_2)_2]ClO_4$ are λ 384 nm, ϵ_{384} 133 cm^{-1} M^{-1}, and λ 520 nm, ϵ_{520} 171 cm^{-1} M^{-1}. Those reported by Garnett and Watts[4] are λ 383 nm, ϵ_{383} 137 cm^{-1} M^{-1}, and λ 515 nm, ϵ_{515} 180 cm^{-1} M^{-1}. Repeated ion exchange chromatography of our β-*cis*-$Co(EDDA)(OH_2)_2^+$ samples indicated no impurities in our preparations and further, numerous crystallization operations gave reproducible peak positions and molar absorptivities. Our samples of α-*cis*-$[Co(EDDA)(OH_2)_2]ClO_4$ gave molar absorptivities identical with those reported by Kuroda and Watanabe[5] and by Garnett and Watts.[4]

The equilibrium constant for the isomerization reaction was determined under two different sets of conditions: (1) $[H^+] = 5.2 \times 10^{-4}$ M, $T = 45.0$ °C, and (2) $[H^+] = 4.77 \times 10^{-2}$ M (HNO_3), $T = 55$ °C. Defining K_{eq} = [α-*cis*-$Co(EDDA)(OH_2)_2^+$]/[β-*cis*-$Co(EDDA)(OH_2)_2^+$] we report $K_{eq} = 25 \pm 4$ as determined from the equilibrium spectrum after 10 half-lives under the above conditions. Within experimental error (mainly associated with uncertainties, ±1 unit, in the molar absorptivities) there appears to be no temperature or pH dependence in this range. No attempt was made to further refine K_{eq} because the above value was sufficient for direction in the following kinetic study.

An aqueous solution of red β-*cis*-$Co(EDDA)(OH_2)_2^+$ slowly changes in color to the purple associated with α-*cis*-$Co(EDDA)(OH_2)_2^+$. The rate of this change depends on the acidity of the solution as well as *T*. Ion-exchange chromatography (Dowex 50W-X8, 100–200 mesh, H^+ form) of equilibrated solutions initially containing pure β-cis isomer showed the presence of only two +1 charged species. These were subsequently identified as the α-*cis*- and β-*cis*-$Co(EDDA)(OH_2)_2^+$ isomers, respectively. Band size indicated the formation of the α-cis isomer was strongly favored at equilibrium. Ion-exchange chromatography of an equilibrated solution initially containing pure α-*cis*-$Co(EDDA)(OH_2)_2^+$ gave results identical with the above. In acidic solution, repetitive spectral scanning between 600 and 350 nm (Cary 14) showed the expected isosbestic point at λ 553 nm indicating a simple interconversion between the isomers.

A series of kinetic runs was made systematically varying *T* and $[H^+]$ in the ranges $1.47 \times 10^{-4} \leq [H^+] \leq 5.00 \times 10^{-2}$ M and $40 \leq T \leq 60$ °C. $[H^+]$ was adjusted using HNO_3 and the ionic strength was held constant at $\mu = 0.50$ using $NaNO_3$. At the lower hydrogen ion concentrations the pH was found to remain constant within ±0.04 pH unit during the first 2–4 half-lives of the reaction. The isomerization reaction was followed for at least 2 half-lives and plots of $-\log (A_t - A_\infty)$ vs. time were linear during this period.

The observed rate constant, k_{obsd}, is the sum of the rate constants for the interconversions β-cis → α-cis (k_β) and α-cis → β-cis (k_α). The value of K_{eq}, however, establishes that k_α is ~4% of k_β in the ranges studied, and hence to an adequate approximation $k_{obsd} \simeq k_\beta$.

Table I lists the various values of k_{obsd} obtained as a function of total hydrogen ion concentration and temperature. Duplicate runs generally gave k_{obsd} values that agreed within 3% of the original. Hydrogen ion concentration affects k_{obsd} in an inverse fashion. In the ranges $50 \leq T \leq 60$ °C and $[H^+] > 1.0 \times 10^{-3}$ M, plots of k_{obsd} vs. $[H^+]^{-1}$ are linear with a positive temperature-dependent intercept. Here $[H^+] \simeq C_{HNO_3}$, i.e., acid dissociation of β-*cis*-$Co(EDDA)(OH_2)_2^+$ does not contribute to total $[H^+]$. This is not surprising since Garnett's measured pK_β (pK_1 for β-*cis*-$Co(EDDA)(OH_2)_2^+$) is 6.0 at 20 °C.[6] Although some temperature dependence is

Table I. Observed Rate Constants for the Isomerization Reaction β-*cis*-Co(EDDA)$(OH_2)_2^+ \rightleftharpoons \alpha$-*cis*-Co(EDDA)$(OH_2)_2^+$

10^4k_{obsd}, s^{-1} ([H^+], M)[a]				
40.00 °C	45.00 °C	50.00 °C	55.00 °C	60.00 °C
9.08 (1.47 × 10^{-4})	19.6 (1.52 × 10^{-4})	40.3 (1.76 × 10^{-4})	3.18 (5.55 × 10^{-3})	6.85 (5.55 × 10^{-3})
7.78 (1.67 × 10^{-4})	17.3 (1.71 × 10^{-4})	34.4 (1.96 × 10^{-4})	2.48 (7.50 × 10^{-3})	5.26 (7.50 × 10^{-3})
6.87 (1.87 × 10^{-4})	14.9 (1.92 × 10^{-4})	28.6 (2.38 × 10^{-4})	1.98 (1.00 × 10^{-2})	2.83 (1.67 × 10^{-2})
4.61 (2.75 × 10^{-4})	9.95 (2.79 × 10^{-4})	23.5 (2.82 × 10^{-4})	1.30 (1.67 × 10^{-2})	1.46 (5.00 × 10^{-2})
2.42 (5.14 × 10^{-4})	5.34 (5.15 × 10^{-4})	13.0 (5.17 × 10^{-4})	0.654 (5.00 × 10^{-2})	
1.64 (7.59 × 10^{-4})	3.70 (7.60 × 10^{-4})	9.30 (7.62 × 10^{-4})		
	2.76 (1.01 × 10^{-3})	6.84 (1.01 × 10^{-3})		
		3.60 (2.00 × 10^{-3})		
		1.88 (4.00 × 10^{-3})		
		1.08 (7.50 × 10^{-3})		
		0.841 (1.00 × 10^{-2})		

[a] $[H^+]_T = C_{HNO_3}$ + [H^+] from acid dissociation of β-*cis*-Co(EDDA)$(OH_2)_2^+$. Listed in the table is $[H^+]_T$.

Scheme I

$$\begin{tikzcd}
\beta\text{-}cis\text{-Co(EDDA)}(OH_2)_2^+ \arrow[r, shift left, "K_\beta"] \arrow[d, shift right, "k_1"'] & \beta\text{-}cis\text{-Co(EDDA)(OH)}(OH_2)^0 \arrow[l, shift left] \arrow[d, shift right, "k_2"'] \\
\alpha\text{-}cis\text{-Co(EDDA)}(OH_2)_2^+ \arrow[r, shift left, "K_\alpha"] \arrow[u, shift right, "k_3"'] & \alpha\text{-}cis\text{-Co(EDDA)(OH)}(OH_2)^0 \arrow[l, shift left] \arrow[u, shift right, "k_4"']
\end{tikzcd}$$

expected in K_β this effect is apparently not large enough to cause [H^+] to deviate from C_{HNO_3} when $C_{HNO_3} > 1.0 \times 10^{-3}$ M.

The slope of the k_{obsd} vs. $[H^+]^{-1}$ plot is known at 50 °C when $C_{HNO_3} > 1.0 \times 10^{-3}$ M, i.e., $[H^+] \simeq C_{HNO_3}$. Hence the value of K_β at 50 °C can be determined by floating K_β until a plot of k_{obsd} vs. $[H^+]_T^{-1}$ ($[H^+]_T < 1.0 \times 10^{-3}$ M) is linear and of identical slope with that obtained when $[H^+]_T > 1.0 \times 10^{-3}$ M.[7] Similarly at 40 and 45 °C, K_β is allowed to float until a plot of k_{obsd} vs. $[H^+]_T^{-1}$ is linear. At 40 and 45 °C the intercept term is so small as to be indistinguishable from zero in a least-squares analysis.

The data show k_{obsd} is of the form $k + k'/[H^+]$. A reasonable interpretation of these data indicates involvement of both β-*cis*-Co(EDDA)$(OH_2)_2^+$ and β-*cis*-Co(EDDA)(OH)$(OH_2)^0$ in the isomerization process. A mechanism which is in agreement with all the experimental data in the isomerization reaction is shown in Scheme I. By appropriate substitution the observed rate constant for the process β-cis → α-cis is given as

$$k_\beta = \frac{k_1[H^+]}{[H^+] + K_\beta} + \frac{k_2K_\beta}{[H^+] + K_\beta}$$

Similarly the observed rate constant for the process α-cis → β-cis is given by

$$k_\alpha = \frac{k_3[H^+]}{[H^+] + K_\alpha} + \frac{k_4K_\alpha}{[H^+] + K_\alpha}$$

Hence

$$k_{obsd} = \frac{k_1[H^+]}{[H^+] + K_\beta} + \frac{k_2K_\beta}{[H^+] + K_\beta} + \frac{k_3[H^+]}{[H^+] + K_\alpha} + \frac{k_4K_\alpha}{[H^+] + K_\alpha}$$
$$\simeq \frac{k_1[H^+]}{[H^+] + K_\beta} + \frac{k_2K_\beta}{[H^+] + K_\beta}$$

One sees that if $[H^+] >> K_\beta$, k_{obsd} reduces to the form defined by our data. It is to be noted that under all our experimental conditions [H^+] is much greater than K_β (see Table II). Hence the slope and intercept from our experimental plots are defined as k_2K_β and k_1, respectively.

A least-squares analysis of k_{obsd} vs. $[H^+]^{-1}$ plots at $[H^+] > 1.0 \times 10^{-3}$ M yields the respective k_1 values for 50, 55, and 60 °C. These are listed in Table II. Similar treatment at 40, 45, and 50 °C and knowing K_β at these temperatures allow for the determination of k_2. The obtained values of k_2 and K_β are also listed in Table II. In the [H^+] range studied the complex β-*cis*-Co(EDDA)(OH)$(OH_2)^0$ is extremely important in the isomerization process. This well-established phenomenon[2,8-11] is easily seen by comparing the magnitudes of k_1 and k_2.

Table II. Kinetic Parameters Describing the β-*cis*-Co(EDDA)$(OH_2)_2^+ \rightleftharpoons \alpha$-*cis*-Co(EDDA)$(OH_2)_2^+$ Isomerization Reaction

T, °C	10^5k_1, s^{-1}	$10k_2$, s^{-1}	10^6K_β
40.00		0.94 ± 0.14	1.4 ± 0.2
45.00		1.9 ± 0.1	1.6 ± 0.1
50.00	1.57 ± 0.04	3.8 ± 0.2	1.8 ± 0.1
55.00	3.6 ± 0.3	7.3[a]	2.1[a]
60.00	8.0 ± 0.2	14[a]	2.4[a]

[a] These k_2 values are extrapolations from the activation parameter plot. The corresponding K_β values are obtained by dividing the slope of the pertinent k_{obsd} vs. $[H^+]^{-1}$ plot by the extrapolated k_2 value.

Table III. Temperature-Dependence Parameters for the β-*cis*-Co(EDDA)$(OH_2)_2^+ \rightleftharpoons \alpha$-*cis*-Co(EDDA)$(OH_2)_2^+$ System

Constant	Species	$\Delta H^\ddagger$, kcal mol^{-1}	$\Delta S^\ddagger$, eu	ΔH, kcal mol^{-1}
k_1	Diaquo	34.1 ± 1.2	+24.9 ± 3.7	
k_2	Hydroxoaquo	27.3 ± 1.4	+24.0 ± 4.4	
K_β				5.7 ± 0.3

The temperature variation in k_1 and k_2 was used to calculate their respective activation parameters. ΔH for K_β was obtained using its temperature dependence. A least-squares analysis of these data is listed in Table III. Using ΔH for K_β and extrapolating to 20 °C yield $pK_\beta = 6.1$ at this temperature, in quite good agreement with Garnett's reported value of 6.0.[6]

It would be useful to have available the results of a water exchange study on the *cis*-Co(EDDA)$(OH_2)_2^+$ system. This would allow comparison of exchange and isomerization results and perhaps allow a suggestion as to the mechanistic nature of the isomerization process. Lacking this information it is still possible to compare present data with exchange and isomerization data in the *cis*- and *trans*-$Co(en)_2(OH_2)_2^{3+}$ system.[8,12,13] All investigators[8,12,13] have suggested that the data for water exchange and isomerization in the $Co(en)_2(OH_2)_2^{3+}$ system are compatible with a dissociative activation process even though the five-coordinate intermediate generated in each process is most likely of different geometry. Although we have no volumes of activation to report in our system, there is striking similarity between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values in the $Co(en)_2(OH_2)_2^{3+}$ and α- and β-*cis*-Co(EDDA)$(OH_2)_2^+$ systems. Especially when considering the very positive values of $\Delta S^\ddagger$ in the present system, it is tempting to suggest a dissociative activation process in the isomerization reaction.

Without additional information, however, any further speculation concerning the mechanistic activation process in the present system is unwarranted.

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Registry No. β-*cis*-Co(EDDA)$(OH_2)_2^+$, 26135-75-1.

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(7) In this range $[H^+]_T = C_{HNO_3} + [H^+]_\beta$, where $[H^+]_\beta$ is the proton contribution from acid dissociation of β-*cis*-Co(EDDA)$(OH_2)_2^+$. $[H^+]_T$ could be calculated directly if K_β was known at 50 °C. Since this is not the case K_β is allowed to float generating various $[H^+]_\beta$ values given constant C_{HNO_3} and $C_{complex}$. This process is continued until a K_β is determined which generates $[H^+]_\beta$ values such that a plot of k_{obsd} vs. $[H^+]_T^{-1}$ is linear and has a slope identical with that obtained at 50 °C when $[H^+] > 1.0 \times 10^{-3}$ M.

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o-Quinone Coordination to *cis*-Dioxomolybdenum(VI) Species. Crystal and Molecular Structure of *cis*-Dioxodichloro(9,10-phenanthrenequinone)molybdenum(VI)

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Introduction

Benzoquinones constitute a pervasive component of the environment. They occur naturally in higher plants, fungi, bacteria, and the animal kingdom.[1] Humic substances are probably the most widely distributed natural products on the earth's surface and contain oxidized and reduced quinone functional groups.[2,3] Polycyclic quinones have been found as atmospheric contaminants over major cities.[4] *o*-Quinones in both their reduced (catecholate) and oxidized forms are ideal chelating agents for transition metals, and this property appears naturally in many diverse functions. Hydroquinone complexes of Fe^{3+} serve as microbial iron transport agents in specific systems.[5] Metal–catecholate complexes appear as intermediates in the function of catechol dioxygenases.[6] Humic acids function as chelating agents for a wide variety of metal ions.[2]

Much recent interest has been focused on the π-acceptor activity of *o*-quinone ligands coupled with nucleophilic metals.[7] However, the earliest reports of *o*-quinone coordination concern simple adducts of the metal ions Zn^{2+}, Hg^{2+}, Fe^{3+}, and Mo^{6+}.[8,9] In these complexes the ligand behaves as a simple oxygen donor. Characterization of quinone ligands in these compounds has been confined to little more than infrared analysis. The *cis*-dioxomolybdenum(VI) species forms complexes with both oxidized and reduced quinone ligands. Semiquinone[10] and catecholate[11,12] complexes of this type have been characterized structurally. We now report the synthesis of the 9,10-phenanthrenequinone adduct of MoO_2Cl_2 and its molecular structure.[13] The results of this investigation are compared with the structural features of other quinone, semiquinone, and catecholate complexes of Mo(VI).

Experimental Section

Crystal Preparation and Data Collection. The complex $MoO_2Cl_2(O_2C_{14}H_8)$ was prepared by addition of excess 9,10-phenanthrenequinone to an anhydrous dichloromethane solution of MoO_2Cl_2. Slow evaporation of the solvent gave dark green, monoclinic crystals of the complex. A crystal of dimensions 0.26 × 0.22 × 0.11 mm was mounted and aligned on a Syntex $P\bar{1}$ automated diffractometer. Preliminary precession photographs showed monoclinic symmetry with systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) consistent with space group $P2_1/c$-C_{2h}^5. The settings of 15 reflections with 2θ values greater than 25° were used to give the refined cell constants $a = 6.991$ (1), $b = 10.227$ (1), $c = 21.179$ (3) Å, and $\beta = 107.52$ (2)°. An experimental density of 1.863 (7) g/cm^3 agrees with a calculated value of 1.872 g/cm^3 for four molecules per unit cell. A complete set of intensity data (hkl, $hk\bar{l}$) was collected within the angular range $3° \leq 2\theta \leq 50°$ using Mo Kα radiation. The θ–2θ scan mode was used with a fixed scan rate of 2.0°/min. Scans ranged from 0.6° below the Kα_1 2θ setting to 0.7° above Kα_2. Four check reflections were monitored after every 95 reflections measured. Their variation in intensity over the time required to collect data was less than 2.5%. Values for F_o^2 and $\sigma(F_o^2)$ were calculated for the 3083 reflections measured using procedures described previously.[14] Absorption effects were judged to be insignificant with $\mu = 12.4$ cm^{-1}.

Solution and Refinement of the Structure. The position of the Mo atom was determined from a Patterson map. Phases derived from the Mo position were used to locate all other nonhydrogen atoms of the structure. Positions of the quinone hydrogen atoms were calculated using the refined positions of the ring carbon atoms and an assumed C–H bond length of 0.98 Å. In final cycles of refinement hydrogens were refined as individual atoms. Full-matrix least-squares refinement of the complete structure with anisotropic thermal parameters for nonhydrogen atoms converged with $R_F = 0.029$ and $R_{wF} = 0.040$. In all calculations only the 2192 values with $F_o^2 \geq 3\sigma(F_o^2)$ were included. The final value for the error in an observation of unit weight is 1.58. Atomic scattering factors for the nonhydrogen atoms were taken from Cromer and Waber,[15] and hydrogen scattering factors were taken from Stewart et al.[16] Corrections for anomalous dispersion were applied for the Mo and Cl atoms with values of $\Delta f'$ and $\Delta f''$ taken from Cromer and Liberman.[17] Final positional and thermal parameters for nonhydrogen atoms are presented in Table I. Tables containing positional and thermal parameters of hydrogen atoms and observed and calculated structure factor amplitudes are available in the supplementary material.

Description of the Structure

The crystal structure of $MoO_2Cl_2(O_2C_{14}H_8)$ consists of stacks of molecules along the crystallographic b axis. A view of the complex molecule is shown in Figure 1. Bond lengths and angles are presented in Table II. Closest intermolecular contacts along the screw axis occur for Cl(1) with separations of 3.34 and 3.37 Å to carbonyl carbons C(1) and C(2) of the adjacent molecule (Figure 2). Chlorine Cl(2) interacts weakly with ring carbons C(9) and C(14) of the lower molecule in Figure 2 with contacts of 3.60 and 3.45 Å, respectively. The somewhat stronger Cl(1) contact contributes to a longer Mo–Cl(1) length of 2.370 (3) Å compared with the Mo–Cl(2) value of 2.343 (3) Å. Both chloro ligands are bent toward the weakly coordinated quinone by bonding electron-pair repulsions with the strongly bound oxo ligands. The Cl(1)–Mo–Cl(2) angle is 156.3 (1)° with angles between chloro ligands and quinone oxygens of approximately 80°. The cis oxo ligands have characteristically short Mo–O lengths of 1.671 (3) Å with a O(3)–Mo–O(4) angle of 104.8 (2)°. Much the same geometry has been reported for the MoO_2Cl_2 portion of $MoO_2Cl_2(DMF)_2$.[18] Phenanthrenequinone oxygens are