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Cyclization and Hydrolysis of Monodentate Oxalate in *trans*-$[Co(en)_2(C_2O_4/H)(OH/H_2O)]^{0,+,2+}$

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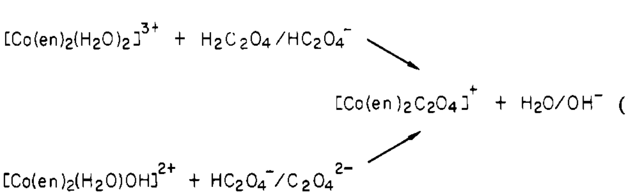
Formation of *trans*-$[Co(en)_2(C_2O_4)OH]$ from $[Co(en)_2(OH)(H_2O)]^{2+}$ and $HC_2O_4^-/C_2O_4^{2-}$ involves displacement of water from the metal center, and the reverse base hydrolysis reaction to form *cis*-$[Co(en)_2(OH)_2]^+$ involves >98% Co–O fission; the latter reaction follows first-order kinetics in OH^- with $k_{OH} = (6.5 \pm 0.4) \times 10^{-4}$ mol^{-1} dm^3 s^{-1} at 25.0 °C, $\mu = 1.0$ ($NaNO_3$). Chelation of oxalate in the *trans*-$[Co(en)_2(C_2O_4H)OH_2]^{2+}$ and *trans*-$[Co(en)_2(C_2O_4)OH_2]^+$ ions is slow, $k_{ch} = 8 \times 10^{-6}$ s^{-1}, and for the latter ion at least proceeds quantitatively via *cis*-$[Co(en)_2(C_2O_4)OH_2]^+$. The various trans species have been characterized, and a crystal structure of *trans*-$[Co(en)_2(C_2O_4)OH_2]CF_3SO_3 \cdot 2H_2O$ ($P2_1/c$, 972 reflections, $R = 0.0518$, $R_w = 0.0514$) is reported.

Introduction

Harris and his colleagues in a series of papers[1-4] have investigated the anation of $[Co(en)_2(H_2O)_2]^{3+}$ and $[Co(en)_2(H_2O)OH]^{2+}$ by $H_2C_2O_4$, $HC_2O_4^-$, and $C_2O_4^{2-}$ (reactions 1).



(1)

These studies led to the detection[1] and reported isolation[2] of the cis intermediate monodentate oxalate complex *cis*-$[Co(en)_2(C_2O_4)OH]$ and to the prediction of a similar intermediate in the anation of the related tetraammine system.[5] The same intermediate has been postulated in the ring opening of $[Co(en)_2C_2O_4]^+$, especially at high $[OH^-]$ and low temperatures[6,7] (reaction 2). Prior to these investigations, Andrade and Taube[8] had suggested this species as an intermediate in the OH^--catalyzed oxygen exchange of the chelate although it is clear from a later publication on the acid-catalyzed process[9] that ring opening was not a prerequisite of their mechanism.

$$[Co(en)_2C_2O_4]^+ + OH^- \rightarrow [Co(en)_2(C_2O_4)OH]$$

$$[Co(en)_2(C_2O_4)OH] + OH^- \rightarrow [Co(en)_2(OH)_2]^+ + C_2O_4^{2-} \quad (2)$$

Although Chan and Harris[2] have published some data on the rates of chelation and hydrolysis of $[Co(en)_2(C_2O_4)OH]$, our recent studies[10,11] on the analogous *cis*- and *trans*-$[Co(en)_2(NH_2CH_2CO_2)(H_2O/OH)]^{2+,+}$ ions have led us to question the configurational integrity of the substrate they used. Also, the possibility of an intramolecular cyclization process involving coordinated water or hydroxide had apparently been overlooked despite the Andrade and Taube study in alkaline solution[8] that requires it of the cis hydroxo species. We have now separated the *cis*- and *trans*-$[Co(en)_2(C_2O_4)OH]$ products of the anation reaction[2] and have examined in some detail the cyclizations and alkaline hydrolyses of these species. This paper reports our results on the *trans*-$[Co(en)_2(C_2O_4/C_2O_4H)(OH_2/OH)]^{0,+,2+}$ species.

Experimental Section

Reagents used in all syntheses were LR grade and were used without further purification. Solutions for kinetic experiments were prepared with use of AR $NaNO_3$ to control ionic strength ($\mu = 1.0$ mol dm^{-3}).

Spectra and kinetic data were recorded on a Cary 219 spectrophotometer using a thermostated five-sample turret (25.0 °C). pK_a measurements were carried out spectrophotometrically with use of a thermostated cell (3.2 cm), and pH was measured by using a Radiometer PHM 65 pH meter equipped with a G2040B glass electrode and K4040 reference electrode. These were standardized with phosphate and borate buffers.

trans-$[Co(en)_2(OH_2)OH](ClO_4)_2$ was prepared according to the method of Kruse and Taube as modified by Harrowfield[12] and was recrystallized from hot water before use. $[Co(en)_2C_2O_4]Cl \cdot H_2O$ was prepared according to Dwyer[13] and was purified by ion-exchange chromatography (Dowex 50W-X2, 0.5 M HCl eluent). Anal. Calcd for $CoC_6H_{18}O_5N_4Cl$: C, 22.5; H, 5.7; N, 17.5. Found: C, 22.9; H, 5.6; N, 17.5. ($\epsilon_{497} = 113$ mol^{-1} dm^3 cm^{-1} in water). A mixture of *cis*- and *trans*-$[Co(en)_2(C_2O_4)OH]$ was prepared by using a modification of the method reported by Chan and Harris.[2] $[Co(en)_2(OH_2)OH]^{2+}$ (0.1 mol dm^{-3}) was reacted with $C_2O_4^{2-}$ (0.2 mol dm^{-3}) at room temperature (~18 °C) for 2 h. The solution was filtered and then passed down an anion-exchange column (Dowex AG1-X8, NO_3^- form, H_2O eluent) to remove free oxalate and anionic cobalt species. The eluate was then loaded onto a cation-exchange column (Dowex 50W-X2, Na^+ form) and the trans isomer eluted with 0.05 M morpholine in water (pH ~9). The cis isomer was subsequently eluted with a 0.10 M $NaNO_3$ solution. The isolated trans solution was used immediately or was stored at 4 °C for a maximum of 12 h. *trans*-$[Co(en)_2(C_2O_4)OH_2]^+$ salts were isolated with use of the counterions PF_6^-, $CF_3SO_3^-$, and ClO_4^-. Anal. Calcd for $[Co(en)_2(C_2O_4)OH_2]CF_3SO_3 \cdot 2H_2O$: C, 17.9; H, 4.7; N, 11.6. Found: C, 17.9; H, 4.9; N, 11.6. Calcd for $[Co(en)_2(C_2O_4)OH_2]PF_6 \cdot H_2O$: C, 16.1; H, 4.5; N, 12.5. Found: C, 16.3; H, 4.8; N, 12.7. Absorption spectra: *trans*-$[Co(en)_2(C_2O_4H)OH_2]^{2+}$ $\epsilon_{547} = 41.1$, $\epsilon_{440} = 30.7$; *trans*-$[Co(en)_2(C_2O_4)OH_2]^+$ $\epsilon_{546} = 45.7$, $\epsilon_{444} = 30.9$; *trans*-$[Co(en)_2(C_2O_4)OH]$ $\epsilon_{528} = 56.1$.

pK_a Measurements. pK_{a1} and pK_{a2} values were measured spectrophotometrically (375 nm) by quickly titrating a freshly prepared solution of *trans*-$[Co(en)_2(C_2O_4)OH]$ in 1.0 mol dm^{-3} $NaNO_3$ with ~15 mol dm^{-3} HNO_3 over the pH range 9.0–0.7 at 25.0 °C.

Kinetic Measurements. Cyclizations of *trans*-$[Co(en)_2(C_2O_4/H)(OH/H)]^{0,+,2+}$ species were followed spectrophotometrically at 497 nm ($\mu = 1$ mol dm^{-3}, $NaNO_3$) at 25.0 ± 0.1 °C. The reaction was identified as biphasic: trans $\xrightarrow{k_1}$ cis $\xrightarrow{k_2}$ chelate (vide infra). However,

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(2) S. C. Chan and G. M. Harris, *Inorg. Chem.*, **10**, 1317 (1971).
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$k_b > 5k_a$,[19] and at 497 nm and pH <7, ϵ(trans) ≈ 27, ϵ(cis) ≈ 117, and ϵ(chelate) = 113. Thus, plots of ln $(A_\infty - A_t)$ vs. time were linear after ~12 h, and their slopes (k_{obsd}) could be equated with k_a.[36] pH was controlled by using 0.02 mol dm^{-3} solutions of chloroacetate, acetate, Pipes (piperazine-*N,N'*-bis(2-ethanesulfonic acid)), and Hepes (*N*-(2-hydroxyethyl)piperazine-*N'*-2-ethanesulfonic acid) buffers. Hydrolyses were followed spectrophotometrically at 510 nm in 0.1–1.0 mol dm^{-3} NaOH (μ = 1.0 mol dm^{-3}, $NaNO_3$) at 25.00 ± 0.05 °C.

Detection of *cis*-[Co(en)$_2$(C$_2$O$_4$)OH]$^+$ during Cyclization. A solution of *trans*-$[Co(en)_2(C_2O_4)OH_2]^+$ was allowed to stand for 13.3 h at pH 5.0, $\mu \approx$ 0.05 mol dm^{-3}, and 25.0 °C and then was loaded on to cation-exchange resin (Dowex 50W-X2, H^+ form). Trans and cis hydroxo–oxalato species were then removed successively as described above and spectrophotometrically analyzed as *cis*-$[Co(en)_2(OH)_2]^+$ following complete hydrolysis in ~0.5 mol dm^{-3} NaOH.

Crystal Data. A freshly prepared solution of *trans*-$[Co(en)_2(C_2O_4)OH]$ was acidified to pH 4.0 and solid $NaCF_3SO_3$ added. The solution was left at 4 °C for 12 h, and the resulting red crystals were recovered. Diffraction data were collected from an orange-red block with dimensions 0.31 × 0.35 × 0.31 mm. Crystal data for $[Co(en)_2(C_2O_4)H_2O]CF_3SO_3\cdot 2H_2O$ ($C_7H_{22}N_4O_{10}CoSF_3$): mol wt 470.3, monoclinic, $P2_1/c$, a = 9.537 (3) Å, b = 14.708 (6) Å, c = 13.557 (17) Å, β = 102.87 (3)°, V = 1853.84 Å^3, d_{obsd} = 1.70 g cm^{-3}, Z = 4, d_{calcd} = 1.68 g cm^{-3}, μ(Mo Kα) = 50.4 cm^{-1}.

Precession photography using Cu Kα radiation uniquely determined the space group as $P2_1/c$ from the systematic absences $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. Accurate lattice and orientation parameters were obtained from a least-squares refinement of 12 strong, high-angle reflections centered in a 5-mm-diameter circular receiving aperture set 23 cm from the crystal on a Hilger and Watts four-circle computer-controlled diffractometer. The mosaicity of the crystal was examined by means of open-counter μ scans at a takeoff angle of 3°; the widths at half-height for typical, intense, low-angle reflections ranged from 0.15 to 0.18°. Zirconium-filtered Mo Kα radiation and the θ–2θ scan technique were used to collect the intensities of 1906 independent reflections. These were corrected for Lorentz and polarization effects, and from them, 972 unique reflections with $I > 3\sigma(I)$, to be used in the final refinement of structural parameters, were obtained by averaging.[14] Absorption corrections were not applied.

The structure was solved by using the direct methods program MULTAN;[15] an E map derived from the set of phases with the highest observed figure of merit revealed the position of the cobalt atom, five of the six ligand donor atoms, and all atoms of the trifluoromethanesulfonate anion. A difference Fourier synthesis[16] located the remaining non-hydrogen atoms of the cation together with the oxygen atoms of both waters of hydration. Refinement of this model with all atoms assigned isotropic temperature factors converged at R ($\sum||F_o| - |F_c||/|F_o|$) = 0.1053.

Following confirmation that a difference Fourier map showed significant positive electron density in reasonable locations for hydrogen atoms of the cation ligand molecules, these were input in idealized positions (r(E–H) = 1.08 Å) with common isotropic temperature factors. A further difference Fourier synthesis revealed the position of the hydrogen atoms of the waters of hydration, and in subsequent cycles these were refined with the O–H bond lengths constrained at 1.05 (5) Å. Refinement continued with all non-hydrogen atoms assigned anisotropic temperature factors, and a weighting scheme based on counting statistics was introduced. The refinement converged with R = 0.0518 and R_w ($[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$) = 0.0514. No abnormal discrepancies were found between observed and calculated structure factors for those reflections not used in the refinement, and the weighting scheme appeared reasonable. A final difference Fourier synthesis revealed no peaks higher than those previously assigned to hydrogen atoms. Bond lengths and angles together with their estimated standard deviations are presented in Table I and final atomic coordinates and thermal parameters in Table II (supplementary material). A table of observed and calculated structure amplitudes is available (Table III, supplementary material).

Table I. Bond Lengths (Å) and Angles (deg) for $[Co(en)_2(C_2O_4)H_2O]CF_3SO_3\cdot 2H_2O$

Distances			
Co–N1	1.957 (11)	Cx1–Cx2	1.546 (18)
Co–N2	1.935 (10)	Cx1–Ox11	1.281 (14)
Co–N3	1.950 (11)	Cx1–Ox12	1.236 (14)
Co–N4	1.952 (10)	Cx2–Ox21	1.247 (15)
Co–Ox11	1.891 (8)	Cx2–Ox22	1.262 (15)
Co–Ow	1.931 (8)	S–O1	1.436 (11)
N1–C1	1.458 (17)	S–O2	1.441 (13)
N2–C2	1.492 (17)	S–O3	1.414 (12)
C1–C2	1.544 (20)	S–C	1.824 (18)
N3–C3	1.488 (18)	C–F1	1.356 (20)
N4–C4	1.478 (17)	C–F2	1.344 (18)
C3–C4	1.506 (20)	C–F3	1.288 (19)

Angles			
N1–Co–N2	86.0 (0.5)	N3–C3–C4	108.1 (1.2)
N1–Co–N3	94.7 (0.5)	N4–C4–C3	107.8 (1.1)
N1–Co–N4	178.0 (0.5)	Cx2–Cx1–Ox11	115.9 (1.2)
N1–Co–Ox11	93.3 (0.4)	Cx2–Cx1–Ox12	118.0 (1.2)
N1–Co–Ow	92.3 (0.4)	Ox11–Cx1–Ox12	126.1 (1.2)
N2–Co–N3	179.3 (0.5)	Cx1–Cx2–Ox21	116.2 (1.3)
N2–Co–N4	92.3 (0.4)	Cx1–Cx2–Ox22	118.3 (1.2)
N2–Co–Ox11	87.3 (0.4)	Ox21–Cx2–Ox22	125.5 (1.1)
N2–Co–Ow	91.3 (0.4)	Co–Ox11–Cx1	126.4 (0.8)
N3–Co–N4	87.0 (0.5)	O1–S–O2	113.5 (0.7)
N3–Co–Ox11	92.9 (0.4)	O1–S–O3	114.7 (0.8)
N3–Co–Ow	88.3 (0.4)	O1–S–C	103.6 (0.8)
N4–Co–Ox11	87.6 (0.4)	O2–S–O3	116.5 (0.9)
N4–Co–Ow	86.7 (0.4)	O2–S–C	100.7 (0.8)
Ox11–Co–Ow	174.1 (0.4)	O3–S–C	105.4 (0.9)
Co–N1–C1	109.6 (0.8)	S–C–F1	109.8 (1.2)
Co–N2–C2	109.7 (0.8)	S–C–F2	109.3 (1.3)
N1–C1–C2	105.7 (1.2)	S–C–F3	112.7 (1.3)
N2–C2–C1	106.0 (1.1)	F1–C–F2	105.4 (1.5)
Co–N3–C3	108.7 (0.8)	F1–C–F3	110.1 (1.6)
Co–N4–C4	108.4 (0.8)	F2–C–F3	109.2 (1.5)

^{18}O-Tracer Studies. ^{18}O-labeled $H_2C_2O_4$ was prepared by refluxing anhydrous $H_2C_2{}^{16}O_4$ (2 g) in 10 atom % $H_2{}^{18}O$ (5 cm^3) for 8 h; the water was removed by distillation and the oxalic acid and dried overnight at 10^{-2} mmHg on a vacuum line. ^{18}O-labeled *trans*-$[Co(en)_2(C_2O_4)OH]$ was prepared as described above with 4.0 g of *trans*-$[Co(en)_2(OH_2)OH](ClO_4)_2$, 1.33 g of NaOH, and 1.5 g of $H_2C_2{}^{18}O_4$, the pH being adjusted to 7.3 as required. Oxalate was recovered as $Ag_2C_2O_4$ as follows: *trans*-$[Co(en)_2(C_2{}^{18}O_4)OH]$ was reduced electrochemically at −1.00 V vs. SCE and $Co_{aq}{}^{2+}$ removed on Sephadex SP-C25 cation-exchange resin (Na^+ form). The eluate was reduced to ~40 cm^3 by rotary evaporation and filtered and 2% aqueous $AgNO_3$ added. The precipitated $Ag_2C_2O_4$ was coagulated by stirring (5 min), filtered (porosity 4, sinter), washed with water (4 × 20 cm^3), ethanol (2 × 20 cm^3), and ether (1 × 20 cm^3), and dried at 10^{-3} mmHg for 12 h. The 50-mg samples were sealed under vacuum in break-seal tubes and pyrolyzed at ~400 °C, and the released CO_2 was analyzed on a ratio-measuring mass spectrometer. For the alkaline hydrolysis reaction, $C_2O_4{}^{2-}$ released from *trans*-$[Co(en)_2(C_2O_4)OH]$ (90 min, 0.5 mol dm^{-3} NaOH) was isolated by passing the quenched (pH ~ 7) solution through cation-exchange resin (Dowex 50W-X2, Na^+ form) and precipitated as $Ag_2C_2O_4$, which was treated as above.

Results and Discussion

When *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ is treated with an excess (5–10-fold) of oxalate ions at pH ~7, a mixture of *trans*- and *cis*-$[Co(en)_2(C_2O_4)OH]$, together with chelated $[Co(en)_2C_2O_4]^+$ and unreacted *cis*- and *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ results (reaction 3). With ^{18}O-enriched $H_2C_2O_4$ (6.146 atom %), a trans product containing 5.893 atom % ^{18}O in the oxalate moiety was recovered. This indicates that the anation proceeds substantially (>85%) via substitution at the Co(III) center. Other results[18] have established that O exchange in the oxalate moiety of the trans monodentate is very slow under

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[14] Data processing program HILGOOT, based on programs DRED (J. F. Blount) and PICKOUT (R. J. Doedens).

[15] P. Main, M. M. Woolfson, and G. Germain, "Multan 77, Direct Methods Program".

[16] G. M. Sheldrick, "SHELX, a Program for Crystal Structure Determination", University of Cambridge, Cambridge, England, 1977.

[17] Similar spectra were obtained for the uncharged species formed in the base hydrolysis of $[Co(en)_2mal]^+$; cf. ref 33 and 34.

[18] G. M. Miskelly, unpublished results.

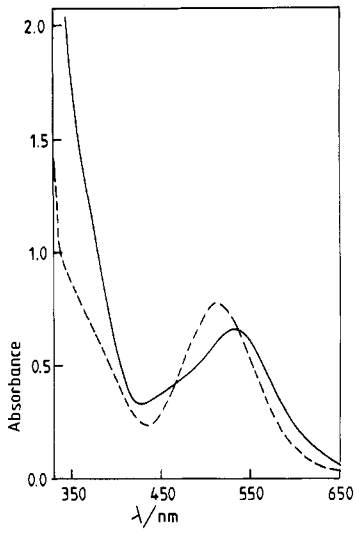

Figure 1. Visible spectra of *trans*- (—) and *cis*-$[Co(en)_2(C_2O_4)OH]$ (--) as isolated from the cation-exchange column.

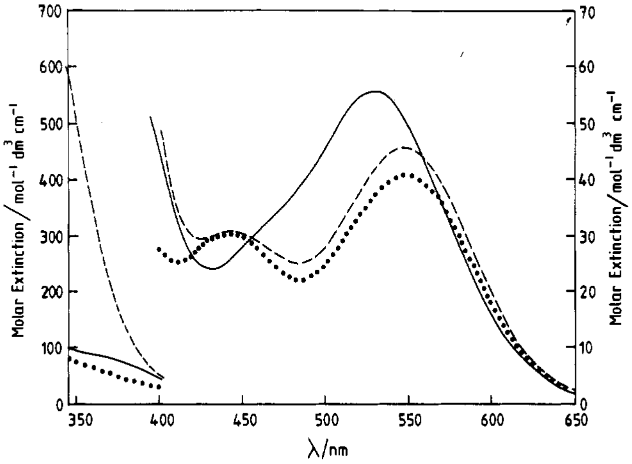

Figure 2. Extinction in the visible region for *trans*-$[Co(en)_2(C_2O_4H)OH_2]^{2+}$ at pH 0 (···), *trans*-$[Co(en)_2(C_2O_4)OH_2]^+$ at pH 4 (--), and *trans*-$[Co(en)_2(C_2O_4)OH]$ at pH 9 (—).

the preparative conditions so that the difference from 100% probably reflects the workup procedure.

The products of reaction 3 can be readily separated by

$$trans\text{-}[Co(en)_2(OH_2)OH]^{2+} + cis\text{-}[Co(en)_2(OH_2)OH]^{2+} + HC_2O_4^-/C_2O_4^{2-} \xrightarrow[2\ h]{\sim 18\ °C} trans/cis\text{-}[Co(en)_2(C_2O_4)OH] + [Co(en)_2C_2O_4]^+ \quad (3)$$

ion-exchange chromatography, and elution with water at pH ~9 removes only the purple nonelectrolyte *trans*-$[Co(en)_2(C_2O_4)OH]$. This is easily distinguished from the mauve cis species (Figure 1).[17] Visible absorption spectra for the trans complexes at pH 0, 4, and 9 are given in Figure 2; these pHs correspond to $[Co(en)_2(C_2O_4H)OH_2]^{2+}$, $[Co(en)_2(C_2O_4)OH_2]^+$, and $[Co(en)_2(C_2O_4)OH]$, respectively. pK_{a1} and pK_{a2} values for eq 4, obtained by spectrophotometric titration in

$$trans\text{-}[Co(en)_2(C_2O_4H)OH_2]^{2+} \overset{K_{a1}}{\rightleftharpoons} trans\text{-}[Co(en)_2(C_2O_4)OH_2]^+ + H^+$$

$$trans\text{-}[Co(en)_2(C_2O_4)OH_2]^+ \overset{K_{a2}}{\rightleftharpoons} trans\text{-}[Co(en)_2(C_2O_4)OH] + H^+ \quad (4)$$

1.0mol dm^{-3} $NaNO_3$ at 25.0 °C, are 1.66 ± 0.04 and 6.31 ± 0.02, respectively. In the time scale of these experiments, there was no significant trans → cis isomerization.

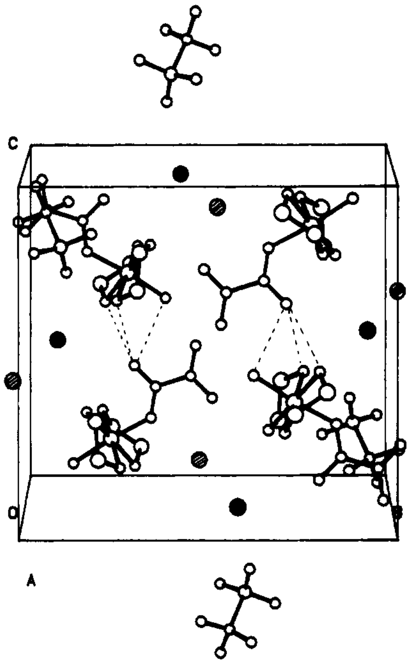

Figure 3. Projection of the unit cell contents of *trans*-$[Co(en)_2(C_2O_4)OH_2](CF_3SO_3)\cdot 2H_2O$ down the *a* axis. The dashed lines show hydrogen bonding mentioned in the text. Solid circles represent WC1 and hatched circles WC2 oxygen atoms.

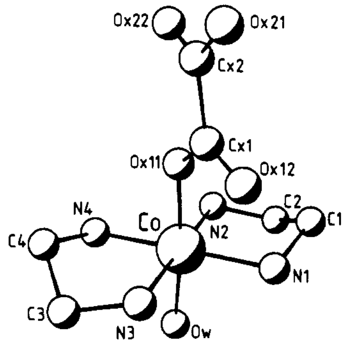

Figure 4. Perspective drawing of the *trans*-$[Co(en)_2(C_2O_4)OH_2]^+$ cation showing the atom-numbering scheme.

The *trans*-$[Co(en)_2(C_2O_4)OH_2]^+$ ion, which is the major species present from pH 2 to 6, was isolated as its $CF_3SO_3^-$, PF_6^-, and ClO_4^- salts, and the solution properties of the isolated complexes were identical with those obtained from the eluate off the column.

Infrared spectra of the isolated trans salts differed from those of the chelate $[Co(en)_2C_2O_4]X$ (X = NO_3^-, Cl^-) in addition to showing anion differences. Indeed, spectra of the latter were similar to that reported by Chan and Choi[3] for *cis*-$[Co(en)_2(C_2O_4)OH]$. We have been unable to crystallize the cis species despite many attempts; only $[Co(en)_2C_2O_4]X$ chelates were obtained, presumably as a result of the rather rapid cyclization of the cis isomer[19] and the relative insolubility of the chelate salts. In any event, we believe that this method of structural characterization is unreliable.

Structure of *trans*-$[Co(en)_2(C_2O_4)H_2O]CF_3SO_3\cdot 2H_2O$. The structure consists of independent cations, anions, and waters of hydration interlinked by a network of hydrogen bonds (Table IV, supplementary material). A projection of the unit cell contents down the *a* axis (Figure 3) shows the $[Co(en)_2(C_2O_4)H_2O]^+$ cations to be hydrogen bonded in a head-to-tail fashion along the *c* axis. Other possible hydrogen bonds

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(19) G. M. Miskelly, C. R. Clark, and D. A. Buckingham, manuscript in preparation.

Table VI. Spectrophotometric (510 nm) Rate Data for Alkaline Hydrolysis of *trans*-[Co(en)$_2$(C$_2$O$_4$)OH] at 25.0 °C, μ = 1.0 (NaNO$_3$), and [Co] = 5 × 10^{-3} mol dm^{-3}

[OH$^-$]/M	$10^4 k_{\text{obsd}}$/s^{-1}	$10^4 k_{\text{OH}} = k_{\text{obsd}}[\text{OH}^-]^{-1}$/ M^{-1} s^{-1}
0.50	2.62	5.2
0.375	1.92	5.2
0.25	1.32	5.3
0.125	0.755	6.0

link the cation to the anion and the waters of hydration. Figure 4 shows the structure of the [Co(en)$_2$(C$_2$O$_4$)H$_2$O]$^+$ cation. The cobalt atom is coordinated octahedrally by the two ethylenediamine ligands together with a water molecule situated trans to the oxalato ligand. The oxalato anion coordinates in an unusual[20] monodentate fashion, with the ligand oriented in such a way as to adopt a staggered conformation with respect to the adjacent ethylenediamine ligands. The Co–Ox11 bond distance, 1.891 (8) Å, is slightly shorter than those observed in Co(III) complexes with bidentate oxalate coordination, but the Cx–Cx and Cx–Ox distances are unremarkable.[21-23] The coordinated oxalato anion deviates slightly from the strict planarity observed in potassium oxalate[24,25] with a mean deviation of 0.03 (1) Å for the six atoms (Table V, supplementary material). The distortion arises from a slight twisting around the Cx1–Cx2 bond, resulting in an angle of 5.3° between the Ox11–Cx1–Ox12 and Ox21–Cx2–Ox22 planes. A similar distortion was observed in the other monodentate oxalate complex to have been structurally characterized[20] and may be ascribed to dissimilar interactions involving the oxygen atoms of the anion.

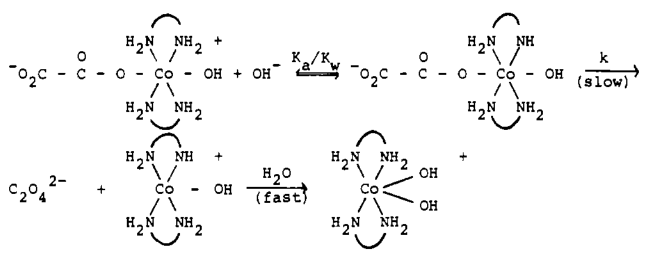
The Co–Ow bond to the aqua ligand [1.931 (8) Å] is considerably shorter than that observed in *trans*-[Co(en)$_2$(H$_2$O)(SO$_3$)]ClO$_4$·H$_2$O.[26] In this latter system however the well-characterized trans effect of the sulfite ligand[27] is clearly instrumental in determining the extension of the Co–O vector. The Co–Ow bond length reported here is more reasonably comparable to that found in *cis*-[Co(en)$_2$(H$_2$O)$_2$][Co(CN)$_6$]·3H$_2$O[28] so that no structural trans effect to the coordinated water is evident.

The ethylenediamine ligands are normal, with C–C and N–C bond lengths within the anticipated range.[29] They are coordinated in $\delta\delta$ (or $\lambda\lambda$) conformations, with C–C dihedral angles of 51.5 and 49.0°, respectively (Table V).

Base Hydrolysis. Hydrolysis of oxalate in reaction 5 competes with the cyclization process (see below) at pHs >7 but is the sole process above pH 9. The rate of hydrolysis was measured over the [OH$^-$] range 0.1–0.5 mol dm^{-3} (Table VI) and conforms to the simple rate law $k_{\text{obsd}} = k_{\text{OH}}[\text{OH}^-]$ with k_{OH} = (5.6 ± 0.4) × 10^{-4} mol^{-1} dm^3 s^{-1}, at μ = 1.0 and 25 °C. The reaction product was identified as the cis dihydroxo isomer (>95%) by its characteristic absorption spectrum (ϵ_{369} = 102, ϵ_{515} = 94),[30] following hydrolysis in 1.0 mol dm^{-3} NaOH (2 h, 6$t_{1/2}$). Under these conditions isomerization of *cis*- to *trans*-[Co(en)$_2$(OH)$_2$]$^+$ is slow ($t_{1/2} \simeq$ 30 h). At the lower OH$^-$ concentrations (Table VI), the cis → trans process did interfere (510 nm) and Guggenheim plots were used to obtain k_{obsd}.

$$\textit{trans}\text{-}[\text{Co(en)}_2(\text{C}_2\text{O}_4)\text{OH}] + \text{OH}^- \rightarrow \textit{cis}\text{-}[\text{Co(en)}_2(\text{OH})_2]^+ + \text{C}_2\text{O}_4^{2-} \quad (5)$$

Scheme I



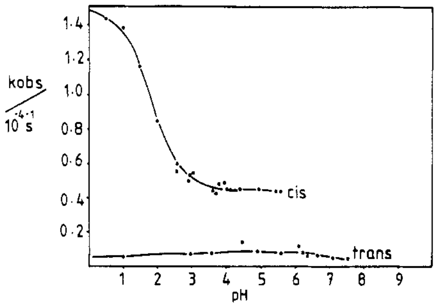


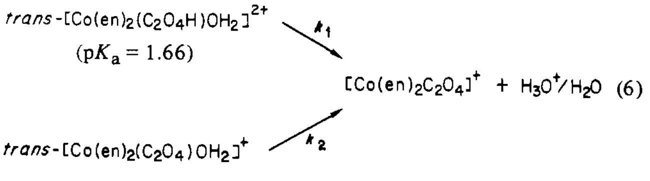
Figure 5. Rate–pH profiles for cyclizations of trans and cis monodentate oxalate species (μ = 1.0 (NaClO$_4$), 25.0 °C).

trans-[Co(en)$_2$(C$_2$^{18}O$_4$)OH] was used to establish the cleavage pattern. The enrichment of the CO$_2$ recovered from oxalato in the trans reactant (4.893 atom %) is to be compared with that in the released C$_2$O$_4$$^{2-}$ (4.868 atom %) following hydrolysis. Clearly only Co–O bond rupture is involved.

k_{OH} found here is comparable with that found for [Co(NH$_3$)$_5$C$_2$O$_4$]$^+$, k_{OH} = 2.45 × 10^{-4} mol^{-1} dm^3 s^{-1}.[37] Alkaline hydrolysis of the latter complex however contains a path second order in [OH$^-$] that probably involves C–O bond cleavage.[37] This path is not apparent in either our kinetic or our ^{18}O data (1.0 mol dm^{-3} NaOH).

The mechanism of alkaline hydrolysis is probably the commonly encountered S_N1CB process, viz. Scheme I, with $k_{\text{OH}} = kK_a/K_w$. K_a for deprotonation of the amine residue is clearly <10^{-14} since no curvature in the k_{obsd} vs. [OH$^-$] plot is observed. The apparent complete stereochemical change trans → cis is in keeping with other results on the base hydrolysis of *trans*-[Co(en)$_2$X(OH)]$^+$ species (X = Cl,[32] Br,[32] OAc[33]) where <10% retention of the trans configuration is observed.

Chelation. Cyclization of oxalate predominates at pHs <7, and rate data (497 nm) for this process (reaction 6), at 25.0 °C and μ = 1.0 (NaNO$_3$), is given as a plot of k_{obsd} vs. pH



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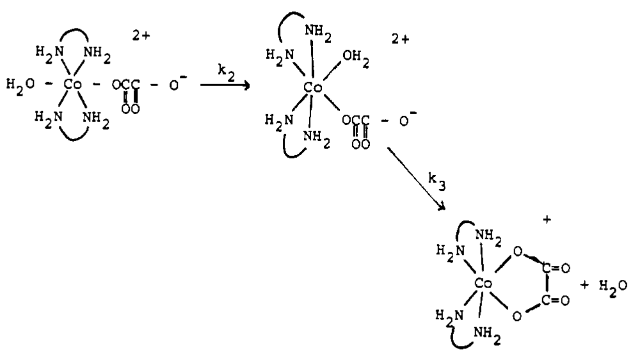
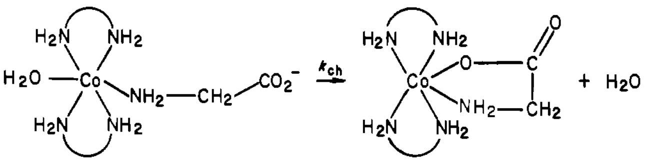
Scheme II



(0–7.6) in Figure 5. Clearly there is little pH dependence whence $k_1 \simeq k_2$. Spectral data at 350 nm suggested the presence of two consecutive processes at pHs 3–7 with the absorbance initially changing slightly with time and then, after ca. 14 h, decreasing exponentially. From a knowledge of the spectral characteristics of the cis monodentate,[19] this suggested that the reaction proceeded via the cis species. Also, from the known rate of conversion of the cis monodentate to the chelate at a particular condition ($k_{obsd} = 4.43 \times 10^{-5}$ s^{-1}, pH 5.0),[19] it was possible to calculate the time at which the maximum amount of *cis*-$[Co(en)_2(C_2O_4)OH_2]^+$ would be present. This gave $t_{max} = 13.1$ h with a [cis]/[trans] ratio of 0.18 together with 20% $[Co(en)_2C_2O_4]^+$. An experiment under these conditions, with ion-exchange separation of the products, positively identified *cis*-$[Co(en)_2(C_2O_4)OH_2]^+$ and gave an observed [cis]/[trans] ratio of 0.17. Clearly, chelation proceeds via the cis monodentate, and the rate data given in Figure 5 (k_2) relate to trans → cis isomerization. The data also demonstrate that the isomerization process is not reversible under the conditions ($k_{obsd} = k_2$, for 6 > pH > 3, $k_{-2} \simeq 0$). This observation has been separately confirmed for the cis isomer.[19] Chelation of the trans reactant thus proceeds via the more rapid cyclization in the cis intermediate (k_3, Scheme II).

A similar isomerization has been proposed for the related malonate complex *trans*-$[Co(en)_2(malH)OH_2]^{2+}$ at pH 0.5–2.5[34] with a rate of 4.2×10^{-6} s^{-1} (18 °C); this rate is comparable to that found here. It is likely that k_2 is controlled by H_2O exchange since related isomerizations appear to occur in this manner. Thus k_{ex} and k_{isom} are similar for *trans*-$[Co(en)_2(H_2O)_2]^{3+}$ ($\sim 10^{-5}$ s^{-1}) and for *trans*-$[Co(en)_2(H_2O)OH]^{2+}$ ($\sim 10^{-3}$ s^{-1}),[31] whereas for *trans*-$[Co(en)_2(NH_3)OH_2]^{3+}$ k_{ex} exceeds k_{isom} by a factor of $\sim$100 ($k_{ex} = 4.5 \times 10^{-6}$ s^{-1}, $k_{isom} = 5 \times 10^{-8}$ s^{-1}, 30 °C).[35] The isomerization rate constant found here, $k_2 \simeq 8 \times 10^{-6}$ s^{-1}, lies close to that for the diaqua species and, as mentioned above, is in agreement with that found for the analogous monodentate malonate complex.

Scheme II for chelation of oxalate differs from that found recently for chelation of monodentate glycinate in *trans*-$[Co(en)_2(NH_2CH_2CO_2)OH_2]^{2+}$.[11] For the latter complex the cis species is not involved as an intermediate, and chelation was proposed to occur directly via back-side expulsion of water by the carboxylate function[11] (eq 7; $k_{ch} = 2 \times 10^{-6}$ s^{-1}, 25 °C).



(7)

The reason for the difference in mechanism for the two complexes is not apparent at this stage and is indeed surprising in view of the similarity in the chelation rates.

Finally, included in Figure 5 are rate data for chelation in the *cis*-$[Co(en)_2(C_2O_4/H)OH_2]^{+,2+}$ ions. Now the rate for the protonated carboxylate function is substantially greater than that for the carboxylate anion, and in a subsequent paper[19] we will show how these processes involve (at least in part) intramolecular attack by coordinated water at the carboxylate center; i.e., Co–O bond fission is not important in the chelation of the cis oxalate species.

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Registry No. *trans*-$[Co(en)_2(OH_2)OH](ClO_4)_2$, 14099-22-0; *cis*-$[Co(en)_2(OH_2)OH]^{2+}$, 21247-60-9; $[Co(en)_2C_2O_4]Cl$, 17439-00-8; *trans*-$[Co(en)_2(C_2O_4)OH]$, 86992-63-4; *cis*-$[Co(en)_2(C_2O_4)OH]$, 59982-23-9; *trans*-$[Co(en)_2(C_2O_4)OH_2]PF_6$, 86941-94-8; *trans*-$[Co(en)_2(C_2O_4)OH_2]CF_3SO_3{\cdot}2H_2O$, 86941-96-0; *trans*-$[Co(en)_2(C_2O_4H)OH_2]^{2+}$, 86941-97-1; *cis*-$[Co(en)_2(C_2O_4)OH_2]^+$, 87036-83-7; *trans*-$[Co(en)_2(OH)_2]^+$, 21772-94-1; *cis*-$[Co(en)_2(OH)_2]^+$, 21247-61-0.

Supplementary Material Available: Final positional and thermal parameters (Table II), observed and calculated structure factors (Table III), H-bonding distances, angles, and symmetry operations (Table IV), and selected dihedral angles for *trans*-$[Co(en)_2(C_2O_4)H_2O]CF_3SO_3{\cdot}2H_2O$ (Table V) (10 pages). Ordering information is given on any current masthead page.

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