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# Chelation and Hydrolysis of Monodentate Oxalate in *cis*-$[Co(en)_2(OC_2O_3)(OH)]$, *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$, and *cis*-$[Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$ and the Alkaline Hydrolysis of Chelated Oxalate in $[Co(en)_2(O_2C_2O_2)]^+$

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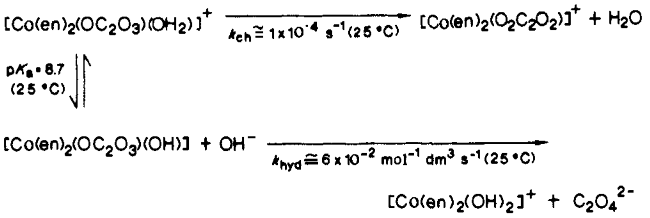
**Abstract:** *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]PF_6$ has been isolated and characterized as the solid and in solution ($\epsilon_{495}$ = 110 mol$^{-1}$ dm$^3$ cm$^{-1}$, p$K_{a1}$ = 1.76 ± 0.04 for *cis*-$[Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$; $\epsilon_{501}$ = 119, p$K_{a2}$ = 7.67 ± 0.04 for *cis*-$[(Co(en)_2(OC_2O_3)(OH_2)]^+$; $\epsilon_{511}$ = 122 for *cis*-$[Co(en)_2(OC_2O_3)(OH)]$, $I$ = 1.0 ($NaNO_3$) 25 °C). In alkaline solution, *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ hydrolyzes to *cis*-$[Co(en)_2(OH)_2]^+$ with Co–O bond cleavage following the rate expression $k_{obsd} = k_c + k_{OH}{}^c[OH^-]$ ($k_c = 5.2 \times 10^{-5}$ s$^{-1}$, $k_{OH}{}^c = (6.3 \pm 0.3) \times 10^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$, $I$ = 1.0 ($NaNO_3$), 25 °C). For 0 < pH < 9, *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ and *cis*-$[Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$ cyclize to the oxalate chelate $[Co(en)_2(O_2C_2O_2)]^+$ following the rate expression $k_{obsd} = (k_1[H^+] + k_2K_{a1})/([H^+] + K_{a1})$ ($k_1 = (1.51 \pm 0.05) \times 10^{-4}$ s$^{-1}$, $k_2 = (4.6 \pm 0.2) \times 10^{-5}$ s$^{-1}$, p$K_{a1}$ = 1.76, $I$ = 1.0 ($NaNO_3$), 25 °C). This reaction is subject to acetate, chloroacetate, and phosphate catalysis which has been interpreted as general acid catalyzed cyclization of *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$. The unassisted reaction occurs with 40% O–C and 60% Co–O bond formation, with the former being attributed to attack by coordinated water at the dangling carboxylate function and the latter to displacement of coordinated water by carboxylate. In the presence of 0.2 mol dm$^{-3}$ $C_2O_4{}^{2-}$, the former path increases to 75%; in the presence of HOAc, the reaction occurs entirely by O–C bond formation. It is suggested that *cis*-$[Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$ also cyclizes entirely with retention of the O atom of coordinated water. Alkaline hydrolysis of $[Co(en)_2(O_2C_2O_2)]^+$ forms *cis*-$[Co(en)_2(OH)_2]^+$ following the rate expression $k_{obsd} = k^1{}_{OH}[OH^-] + k^2{}_{OH}[OH^-]^2$ ($k^1{}_{OH} = 8.3 \times 10^{-6}$ mol$^{-1}$ dm$^3$ s$^{-1}$, $k^2{}_{OH} = 6.3 \times 10^{-5}$ mol$^{-2}$ dm$^6$ s$^{-1}$, $I$ = 1.0 ($NaNO_3$), 25 °C). The two outer oxygen atoms of $[Co(en)_2(O_2C_2O_2)]^+$ exchange rapidly with the solvent before ring opening, $k_{obsd} = k_{ex}[OH^-]$ ($k_{ex} = 2.9 \times 10^{-2}$ mol$^{-1}$ dm$^3$ s$^{-1}$, 25 °C). Ring opening occurs via 100% O–C bond cleavage for the $k^2{}_{OH}$ path and by 40% O–C bond cleavage for the $k^1{}_{OH}$ path with the remainder occurring by substitution at the metal with Co–O bond cleavage.

In an earlier paper[1] we described the chelation of monodentate oxalate in *trans*-$[Co(en)_2(OC_2O_3)OH)]^0$, *trans*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$, and *trans*-$[Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$. It was shown that in neutral to acidic aqueous solution, this occurs via isomerization to the cis isomer. In this paper we discuss the properties and reactions of the latter complex and also report on a reinvestigation of O-exchange and hydrolysis of oxalate in the five-membered $[Co(en)_2(O_2C_2O_2)]^+$ chelate.

Much uncertainty remains concerning the rate-determining step and rate law for the alkaline hydrolysis of $[Co(en)_2(O_2C_2O_2)]^+$. Sheel et al.[2] reported that at $[OH^-] \leq 0.024$ mol dm$^{-3}$ and $T$ = 71 °C, hydrolysis, oxalate exchange, and loss of optical activity occurred at the same rate, $k_{obsd} = k[OH^-]$, with $k = (2.8 \pm 0.5) \times 10^{-2}$ mol$^{-1}$ dm$^3$ s$^{-1}$. They interpreted this in terms of rate-determining opening of the chelate with rapid subsequent hydrolysis of the monodentate oxalate in $[Co(en)_2(OC_2O_3)(OH)]$ and eventual formation of an equilibrium mixture of *trans*- + *cis*-$[Co(en)_2(OH)_2]^+$. Subsequently, an $^{18}O$-tracer study by Andrade and Taube[3] showed that chelate ring opening involved C–O bond cleavage but that the subsequent hydrolysis of *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ occurred largely via substitution at the metal. Uncertainty remained if a more detailed analysis of Andrade and Taube's data was attempted since the rate laws for the two processes under their conditions were unknown at the time. It did appear, however, that both hydrolysis and exchange into the oxalate were important properties of a monodentate species since varying amounts of exchange into released $C_2O_4{}^{2-}$ were found depending on the reaction time and other experimental conditions. Farago and Mason[4,5] followed hydrolysis of $[Co(en)_2(O_2C_2O_2)]^+$ spectrophotometrically and polarimetrically in strong alkali solution ($[NaOH]$ = 0.125–3.6 mol dm$^{-3}$) over the temperature range 4–47 °C. At 25 °C an initial first-order change in $[OH^-]$ was followed by a slower reaction, and the final products were racemic *cis*-$[Co(en)_2(OH)_2]^+$ and $C_2O_4{}^{2-}$. The two processes were interpreted as ring opening of $[Co(en)_2(O_2C_2O_2)]^+$ and hydrolysis of *cis*-$[Co(en)_2(OC_2O_3)(OH)]$, respectively, but neither the data nor the interpretation was convincing. Bark et al.[6] then studied the hydrolysis of $[Co(NH_3)_4(O_2C_2O_2)]^+$, but precipitation of $Co(OH)_3$ prevented any sensible conclusion regarding the oxalate moiety, and Mason and Farago[7] refuted a claim that a similar decomposition occurs with $[Co(en)_2(O_2C_2O_2)]^+$.

Scheme I



Information concerning the behavior of monodentate oxalate in alkali solution is more certain. Angerman and Jordan[8] found a two-term rate law, $k_{obsd} = k_1[OH^-] + k_2[OH^-]^2$, for hydrolysis of $[Co(NH_3)_5(OC_2O_3)]^+$ ($k_1 = 2.5 \times 10^{-4}$ mol$^{-1}$ dm$^3$ s$^{-1}$, $k_2 = 6.1 \times 10^{-5}$ mol$^{-2}$ dm$^6$ s$^{-1}$, 25 °C) and by using the earlier data of Andrade and Taube[3] attributed the third-order term to C–O cleavage and the second-order term to Co–O cleavage. They also estimated a rate of ~4 × $10^{-5}$ mol$^{-1}$ dm$^3$ s$^{-1}$ for O-exchange in the monodentate if this was attributed to equivalent exchange of the two oxygens nearest to the metal. Dash and Nanda[9] showed that various anions, notably $PO_4{}^{3-}$, $SO_4{}^{2-}$, and $CO_3{}^{2-}$, retarded

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hydrolysis. In a separate study[10] they determined $k_1 = 1 \times 10^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$ (25 °C) for the alkaline hydrolysis of $[Co(en)_2(NH_3)(OC_2O_3)]^+$. However, the study most relevant to the present investigation is that by Chan and Harris.[11] They isolated $[Co(en)_2(OC_2O_3)(OH)]$ from a mixture of *trans*- + *cis*-$[Co(en)_2(OH_2)(OH)]^{2+}$ + $C_2O_4^{2-}$, reported its p$K_a$ (6.7), and discussed its hydrolysis and cyclization. Although it is now apparent that the reactant they used was a mixture of the cis + trans isomers,[1] their data are relevant and are given in Scheme I.

They reported that hydrolysis of the monodentate was some 500 times faster than hydrolysis of the chelate, explaining the earlier inability to detect this intermediate.[2] Stranks and Vanderhoek[12] found $\Delta V^{\ddagger} = 0 \pm 1.2$ cm$^3$ mol$^{-1}$ for $k_{ch}$ and interpreted this in terms of $I_a$ interchange of coordinated water by carboxylate at the metal.

The results given here are discussed with this background in mind.

## Experimental Section

$[Co(en)_2(O_2C_2O_2)]Cl{\cdot}H_2O$ was prepared as described by Dwyer et al.,[19] purified by ion-exchange chromatography (Dowex 50W × 2, 0.5 mol dm$^{-3}$ HCl), and finally crystallized from 2 mol dm$^{-3}$ HCl. Anal. Calcd: C, 22.48; H, 5.66; N, 17.46. Found: C, 23.0; H, 5.6; N, 17.5. $\epsilon_{497} = 113$ mol$^{-1}$ dm$^3$ cm$^{-1}$ in $H_2O$. The sparingly soluble $ClO_4^-$ salt was easily obtained by adding $NaClO_4$ to an aqueous solution of the $Cl^-$ salt, and the $OAc^-$ salt was prepared by using Ag(OAc). *cis*- and *trans*-$[Co(en)_2(OC_2O_3)(OH)]$ were prepared and separated as described previously.[1] *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]PF_6$ was isolated by freeze drying a freshly prepared solution, redissolving in the minimum amount of water, and adding $NaPF_6$ to the resulting solution at pH ~ 5. The orange-red solid which formed on cooling was recovered, washed with MeOH, and air dried. Other salts were too soluble to be isolated as solids, and recrystallization of the $PF_6^-$ salt resulted only in the chelate being recovered. The initial sample was shown by RP-HPIPC[24] to contain only minor contaminants of the trans isomer and chelate.

**p$K_a$ Measurements.** p$K_a$ values for *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ and *cis*-$[Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$ were measured spectrophotometrically (330 and 360 nm, respectively) in 1.0 mol dm$^{-3}$ $NaNO_3$ by quickly titrating a freshly prepared solution of *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ at pH ~ 9 with ~15 mol dm$^{-3}$ $HNO_3$ in a thermostated cell (3.2 cm) fitted with pH electrodes. The p$K_{a2}$ was calculated by the method of Albert and Serjeant,[20] and the p$K_{a1}$ was obtained by a graphical procedure.[21]

**Kinetic Measurements.** Rate data were obtained spectrophotometrically (355 nm, pH < 1.5; 330 nm, pH > 1.5) in 1.0 mol dm$^{-3}$ $NaNO_3$ (or $NaClO_4$) by using a Cary 219 spectrophotometer. Buffer solutions (0.2 mol dm$^{-3}$) were mixed with an equal volume of the complex solution, and the pH was measured at the beginning and conclusion of each run. Data were collected for at least $4t_{1/2}$ before leaving for an infinity reading. Plots of ln $(A_t - A_\infty)$ or ln $(A_t - A_{t+T})$ vs. time were used for the cyclization and hydrolysis of the cis monodentate, and initial rate plots at 497 nm ($A_\infty = 0.735A_0$) were used for the alkaline hydrolysis of $[Co(en)_2(O_2C_2O_2)]^+$.

Reaction products were identified by absorption spectra or by their ion-exchange or RP-HPIPC behavior.

Data for the reactions of *cis*-$[Co(en)_2(OC_2O_3)(OH)]^0$ and *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ at pH 7.11, 7.70, 8.97, and 10.77 were obtained by sampling the reaction at varying times, acidifying with HCl, and storing at −179 °C before analyzing by reversed-phase high-performance ion-pair chromatography (RP-HPIPC). The eluents were at pH ~ 3, so that the species analyzed were *cis*- and *trans*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$, $[Co(en)_2(O_2C_2O_2)]^+$, and *cis*- and *trans*-$[Co(en)_2(OH_2)_2]^{3+}$. The 1+ and 3+ ions were analyzed separately. Conditions for the analysis are given in Figure 1, which shows the concentrations of the various species after one half-life.

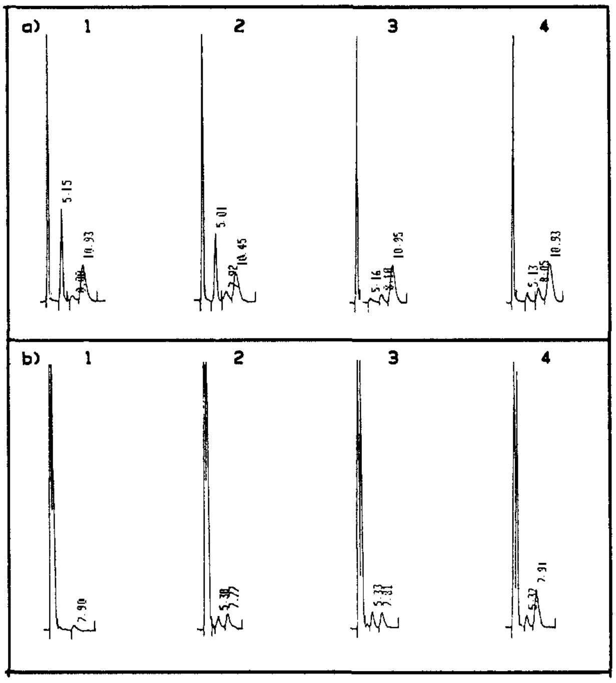

Figure 1. RP-HPIP chromatograms of products formed from *cis*-$[Co(en)_2(OC_2O_3)(OH)]^0$ and *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ at pH 7.11 (1), 7.70 (2), 8.97 (3), and 10.77 (4) after 242, 299, 242, and 242 min, respectively (about $1t_{1/2}$ for reaction). (a) Analysis of 1+ ions. Eluents: 20 mM sodium *n*-octanesulfonate, 35 mM triethylammonium phosphate, 15% methanol, pH 2.75. Elution order: anions, $[Co(en)_2(O_2C_2O_2)]^+$, *trans*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$, *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$. (b) Analysis of 3+ ions. Eluents: 25 mM sodium *n*-hexanesulfonate, 70 mM triethylammonium phosphate, 12% methanol, pH 2.9. Elution order: anions, 1+ ions, *trans*-$[Co(en)_2(OH_2)_2]^{3+}$, *cis*-$[Co(en)_2(OH_2)_2]^{3+}$. $\mu$-Bondapak radial compression column, flow rate 2 cm$^3$ min$^{-1}$; $\lambda = 250$ nm. Elution time in minutes.

**$^{18}$O-Tracer Experiments.** These were carried out by using either enriched oxalic acid (~6 atom %)[1] or enriched water (~1–2 atom %). Ionic and complexed oxalate was recovered as $Ag_2C_2O_4$ and analyzed as described previously.[1] Care was needed with this procedure, and trial experiments demonstrated some sources of contamination. Thus, thoroughly washed and dried $Ag_2C_2O_4$ recovered from an aqueous solution of labeled $Na_2C_2O_4$ contained 7.04 atom % $^{18}$O, but when recovered from a solution 1 mol dm$^{-3}$ in $NaNO_3$ with inadequate washing contained 6.44 atom %. Dissolution of the $Ag_2C_2O_4$ in dilute $NH_4OH$ and reprecipitation with $HNO_3$ reduced the $^{18}$O content from 7.04 to 5.48 atom %. These results led to a standard procedure of precipitating from acidified (pH 2–4) dilute solutions and washing with large amounts of water (pH ~ 4) and finally ethanol and ether. $Ag_2C_2O_4$ (25–30 mg) was adequate for analysis purposes, but usually larger amounts (75–100 mg) were recovered. Samples were kept in aluminum-wrapped vials until required. Enriched solvent was analyzed by distillation of a ca. 0.5-cm$^3$ solution sample on the vacuum line and equilibration with normal $CO_2$ at 80 °C.[22] Details of the many experiments requiring variations of the standard separation and isolation procedure are given elsewhere.[21]

The ratios $R_{45} = M_{45}/M_{44}$ and $R_{46} = M_{46}/(M_{44} + M_{45})$ were measured on a VG Micromass 1202E double-collector mass spectrometer. Calculations of atom % $^{18}$O were made by using either atom % = $100R_{46}/(1.97 + R_{46})$ or

$$\text{atom \%} = [3.868(R_{45} + 1)R_{46} - (0.9889R_{45} - 0.0111) \times (0.0329 - 0.978R_{45})]100/[3.868(R_{45} + 1)R_{46} - 0.9889(0.9889R_{45} - 0.0111)^2 + 7.693 + 3.825R_{45}]$$

The extended version is necessary for high (~5 atom %) enrichments of unnormalized $^{18}$O, which may contain significant (~2 atom %) amounts of $^{17}$O.

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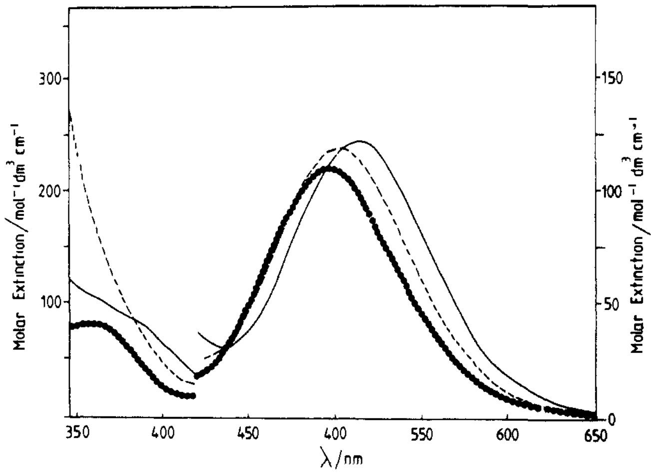


**Figure 2.** Visible absorption spectra for *cis*-$[Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$ (···), $\epsilon_{495}$ = 110 mol$^{-1}$ dm$^3$ cm$^{-1}$; *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ (---), $\epsilon_{501}$ = 119 mol$^{-1}$ dm$^3$ cm$^{-1}$; *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ (—), $\epsilon_{511}$ = 122 mol$^{-1}$ dm$^3$ cm$^{-1}$; in water at pH ~ 0, 4, and 9, respectively.

## Results and Discussion

**Properties of *cis*-$[Co(en)_2(OC_2O_3)(OH)]^0$, *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$, and *cis*-$[Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$.** The method of preparation and isolation has been described previously,[1] and details of the anation of *cis*- and *trans*-$[Co(en)_2(OH_2)(OH)]^{2+}$ by $C_2O_4^{2-}$ will be discussed in a separate paper.[23] It is sufficient to report here that the cis isomer can be isolated in solution at pH ~ 9 as the nonelectrolyte *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ and has been crystallized as *cis*-$[Co(en)_2(OC_2O_3)(OH_2)](PF_6)$. The IR spectrum of the latter does not differ appreciably from that of the chelate $[Co(en)_2(O_2C_2O_2)](PF_6)$ or *trans*-$[Co(en)_2(OC_2O_3)(OH_2)](PF_6)$ so that this method of identification is inappropriate. $^{18}$O-tracer results, Table I (experiments 4 and 5), establish that the preparative procedure involves displacement of coordinated water or hydroxide, by carboxylate oxygen, eq 1.

$$cis\text{-} + trans\text{-}[Co(en)_2(OH)(OH_2)]^{2+} + C_2{}^{18}O_4{}^{2-} \rightarrow cis\text{-}[Co(en)_2({}^{18}OC_2{}^{18}O_3)(OH)] + trans\text{-}[Co(en)_2({}^{18}OC_2{}^{18}O_3)(OH)] + H_2O \quad (1)$$

Visible absorption spectra at pH 0, 4, and 9 are given in Figure 2, and spectrophotometric titration in 1.0 mol dm$^{-3}$ $NaNO_3$ (25.0 °C) gave p$K_a$ values of (1.76 ± 0.04) and (7.67 ± 0.04) for processes 2 and 3.

$$cis\text{-}[Co(en)_2(OC_2O_3H)(OH_2)]^{2+} \underset{}{\overset{K_{a1}}{\rightleftharpoons}} cis\text{-}[Co(en)_2(OC_2O_3)(OH_2)]^+ + H^+ \quad (2)$$

$$cis\text{-}[Co(en)_2(OC_2O_3)(OH_2)]^+ \overset{K_{a2}}{\rightleftharpoons} cis\text{-}[Co(en)_2(OC_2O_3)(OH)] + H^+ \quad (3)$$

The spectra in Figure 2, therefore, characterize *cis*-$[Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$, *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$, and *cis*-$[Co(en)_2(OC_2O_3)(OH)]$.

**Hydrolysis of *cis*-$[Co(en)_2(OC_2O_3)(OH)]$.** In alkaline solution hydrolysis results in *cis*-$[Co(en)_2(OH)_2]^+$. The cis configuration was established from the final absorption spectrum in strong alkali solution (0.5–1.0 mol dm$^{-3}$), $\epsilon_{369}$ = 102, $\epsilon_{515}$ = 94 mol$^{-1}$ dm$^3$ cm$^{-1}$. Under such conditions isomerization to *trans*-$[Co(en)_2(OH)_2]^+$ is a much slower process ($t_{1/2} \simeq$ 30 h).[30] The cis configuration was also established by quenching and RP-HPIPC analysis for strongly alkaline solutions and by RP-HPIPC analysis during the course of slower hydrolyses at pH 7.7–10.8. This method of analysis allows for the rapid separation and identification of *cis*- and *trans*-$[Co(en)_2(OH_2)_2]^{3+}$, c.f., Figure 1, and in all cases formation of *trans*-$[Co(en)_2(OH)_2]^+$ could be accounted for as resulting from isomerization of the initially formed *cis*-$[Co(en)_2(OH)_2]^+$ product.

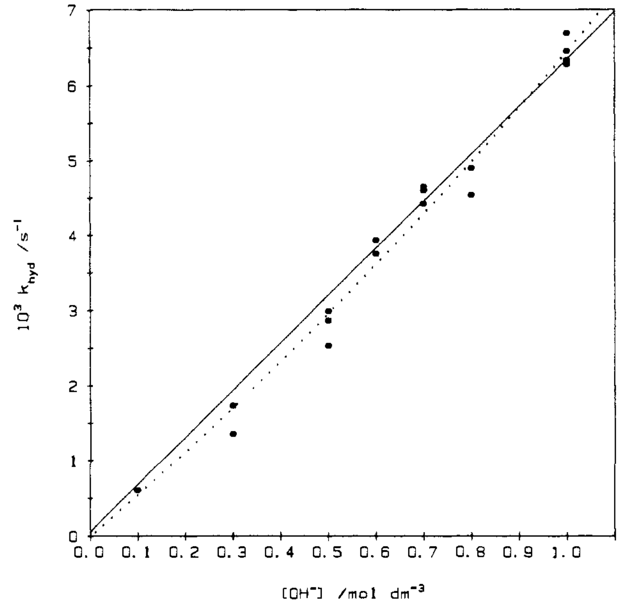
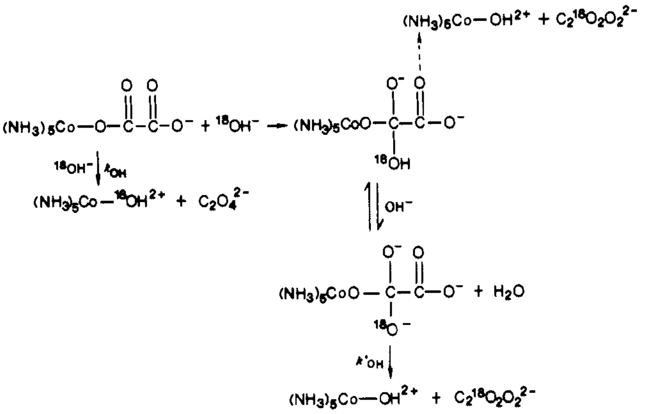


**Figure 3.** Plot of $k_{hyd}$ vs. [OH$^-$] for the alkaline hydrolysis of *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ at 25.0 °C, $I$ = 1.0 ($NaNO_3$) mol dm$^{-3}$. The straight line (—) is for the expression $k_{obsd} = k^c + k_{OH}{}^c[OH^-]$ using $k^c = 5.2 \times 10^{-5}$ s$^{-1}$ and $k_{OH}{}^c = 6.3 \times 10^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$, and the curved best fit (---) is for the expression $k_{obsd} = k^c + k_{OH}{}^c[OH^-] + k_{OH}{}^{cl}[OH^-]^2$ using $k^c = 3.7 \times 10^{-5}$ s$^{-1}$, $k_{OH}{}^c = 5.3 \times 10^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$, and $k_{OH}{}^{cl} = 1.2 \times 10^{-3}$ mol$^{-2}$ dm$^6$ s$^{-1}$ (c.f. Table II, supplementary material).

**Scheme II**



$^{18}$O-tracer results given in table I (experiment 1) demonstrate that only Co–O bond cleavage, eq 4, is involved in strongly alkaline solution. No O-exchange into the oxalate function has occurred.

$$cis\text{-}[Co(en)_2({}^{18}OC_2{}^{18}O_3)(OH)] + OH^- \rightarrow cis\text{-}[Co(en)_2(OH)_2]^+ + C_2{}^{18}O_4{}^{2-} \quad (4)$$

Rate data (Table II, supplementary material) are given as a plot of $k_{obsd}$ vs. [OH$^-$] in Figure 3. The scatter of the data allows it to be analyzed as either $k_{obsd} = k^c + k_{OH}{}^c[OH^-]$ with $k^c = 5.2 \times 10^{-5}$ s$^{-1}$, $k_{OH}{}^c = (6.3 \pm 0.3) \times 10^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$, or $k_{obsd} = k^c + k_{OH}{}^c[OH^-] + k_{OH}{}^{cl}[OH^-]^2$ with $k^c = 3.7 \times 10^{-5}$ s$^{-1}$, $k_{OH}{}^c = 5.3 \times 10^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$, and $k_{OH}{}^{cl} = 1.2 \times 10^{-3}$ mol$^{-2}$ dm$^6$ s$^{-1}$. If the $k_{OH}{}^{cl}$ term is real, it contributes 10% in 0.5 mol dm$^{-3}$

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**Table I.** $^{18}O$-Tracer Experiments

| expt | reactant | atom % enrichment | reaction/comments | product | atom % enrichment in oxalate moiety |
|---|---|---|---|---|---|
| A. Labeled $C_2O_4^{2-}$ | | | | | |
| 1 | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.65 | base hydrolysis, 0.5 M NaOH, 270 min | $C_2O_4^{2-}$ | 5.81 |
| 2 | *trans*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.69 | base hydrolysis, 0.5 M NaOH, 100 min | $C_2O_4^{2-}$ | 5.69 |
| 3 | $C_2O_4^{2-}$ | | anation, pH 7.5, 2.5 h, unreacted, $C_2O_4^{2-}$ recovered | $C_2O_4^{2-}$ | 5.40 |
| 4 | $C_2O_4^{2-}$ | 5.40 | anation, pH 7.5, 2.5 h | *trans*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.35 |
| 5 | $C_2O_4^{2-}$ | 5.40 | anation, pH 7.5, 2.5 h | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.45 |
| 6 | $C_2O_4^{2-}$ | 5.40 | chelation, pH 7.5, 2.5 | $[Co(en)_2(O_2C_2O_2)]^+$ | 4.63 |
| 7 | *trans*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.69 | O-exchange, pH 4, 18 h | *trans*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ | 5.48 |
| 8 | *trans*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.69 | chelation, pH 4, 18 h | $[Co(en)_2(O_2C_2O_2)]^+$ | 4.86 |
| 9 | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.45 | O-exchange, pH 4, 1 h | *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ | 5.41 |
| 10 | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.45 | O-exchange, pH 4, 4 h | *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ | 5.39 |
| 11 | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.45 | chelation, pH 4, 4 h | $[Co(en)_2(O_2C_2O_2)]^+$ | 4.71 |
| 12 | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.45 | chelation, pH 4, 6 h | $[Co(en)_2(O_2C_2O_2)]^+$ | 4.92 |
| 13 | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.65 | O-exchange, pH 2, 80 min | *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ | 5.30 |
| 14 | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.65 | chelation, pH 2, 80 min | $[Co(en)_2(O_2C_2O_2)]^+$ | 4.23 |
| 15 | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.65 | O-exchange, pH 1, 160 min | *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ | 3.66 |
| 16 | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.65 | chelation, pH 1, 160 min | $[Co(en)_2(O_2C_2O_2)]^+$ | 3.47 |
| 17 | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.65 | chelation, pH 4, 220 min | $[Co(en)_2(O_2C_2O_2)]^+$ | 5.11 |
| 18 | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 5.65 | chelation, pH 4 + HOAc, 18 h | $[Co(en)_2(O_2C_2O_2)]^+$ | 4.24 |
| B. Labeled Solvent | | | | | |
| 19 | $[Co(en)_2(O_2C_2O_2)]^+$ | 0.787 ($H_2O$) | O-exchange, pH 7, $[C_2O_4^{2-}]$ = 0.2 M, 2.5 h | $[Co(en)_2(O_2C_2O_2)]^+$ | 0.001 |
| 20 | $[Co(en)_2(OH)(OH_2)]^{2+}$[a] | 2.23 ($H_2O$) | anation, pH 7.6, 2.5 h | $[Co(en)_2(O_2C_2O_2)]^+$ | 0.41 |
| 21 | *cis*-$[Co(en)_2(OC_2O_3H)(^{18}OH_2)]^{2+}$[a] | 2.23 | chelation, pH 0.98, 14 h in normal solv | $[Co(en)_2(O_2C_2O_2)]^+$ | 0.03 |
| 22 | *cis*-$[Co(en)_2(OC_2O_3)(^{18}OH_2)]^{+}$[a] | 2.23 | chelation, pH 6.24, 14 h in normal solv | $[Co(en)_2(O_2C_2O_2)]^+$ | 0.02 |
| 23 | *cis*-$[Co(en)_2(OC_2O_3)(^{18}OH_2)]^{+}$[a] | 2.23 | chelation, pH 7.25, 14 h in normal solv | $[Co(en)_2(O_2C_2O_2)]^+$ | 0.01 |
| 24 | $[Co(en)_2(^{18}OH)(^{18}OH_2)]^{2+}$[a] + $C_2O_4^{2-}$ | 1.401 ($H_2O$) | chelation, pH 7.55, 4 h | $[Co(en)_2(O_2C_2O_2)]^+$ | 0.274 |
| 25 | $[Co(en)_2(^{18}OH)(^{18}OH_2)]^{2+}$[a] + $C_2O_4^{2-}$ | 1.401 | anation, pH 7.55, 4 h | *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ | 0.003 |
| 26 | *cis*-$[Co(en)_2(OC_2O_3H)(^{18}OH_2)]^{2+}$[a] | 1.401 | chelation, pH 1, 18 h, normal solvent | $[Co(en)_2(O_2C_2O_2)]^+$ | 0.028 |

[a] Reactant $^{18}O$ enrichment deduced from solvent value.

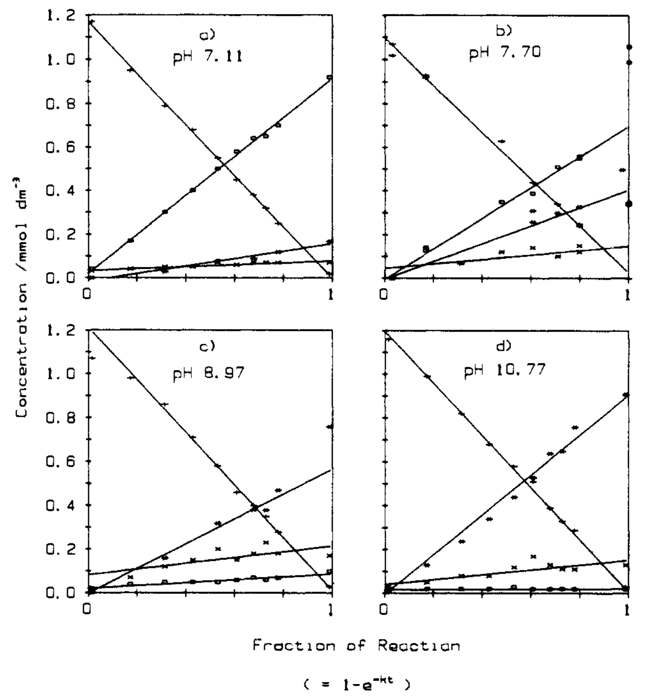


**Figure 4.** Plots for the disappearance of *cis*-[Co(en)$_2$(OC$_2$O$_3$)(OH)] and *cis*-[Co(en)$_2$(OC$_2$O$_3$)(OH$_2$)]$^+$ (+) and the appearance of [Co(en)$_2$(O$_2$C$_2$O$_2$)]$^+$ (⊙), *trans*-[Co(en)$_2$(OC$_2$O$_3$)(OH)]$^0$ and *trans*-[Co(en)$_2$(OC$_2$O$_3$)(OH$_2$)]$^+$ (×), and *cis*- + *trans*-[Co(en)$_2$(OH$_2$)(OH)]$^{2+}$ and [Co(en)$_2$(OH)$_2$]$^+$ (*) as a function of fraction of reaction; $I$ = 1.0 mol dm$^{-3}$ (NaNO$_3$), 25.0 °C (c.f. Table III).

OH$^-$ and 20% in 1.0 mol dm$^{-3}$ OH$^-$. The OH$^-$-independent term becomes significant below pH 11 and along with chelation dominates the rate at pH 7–11. This aspect is considered in detail below.

The tracer data require that hydrolysis at the metal is much faster than OH$^-$ substitution into the monodentate oxalate ligand. This fact argues against the above possibility of a $k_{OH}^{cl}[OH^-]^2$ contribution to the rate since it is difficult to accommodate this without O-exchange. This contrasts with [Co(NH$_3$)$_5$(OCOCF$_3$)]$^{2+}$ [13] and with [Co(NH$_3$)$_5$(OC$_2$O$_3$)]$^+$ [3] where a $k_{OH}^{cl}[OH^-]^2$ term can be associated with OH$^-$-catalyzed exchange into the ligand and CoO–C cleavage. Scheme II details such factors. The faster substitution rate at the metal for *cis*-[Co(en)$_2$(OC$_2$O$_3$)(OH)] ($k_{OH}^c$ = 6.3 × 10$^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$) compared to that for [Co(NH$_3$)$_5$(OC$_2$O$_3$)]$^+$ ($k_{OH}^c$ = 2.45 × 10$^{-4}$ mol$^{-1}$ dm$^3$ s$^{-1}$)[9] is not unexpected from charge considerations; this would not be expected to influence attack at the ligand to the same extent. However, the not too different hydrolysis rate of the trans isomer ($k_{OH}^c$ = 6.5 × 10$^{-4}$ mol$^{-1}$ dm$^3$ s$^{-1}$), where reaction also occurs entirely by Co–O bond fission (Table I, experiment 2), is more difficult to accommodate simply in these terms.

**Chelation of *cis*-[Co(en)$_2$(OC$_2$O$_3$)(OH)]$^0$, *cis*-[Co(en)$_2$(OC$_2$O$_3$)(OH$_2$)]$^+$, and *cis*-[Co(en)$_2$(OC$_2$O$_3$H)(OH$_2$)]$^{2+}$.** Cyclization of monodentate oxalate becomes significant at pH < 9 and is the only reaction below pH 7. Under the latter condition [Co(en)$_2$(O$_2$C$_2$O$_2$)]$^+$ was confirmed as the product by spectrophotometric and chromatographic analysis and by the isolation of sparingly soluble [Co(en)$_2$(O$_2$C$_2$O$_2$)](ClO$_4$) directly from solution ($\epsilon_{354}$ = 147, $\epsilon_{491}$ = 113 mol$^{-1}$ dm$^3$ cm$^{-1}$). Similar observations were made by Chan and Harris using cis,trans mixtures of the monodentates.[11] Figure 4 and Table III (supplementary material) give reaction products (c.f. Figure 1) for pH 7.1, 7.7, 9.0, and 10.8, and it is clear that both cyclization and hydrolysis occur, with the former decreasing in importance with increasing pH. Also, some *trans*-[Co(en)$_2$(OC$_2$O$_3$)(OH)] is formed, and the amount (10%) appears to have little pH dependence above pH 7.7. RP-HPIP chromatography also showed the absence of additional products in the presence of buffer species (see below).

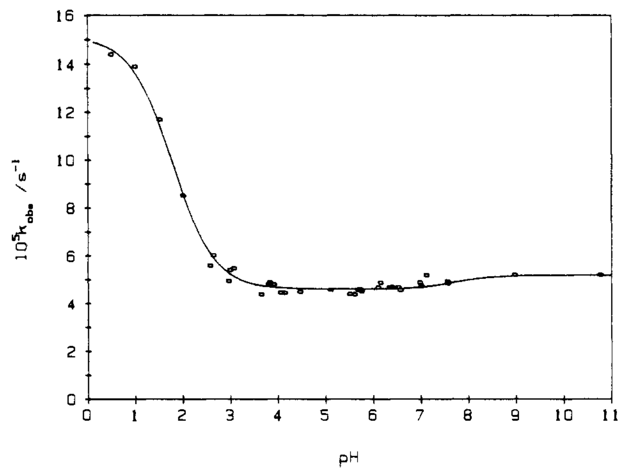


**Figure 5.** Plot of $k_{obsd}$ ($I$ = 1.0 mol dm$^{-3}$ (NaNO$_3$), 25.0 °C) for reaction of *cis*-[Co(en)$_2$(OC$_2$O$_3$)(OH)]$^0$, *cis*-[Co(en)$_2$(OC$_2$O$_3$)(OH$_2$)]$^+$, and *cis*-[Co(en)$_2$(OC$_2$O$_3$H)(OH$_2$)]$^{2+}$ species vs. pH (c.f. Table IV in supplementary material).

**Table V.** Effect of Phosphate[a] (0.08 mol dm$^{-3}$) on the Cyclization Rates of *cis*-[Co(en)$_2$(OC$_2$O$_3$)(OH$_2$)]$^{+}$[b] and *cis*-[Co(en)$_2$(OC$_2$O$_3$H)(OH$_2$)]$^{2+}$[b] ($I$ = 1.0 mol dm$^{-3}$ (NaNO$_3$), 25.0 °C)

| pH | $10^5k_{obsd}$, s$^{-1}$ |
|---|---|
| 1.50 | 14.0 |
| 2.23 | 19.7 |
| 3.80 | 20.0 |
| 5.50 | 17.1 |
| 6.54 | 21.7 |
| 7.03 | 22.3 |

[a] p$K_{a1}$ (H$_3$PO$_4$), 2.22; p$K_{a2}$ (H$_2$PO$_4^-$), 6.53. [b] p$K_{a1}$ (monodentate oxalate), 1.79; p$K_{a2}$ (coordinated water) 7.67.

Rate data over the pH range 0–10.8 are given in Figure 5 ($I$ = 1.0 mol dm$^{-3}$ (NaNO$_3$), 25.0 °C). $k_{obsd}$ was obtained using HNO$_3$ solutions or is the extrapolated rate obtained from extensive data in the presence of buffers (Table IV, supplementary material). A small negative ionic strength effect exists ($k_{obsd}$ = 1.69 × 10$^{-4}$, 1.86 × 10$^{-4}$ s$^{-1}$ at $I$ = 1.0, 0.1 mol dm$^{-3}$, [H$^+$] = 0.1 mol dm$^{-3}$), but there is no significant medium effect (ClO$_4^-$, NO$_3^-$, and C$_2$O$_4^{2-}$). Three regions of reactivity are apparent with $k_{obsd}$ being almost pH independent between 0 and 1 and decreasing some threefold to another pH-independent region above 3. For 0 < pH < 6, $k_{obsd}$ agrees with expression 5 with $k_1$ = (1.51 ± 0.05) × 10$^{-4}$ s$^{-1}$, $k_2$ = (4.6 ± 0.2) × 10$^{-5}$ s$^{-1}$, and p$K_{a1}$ = (1.76 ± 0.02) at $I$ = 1.0 (NaNO$_3$), 25 °C. $k_1$ and $k_2$ correspond to cyclization

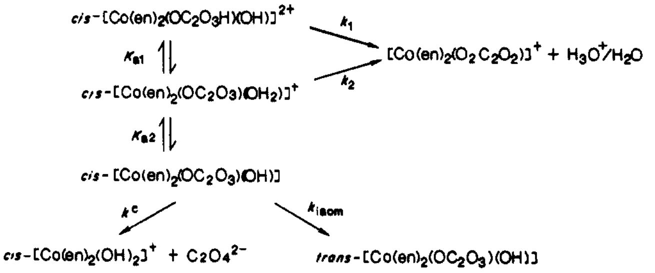
$$k_{obsd} = \frac{k_1[H^+] + k_2K_{a1}}{[H^+] + K_{a1}} \qquad (5)$$

of *cis*-[Co(en)$_2$(OC$_2$O$_3$H)(OH$_2$)]$^{2+}$ and *cis*-[Co(en)$_2$(OC$_2$O$_3$)(OH$_2$)]$^+$, respectively. Chloroacetic, acetic, and phosphoric acids all catalyze cyclization. Table IV (supplementary material) gives detailed rate data, and Table V gives $k_{obsd}$ values for 0.08 mol dm$^{-3}$ phosphoric acid buffer at selected pHs. Considerably catalysis is involved, and the reaction resembles that for cyclization in *cis*-[Co(en)$_2$(glyOH)(OH$_2$)]$^{3+}$.[14] In the latter study catalysis was attributed to general acid catalysis of the anionic component *cis*-[Co(en)$_2$(glyO)(OH$_2$)]$^{2+}$, and the present data are similarly analyzed in terms of *cis*-[Co(en)$_2$(OC$_2$O$_3$)(OH$_2$)]$^+$.[15] For acetic acid (0–0.40 mol dm$^{-3}$; pH 3.39–5.19), the data fit the expression $k_{obsd} = k_0 + k_{HOAc}[HOAc]$ with $k_0$ representing the uncatalyzed rate and $k_{HOAc}$ = 7.1 × 10$^{-4}$ mol$^{-1}$ dm$^3$ s$^{-1}$. For chloroacetic acid, the data (0–0.4 mol dm$^{-3}$; pH 1.96–3.36) fit expression 6 with p$K_{HOClAc}$ = 2.70 and $k_{HOClAc}$ = 9.8 × 10$^{-4}$ mol$^{-1}$ dm$^3$ s$^{-1}$. The

$$k_{obsd} = k_0 + \frac{k_{HOClAc}K_{a1}[H^+][HOClAc]_T}{([H^+] + K_{a1})([H^+] + K_{HOClAc})} \qquad (6)$$

phosphate–phosphoric acid data are more complex, with curvature occurring in plots of $k_{obsd}$ vs. [phosphate]$_T$ at pH ≥ 5. No such curvature was found previously in the cyclization of monodentate

**Scheme III**

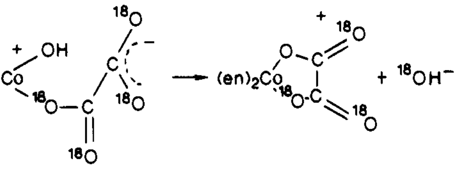


glycinate.[14] In more acidic solutions $H_3PO_4$ and $H_2PO_4^-$, both appear to catalyze cyclization, Table IV, but this aspect was not investigated further.

Rate data at pH > 7 (Table III, Figure 4) show little pH dependence, $k_{obsd} \simeq 5.0 \times 10^{-5}$ s$^{-1}$, even though the product results given above require this part of the reaction to lead to both cyclization and loss of $C_2O_4^{2-}$. At pH 7.7 no buffer dependence was found (0.05, 0.10 mol dm$^{-3}$ Hepes), and the presence of 0.1 mol dm$^{-3}$ $C_2O_4^{2-}$ at pH 6.4 did not alter the rate although it increased the observed absorbance change (decrease) by a factor approaching 2.

Consideration of the product and rate data leads to Scheme III. Cyclization occurs via *cis*-$[Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$ ($k_1$ = (1.51 ± 0.5) × 10$^{-4}$ s$^{-1}$) and *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$, and hydrolysis occurs via *cis*-$[Co(en)_2(OC_2O_3)(OH)]$, with the pH-independent rates for the latter two processes being similar, $k_2$ = (4.6 ± 0.2) × 10$^{-5}$ s$^{-1}$, $k^c$ = 5.2 × 10$^{-5}$ s$^{-1}$; $k_{isom}$ has a value of about 5 × 10$^{-6}$ s$^{-1}$ ($I$ = 1.0 mol dm$^{-3}$, 25.0 °C).

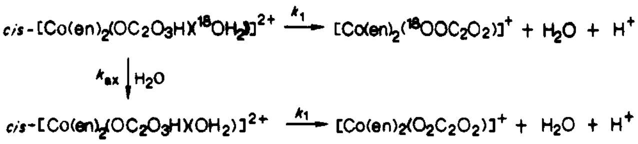
The $^{18}O$-tracer data, Table I, define cyclization in terms of substitution by coordinated water or hydroxide at carboxylic acid carbon or displacement by carboxylate oxygen at the metal. The data of Andrade and Taube[3] require cyclization by the former route under strongly alkaline conditions, eq 7, but it is now clear that hydrolysis to *cis*-$[Co(en)_2(OH)_2]^+ + C_2O_4^{2-}$ occurs under these conditions. Our data concern the reactions of the cis



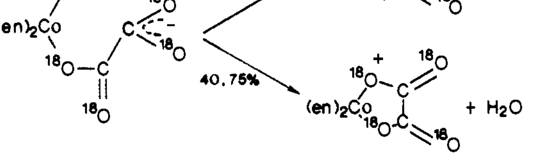
(7)

monodentate in neutral and mildly acidic conditions appropriate to the kinetic paths $k_1$ and $k_2$, of Scheme III. Experiments listed in Table I used both labeled oxalate ligand in normal water and labeled coordinated water in enriched or normal solvent. At the outset it was necessary to establish the exchange pattern for the monodentate reactant and chelated $[Co(en)_2O_2C_2O_2]^+$ complexes under the experimental conditions. As background it was already known that the oxygens of $[Co(NH_3)_5(OC_2O_3H)]^{2+}$ undergo exchange in acid ([H$^+$] > 0.4 mol dm$^{-3}$), with the carbonyl oxygen exchanging via an acid-catalyzed path ($k_{ex}$ = 4.5 × 10$^{-4}$ mol$^{-1}$ dm$^3$ s$^{-1}$) and the two remote carboxylic acid oxygens by an acid-independent route ($k_{ex}'$ = 2.1 × 10$^{-5}$ s$^{-1}$); in dilute acid all four oxygens exchange at the same acid-dependent rate ($k'_{ex}$ = 1.3 × 10$^{-3}$ s$^{-1}$, [H$^+$] = 0.01 mol dm$^{-3}$) possibly via the carbonyl oxygen and equilibration at the metal.[16] Our results are appropriate to the latter condition and are in general agreement with it. Experiment 7 shows some 4% exchange (of four oxygen atoms) after 18 h at pH 4 with *trans*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$, and experiments 9 and 10 suggest a similar rate for the cis isomer. At pH 2 and 1 where the monodentate oxalate is partly or fully protonated, exchange is more rapid, with 6% and 35% exchange after 80 and 160 min, respectively (experiments 13 and 15). Clearly such factors need to be considered if cyclization is carried out using labeled oxalate at pH ≤ 2, but not at pH 4. Exchange of the two exocyclic oxygens in $[Co(en)_2(O_2C_2O_2)]^+$ occurs at an acid-dependent rate of 2.3 × 10$^{-5}$ mol$^{-1}$ dm$^3$ s$^{-1}$.[16] This again suggests that some allowance is necessary at pH ≤ 2 but not otherwise. Experiment 19 confirms the absence of exchange into the chelate at pH 7 in the presence of 0.2 mol dm$^{-3}$ $C_2O_4^{2-}$. It is known that $C_2O_4^{2-}$ itself undergoes only very slow exhange in the pH range 1–7[25,26] and in strong alkali solutions,[3] such that it can be ignored over the time periods and temperatures used here. Our own experiments[21] confirm zero exchange at pH 4–7 at 25 °C. With this information in mind, the cyclization results can be interpreted.

**Scheme IV**



Experiments 11, 12, and 17 require some 40% exchange of one oxalate oxygen on cyclization of *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ at pH 4; these data clearly refer to $k_2$ of Scheme III. Also, cyclization of *trans*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ gives a similar amount (experiment 8), confirming the previously established path via prior isomerization to the cis monodentate[1] and in addition showing that isomerization of the reactant does not involve O-exchange into coordinated oxalate. The data suggest two competing paths for cyclization: one involving displacement of coordinated water at the metal (60%) and the other involving substitution at the carboxylate carbon by coordinated water (40%), eq 8.



(8)

At pH 7.5–7.6 under the conditions of the initial anation, the recovered $[Co(en)_2(O_2C_2O_2)]^+$ has lost 57% of one oxygen (experiment 6) or has gained ≈75% of one oxygen (experiment 20 gives 74%; 24 gives 78%) from the solvent. The latter value is considered the more reliable, and experiment 19 shows that $[Co(en)_2(O_2C_2O_2)]^+$ does not itself undergo exchange under the conditions in the presence of $C_2O_4^{2-}$. The increased contribution of the path involving substitution at the carboxylate carbon by coordinated water (75%) must be attributed to the presence of $C_2O_4^{2-}$ in these experiments, and the increased optical density change observed for cyclization in the presence of $C_2O_4^{2-}$ (compared to a $NO_3^-$ medium) is consistent with changes in ion pairing of the 2+ reactant. The unaltered overall rate would require the two processes to be influenced in opposite senses energetically. Such medium effects are not entirely unexpected for competing processes of this nature, and we are currently investigating the effects of $C_2O_4^{2-}$ on water exchange in these complexes.[21]

At pH 1–2 when $[Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$ is the reactant, interpretation of the results is made difficult by exchange into the reactant as outlined above. However, comparisons of experiments 12 and 14 at pH 2 (and to a lesser extent 15 and 16 at pH 1) suggest the loss of close to one oxygen during cyclization. Furthermore, the HOAc-catalyzed reaction at pH 4, which is much faster, gives 100% exchange of one oxygen (experiment 18). A direct demonstration of intramolecular attack by coordinated water is provided by experiments 21 and 26, using *cis*-$[Co(en)_2(OC_2O_3H)(^{18}OH_2)]^{2+}$ in normal water. These results give 5% and 8% incorporation into the chelate at pH 1, but water exchange into the reactant is now a competitive process, Scheme IV. Analysis of the data gives $k_{ex}$ = 1.6 × 10$^{-3}$ and 2.6 × 10$^{-3}$ s$^{-1}$ for the two experiments. Such values are obviously based on complete retention of coordinated oxygen during cyclization and the assumption that no label has been lost in the chromatographic isolation of *cis*-$[Co(en)_2(OC_2O_3)(^{18}OH)]$. Small but experimentally meaningful retention of labeled water is also found at pH 6–7 (experiments 22 and 23) where cyclization is both slower

Table VI. Rate Data[a] for Alkaline Hydrolysis of $[Co(en)_2(O_2C_2O_2)]^+$ ($I$ = 1.0 mol dm$^{-3}$ ($NaNO_3$), 25.0 °C)

| $[OH^-]$, mol dm$^{-3}$ | $10^6k_{obsd}$, s$^{-1}$ | $10^6k_{calcd}$, s$^{-1}$ |
|---|---|---|
| 1.0 | 72.7 | 71.6 |
| 0.7 | 36.8 | 36.7 |
| 0.5 | 20.1 | 19.9 |
| 0.3 | 8.25 | 8.16 |
| 0.1 | 1.63 | 1.46 |

[a] Spectrophotometric (497 nm); initial rates $[Co(en)_2(O_2C_2O_2)]^+$, $\epsilon$ = 111.7 (1 mol dm$^{-3}$ NaOH); 111.5 (1 mol dm$^{-3}$ $NaNO_3$), *cis*-$[Co(en)_2(OH)_2]^+$, 81.9.

and is occurring by the two paths indicated by eq 8.

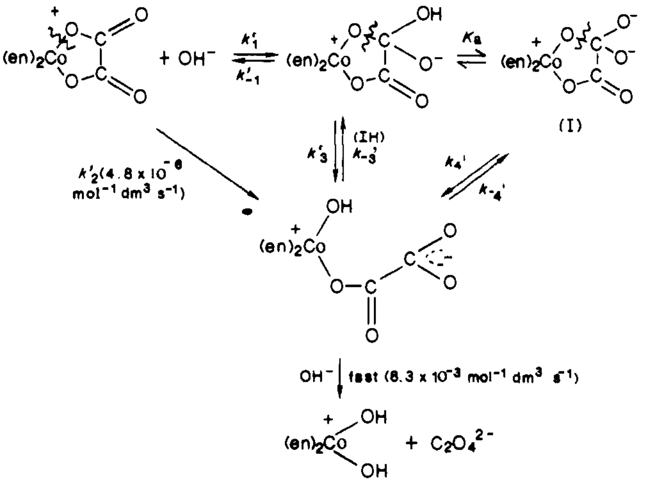
**O-Exchange and Alkaline Hydrolysis of $[Co(en)_2(O_2C_2O_2)]^+$.** Hydrolysis of the chelate ring is slow compared to hydrolysis of monodentate oxalate in *cis*- and *trans*-$[Co(en)_2(OC_2O_3)(OH)]$, so that ring opening is rate determining. The tracer studies of Andrade and Taube[3] as well as those given below require one act of C–O bond cleavage (particularly at high $[OH^-]$) and one Co–O bond cleavage in the complete loss of $C_2O_4^{2-}$. It has been shown above that Co–O cleavage occurs with both *cis*- and *trans*-$[Co(en)_2(OC_2O_3)(OH)]$ so that if either is involved as an intermediate in the overall hydrolysis reaction, C–O bond cleavage must occur in the ring-opening process. This is in agreement with the interpretation given by Andrade and Taube.[3]

It has also been previously stated[4] that the product of complete hydrolysis is *cis*-$[Co(en)_2(OH)_2]^+$, and our observations confirm this. Hydrolysis of both *cis*- and *trans*-$[Co(en)_2(OC_2O_3)(OH)]$ also results in only *cis*-$[Co(en)_2(OH)_2]^+$, and the faster rates of these processes preclude the observation of these species as intermediates. The subsequent change observed by others[4,5] is due to *cis*- to *trans*-$[Co(en)_2(OH)_2]^+$ equilibration which interferes with all spectrophotometric rate data at 25 °C. An attempted kinetic run at 460 nm, close to an isosbestic point for this equilibration, resulted in only a very small optical density change for the chelate, and it was decided to collect data by the initial rate method at the visible maximum of $[Co(en)_2(O_2C_2O_2)]^+$ (497 nm), where a large overall absorbance change occurs. These data are given in Table VI and assume *cis*-$[Co(en)_2(OH)_2]^+$ to be the immediate product. The data fit expression 9 with $k_{OH}{}^1 = 8.3$

$$k_{obsd} = k_{OH}{}^1[OH^-] + k_{OH}{}^2[OH^-]^2 \qquad (9)$$

$\times\ 10^{-6}$ mol$^{-1}$ dm$^3$ s$^{-1}$, $k_{OH}{}^2 = 6.3 \times 10^{-5}$ mol$^{-2}$ dm$^6$ s$^{-1}$ ($I$ = 1.0 mol dm$^{-3}$ ($NaNO_3$), 25.0 °C). In 1.0 and 0.1 mol dm$^{-3}$ $OH^-$, the path second order in $OH^-$ contributes 88% and 43% to the overall rate so that good definition of both contributions has been achieved. The above values agree well with those found for alkaline hydrolysis of $[Co(pn)_2(O_2C_2O_2)]^+$. A recent study on this related system misinterpreted the data,[31] but treatment in a similar fashion to the above, followed by extrapolation to 25 °C, leads to $k_1$ = $6 \times 10^{-6}$ mol$^{-1}$ dm$^3$ s$^{-1}$ and $k_2 = 4 \times 10^{-5}$ mol$^{-2}$ dm$^6$ s$^{-1}$. This study also followed the hydrolysis of $[Co(tmd)_2(O_2C_2O_2)]^+$ which on reanalysis gives $k_1 = 3 \times 10^{-5}$ mol$^{-1}$ dm$^3$ s$^{-1}$ and $k_2 = 2 \times 10^{-4}$ mol$^{-2}$ dm$^6$ s$^{-1}$ at 25 °C.

Scheme V



$^{18}$O-tracer results are given in Table VII. Labeled solvent was used, and both $[Co(en)_2(O_2C_2O_2)]^+$ and released $C_2O_4^{2-}$ were analyzed. As mentioned above exchange into the latter is very slow under alkaline conditions and at 25 °C can be ignored for most of the times employed here. For $[Co(en)_2(O_2C_2O_2)]^+$ experiment 1 in 1.0 mol dm$^{-3}$ NaOH clearly demonstrates very rapid exchange of two out of the four available oxygens. A much slower exchange of a third oxygen is suggested (experiments 1–5). The latter exchange ($k_{obsd} \approx 4 \times 10^{-6}$ s$^{-1}$) will be returned to below, but the fast exchange means that released $C_2O_4^{2-}$ must contain at least two equilibrated oxygens at all times. The smaller exchange values obtained by Andrade and Taube at 71 and 90 °C and at short times[3] would require an unusually large activation energy for the $[OH^-]$-catalyzed cleavage of the ring ($k_2'$, Scheme V) compared to that for oxygen exchange ($k_1'$), and in our view are in error.

Rate data for exchange into the chelate were obtained in 0.02 mol dm$^{-3}$ NaOH (experiments 12–17), giving $k_{ex} = 5.74 \times 10^{-4}$ s$^{-1}$ based on two exchanging oxygens. Experiment 10 in 0.1 mol dm$^{-3}$ NaOH gives $t_{1/2} \approx 5$ min, and complete exchange is achieved in 4 min in 1 mol dm$^{-3}$ NaOH. Clearly a first-order rate law in $[OH^-]$ is applicable, $k_{obsd} = k_1'[OH^-]$, with $k_1' = 2.9 \times 10^{-2}$ mol$^{-1}$ dm$^3$ s$^{-1}$ at 25 °C.

After we allow for this fast exchange into the chelate, released $C_2O_4^{2-}$ in 1.0 mol dm$^{-3}$ NaOH (experiments 1–5) shows on average 94% incorporation of one additional oxygen. This decreases

Table VII. $^{18}$O-Tracer Experiments. Alkaline Hydrolysis of $[Co(en)_2(O_2C_2O_2)]^+$ at 25 °C

| expt | atom % enrichment of solv | reaction conditions | atom % enrichment in recovered $[Co(en)_2(O_2C_2O_2)]^+$ | $n$[a] | atom % enrichment in recovered $C_2O_4^{2-}$ | $n$[a] |
|---|---|---|---|---|---|---|
| 1 | 1.655 | 1 M NaOH, 0.5 h | 0.843 | 2.04 | 1.202 | 2.905 |
| 2 | 1.655 | 1 M NaOH, 1 h | 0.856 | 2.07 | 1.215 | 2.94 |
| 3 | 1.655 | 1 M NaOH, 2.33 h | 0.884 | 2.14 | 1.214 | 2.93 |
| 4 | 1.655 | 1 M NaOH, 5 h | 0.888 | 2.15 | 1.199 | 2.90 |
| 5 | 1.655 | 1 M NaOH, 9.2 h | 0.936 | 2.26 | 1.208 | 2.92 |
| 6 | 1.000 | 0.5 M NaOH, 5 h | | | 0.69 | 2.76 |
| 7 | 1.000 | 0.5 M NaOH, 13 h | | | 0.71 | 2.84 |
| 8 | 1.230 | 0.1 M NaOH, 95.5 h | | | 0.81 | 2.63 |
| 9 | 1.230 | 0.1 M NaOH, 168 h | | | 0.82 | 2.67 |
| 10 | 1.300 | 0.1 M NaOH, 5 min | 0.320 | 0.98 | | |
| 11 | 1.300 | 0.1 M NaOH, 30 min | 0.648 | 1.99 | | |
| 12 | 1.310 | 0.02 M NaOH, 30 s | 0.018 | 0.055 | | |
| 13 | 1.310 | 0.02 M NaOH, 1 min | 0.027 | 0.082 | | |
| 14 | 1.310 | 0.02 M NaOH, 2 min | 0.055 | 0.168 | | |
| 15 | 1.310 | 0.02 M NaOH, 5 min | 0.133 | 0.406 | | |
| 16 | 1.310 | 0.02 M NaOH, 10 min | 0.184 | 0.562 | | |
| 17 | 1.310 | 0.02 M NaOH, 60 min | 0.545 | 1.664 | | |

[a] Represents the number of O atoms enriched out of four.

**Scheme VI**

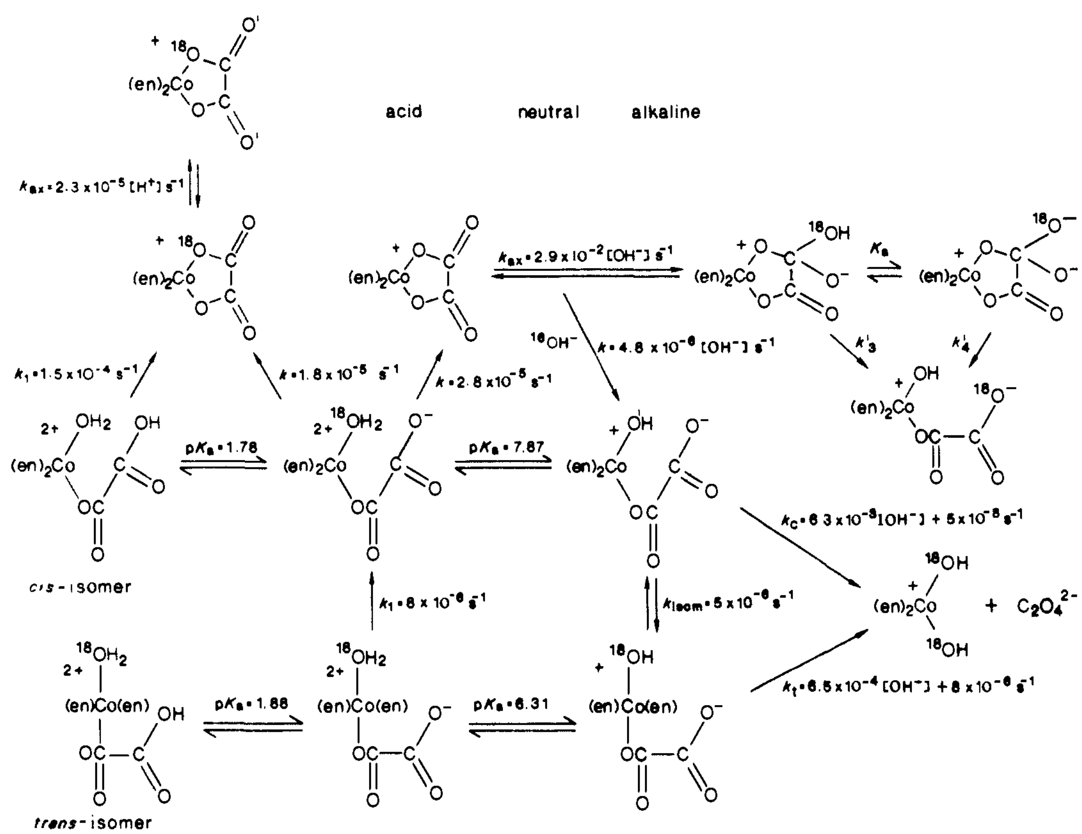


**Table VIII.** Comparisons of Cleavage Paths for Alkaline Hydrolysis of $[Co(en)_2(O_2C_2O_2)]^+$

| $[OH^-]$, mol dm$^{-3}$ | contributions $k_{OH^1}$ | contributions $k_{OH^2}$ | $n^a$ | % C–O cleavage for $k_{OH^1}$ |
|---|---|---|---|---|
| 1.0 | 13 | 87 | 0.94 | 40 |
| 0.5 | 22 | 78 | 0.80 | 5 |
| 0.1 | 60 | 40 | 0.67 | 45 |

[a] $n$ data (Table VII) −2.00.

to 80% in 0.5 mol dm$^{-3}$ NaOH (experiments 6 and 7) and to 67% in 0.1 mol dm$^{-3}$ NaOH (experiments 8 and 9). There is a reasonable correspondence of these data with expression 9 for chelate hydrolysis, Table VIII. The $[OH^-]^2$ contribution clearly involves C–O bond cleavage, but the $[OH^-]$ contribution ($k_{OH}{}^1$) involves both C–O and Co–O cleavage, with the data in 1.0 and 0.1 mol dm$^{-3}$ NaOH suggesting a 40% contribution from the former. This is depicted in Scheme V with $k_4'$ and $k_3'$ involving C–O cleavage and $k_2'$ leading to Co–O bond fission. The latter path can be interpreted as normal $S_N1(CB)$-induced hydrolysis at the metal such as has been found with other chelated carboxylates.[17,18] Its appearance provides a route to the observed small amount of O-exchange into the endocyclic oxygens of $[Co(en)_2(O_2C_2O_2)]^+$ mentioned above ($k_{obsd} \approx 4 \times 10^{-6}$ s$^{-1}$ in 1.0 mol dm$^{-3}$ NaOH) via $k_{-4}'$ or $k_{-3}'$. Hydrolysis at the metal via the $k_2'$ path could also lead to some trans monodentate product such as is found with $[Co(en)_2(\beta\text{-alaO})]^{2+}$ ring opening,[17] but this possibility cannot be tested since both monodentate isomers hydrolyze rapidly to *cis*-$[Co(en)_2(OH)_2]^+$ under the conditions.

Steady-state treatment according to Scheme V leads to expression 10, assuming IH and I are at equilibrium as well as low concentration. The fast exchanging exo oxygens confirm the

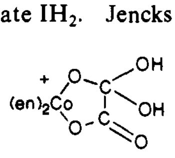
$$k_{obsd} = \frac{k_1'(k_3' + k_4'K_a[OH^-]/K_w)[OH^-]}{k_{-1}' + k_3' + k_4'K_a[OH^-]/K_w} + k_2'[OH^-] \qquad (10)$$

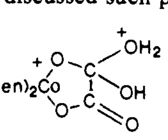
equilibrium assumption, and attempts to observe IH in 1.0 mol dm$^{-3}$ NaOH were unsuccessful, with no rapid change in the spectrum from 310 to 650 nm. Specifically, at 317 nm which is a trough in the near-UV spectrum of $[Co(en)_2(O_2C_2O_2)]^+$, no spectral change with a time constant characteristic of exchange of the exocyclic oxygens ($t_{1/2}$ = 24 s) was observed ($\Delta A < 0.0004$, $A = 0.075$). This region of the spectrum is particularly sensitive to the detection of such intermediates. The first term in expression 10 represents that part of expression 9 leading to C–O bond fission (i.e., $k_{OH}{}^2[OH^-]^2 + 0.4k_{OH}{}^1[OH^-]$). Comparison gives $k_4'/k_3' = 20\ K_w/K_a$, and if $K_a \leq 10^{-14}$, as appears likely in such situations,[14] then $k_4' \geq 20\ k_3'$. The inability to detect IH requires $k_{-1}' \geq 10^2 k_1' \approx 3$ s$^{-1}$. It is interesting to note that $S_N1(CB)$-catalyzed substitution at the metal competes favorably with C–O bond fission in IH.

## General Comments

Most details of the cyclization, hydrolysis, and O-exchange of coordinated oxalate have been examined. A summary of this information is given by Scheme VI.

In acid, cyclization of monodentate oxalate occurs via the cis aqua isomer with retention of the oxygen atom of coordinated water. This requires preferential O-exchange at the carboxylic acid carbon, and such a process is more favorable than exchange at the carboxylate carbon ($k = 1.51 \times 10^{-4}$, $1.8 \times 10^{-5}$ s$^{-1}$, respectively). Acid catalysis of the latter process is found with acetic ($7.1 \times 10^{-4}$ mol$^{-1}$ dm$^3$ s$^{-1}$), chloroacetic ($9.8 \times 10^{-4}$), and phosphoric ($1.6 \times 10^{-3}$) acids, and this is probably a common property. It has previously been observed in the related glycinate cyclization.[14] Such catalysis could be interpreted in terms of base catalysis of the aqua acid, but general base catalysis has not been found with the related aqua-$\beta$-alanine ester system[27] where proton positioning is not equivocal. This step must be rate determining, and it may involve concerted addition–elimination with avoidance of intermediate $IH_2$. Jencks has discussed such possibilities.[28]


$IH_2$

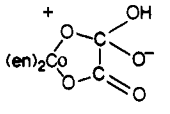

$IH_3$

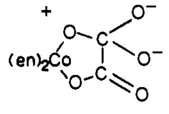
Hydrolysis of the chelate does not occur under acidic conditions, with $[Co(en)_2(O_2C_2O_2)]^+$ being stable for at least 1 year in 1 mol $dm^{-3}$ hydrochloric acid. Acid-catalyzed exchange of the two exocyclic oxygens, however, does occur ($k_{ex} = 2.3 \times 10^{-5}$ $mol^{-1}$ $dm^3$ $s^{-1}$), and there is some suggestion of a much slower exchange of the chelated oxygens.[16] The faster process has been attributed to loss of water from the intermediate $IH_3$.[16]

In neutral conditions cyclization of *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$ occurs by loss of water from either carboxylate carbon or the metal. The former reaction is some 10 times slower than that found for *cis*-$Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$. A similar rate difference was found between the aqua glycinate *cis*-$[Co(en)_2(glyO)(OH_2)]^{2+}$ and aqua glycine acid *cis*-$[Co(en)_2(glyOH)(OH_2)]^{3+}$ where the reaction occurs entirely by attack of coordinated water at the carbon center.[14] The more rapid cyclization in the glycine system avoids water exchange at the metal, and it is this latter process which allows competitive entry of carboxylate in the oxalate system. Water exchange at the metal is likely to dominate all slow cyclization processes.

In more alkaline conditions where ionization of coordinated water has occurred, cyclization of $[Co(en)_2(OC_2O_3)(OH)]$ is relatively unimportant; hydrolysis of the ligand is preferred. A similar, although not identical, situation is found with the glycinate system with cyclization of *cis*-$[Co(en)_2(glyO)(OH)]^+$ being at least 100 times slower than for *cis*-$[Co(en)_2(glyO)(OH_2)]^{2+}$. It is not known whether the latter reaction occurs via attack at the metal center by carboxylate oxygen or by coordinated hydroxide attack at carboxylate carbon,[14] but the slower complete loss of N-bound monodentate glycinate in alkaline solution compared to monodentate oxalate allows cyclization to occur. Attack by coordinated hydroxide is found at the ester[27] and amide[29] carbon, with both $OH^-$-independent and $OH^-$-dependent paths contributing to the rate. Similar paths to IH or I from *cis*-$[Co(en)_2(OC_2O_3)(OH)]$ would accommodate the observed O-exchange into the endocyclic oxygens of $[Co(en)_2(O_2C_2O_2)]^+$, and an analysis of the data requires $(k_{-3}' + k_{-4}')$ to be $\leq 10^{-3}$ $s^{-1}$ in 1.0 mol $dm^{-3}$ $OH^-$. The alternative possibility of switching of O atoms in IH by rotation about the C–C bond[32] is considered unlikely.

Microscopic reversibility requires a path for cyclization via displacement of coordinated hydroxide since hydrolysis of $[Co(en)_2(O_2C_2O_2)]^+$ shows some $OH^-$-catalyzed displacement at the metal. However $OH^-$-catalyzed hydrolysis of the monodentates to give *cis*-$[Co(en)_2(OH)_2]^+$ is preferred in these circumstances. The deprotonated intermediates IH and I lead exclusively to cleavage in the chelate ring. Only intermediate IH is required for O-exchange. Probably CoO–C bond fission occurs via solvent protonation of the bound oxygen atom since $CoO^-$ does not provide an acceptable leaving group in water.


IH


I

Hydrolysis of both the cis and trans monodentates occurs via Co–O bond fission. This is easily reconciled in terms of the commonly encountered $S_N1(CB)$ mechanism for hydrolysis via a deprotonated ethylenediamine precursor.

The above comments could well be of general applicability to cobalt(III) carboxylate systems. Differences will result from variations in the acidity of the monodentate carboxylate or coordinated water functions and possibly from more substantial variations in the rates of water or hydroxide exchange at the metal. Attack at carboxylic acid carbon by coordinated water, or at carboxylate carbon by coordinated hydroxide, should not be appreciably affected by the other ligands on the metal, but this aspect has yet to be tested.

**Acknowledgment.** We thank Dr J. Hulston, Institute of Nuclear Sciences, D.S.I.R., Lower Hutt, for measurement of oxygen isotopic ratios.

**Registry No.** *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]PF_6$, 102920-52-5; *cis*-$[Co(en)_2(OC_2O_3)(OH)]$, 59982-23-9; *cis*-$[Co(en)_2(OC_2O_3)(OH_2)]^+$, 87036-83-7; *cis*-$[Co(en)_2(OC_2O_3H)(OH_2)]^{2+}$, 102920-53-6; $[Co(en)_2(O_2C_2O_2)]^+$, 17835-71-1.

**Supplementary Material Available:** Listings of observed reaction products (Table III) and rate data for hydrolysis (Table II) and cyclization (Table IV) (5 pages). Ordering information is given on any current masthead page.

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(31) Dash, A. C.; Nanda, R. K.; Ray, N.; Rout, K. C. *Int. J. Chem.* **1984**, *23A*, 907. These authors obtained a curved plot with zero intercept when $k_{obsd}$ was plotted againt $[OH^-]$ and a linear plot, interpreted as $k_{obsd} = k_0 + k_2[OH^-]^2$ when $k_{obsd}$ was plotted against $[OH^-]^2$; the two are in obvious disagreement. From plots of $k_{obsd}/[OH^-]$ vs. $[OH^-]$ or when a least-squares quadratic fit is used, the rate law $k_{obsd} = k_1[OH^-] + k_2[OH^-]^2$ is obtained for all the data.

(32) Broomhead, J. A.; Kane-Maguire, N.; Lauder, I.; Nimmo, P. *J. Chem. Soc., Chem. Commun.* **1968**, 747.

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# Design and Synthesis of a New Ferroelectric Liquid Crystal Family. Liquid Crystals Containing a Nonracemic 2-Alkoxy-1-propoxy Unit

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**Abstract:** The synthesis and phase behavior of a new class of nonracemic liquid crystal materials of general structure **1**, possessing a phenyl benzoate core and chiral nonracemic 2-alkoxy-1-propoxy tail unit derived from ethyl acetate, are described. Several of the new materials possess monotropic ferroelectric liquid crystal (FLC) phases at or near room temperature. These materials exhibit the fastest room temperature electro-optical switching characteristics of any known FLC's. A discussion of the ferroelectric polarization in nonracemic tilted smectic liquid crystal phases is given. It is suggested that the phenomenon may be considered in terms of a novel kind of molecular recognition occurring in the liquid crystal phase.

Phenomena involving molecular recognition in complexation have long been of great interest in organic chemistry, and considerable current research is directed toward understanding and utilizing molecular recognition in chemical aggregates. In its