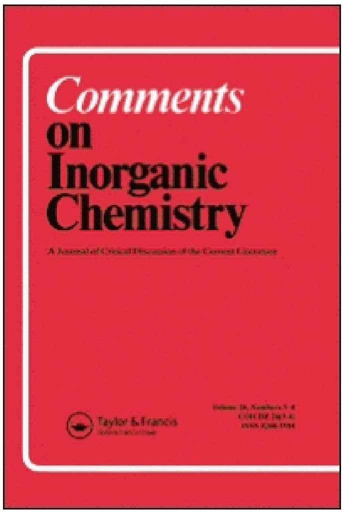

Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Chelation, Hydrolysis, and Oxygen Exchange in the $[Co(en)_2(OH)(H_2O)]^2$ $/C_2O_4^{2-}$ System

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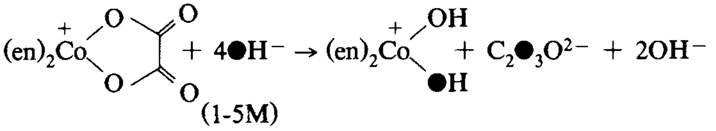
To cite this Article Miskelly, Gordon M. and Buckingham, David A.(1985) 'Chelation, Hydrolysis, and Oxygen Exchange in the $[Co(en)_2(OH)(H_2O)]^2$ $/C_2O_4^{2-}$ System', Comments on Inorganic Chemistry, 4: 3, 163 — 178
To link to this Article: DOI: 10.1080/02603598508072258
URL: http://dx.doi.org/10.1080/02603598508072258

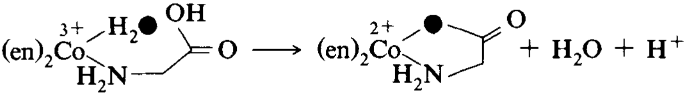
Chelation, Hydrolysis, and Oxygen Exchange in the $[Co(en)_2(OH)(H_2O)]^{2+}/C_2O_4^{2-}$ System

INTRODUCTION

Chelation, hydrolysis, and oxygen exchange have all been studied previously. However, two experimental observations suggested to us that the mechanistic detail was not as straightforward as had been assumed. First, Andrade and Taube in 1964 found that chelated oxalate in (1) incorporated close to *three* oxygen atoms from the solvent during its complete hydrolysis in strongly alkaline


(1)

solution.*[1] Second, we had observed some especially facile intramolecular hydrolysis reactions including the interesting very rapid ($t_{½} \simeq 40$ s, 25 °C) attack of coordinated water at carboxylic acid carbon,[2] *viz.* (2).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*● indicates ^{18}O-enriched species.

Comments Inorg. Chem.
1985, Vol. 4, No. 3, pp. 163–178
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In the context of what this second study told us under alkaline conditions Andrade and Taube's claim of initial acyl-O bond cleavage in (1) seemed perfectly reasonable, but it cast serious doubt on their proposed mechanism. Also, we were interested in establishing the pathway for the reverse process, the cyclization reaction, at lower pH's. So, as is often the case, what started as a two-term B.Sc. (Hons) project has turned out to require much more careful study, and has expanded to cover all aspects of $(en)_2Co^{3+}$-oxalate chemistry.

Probable intermediates in both the hydrolysis and chelation processes are the *cis*- and *trans*-monodentate species; so we began there.

PREPARATION AND PROPERTIES OF MONODENTATE *cis*- AND *trans*-$[Co(en)_2(OH/H)(OC_2O_3/H)]^{0,1+,2+}$ SPECIES

Previous experience suggested that such species should be reasonably stable in slightly alkaline (pH ~ 9) conditions. Initial attempts to prepare the precursor complex *cis*-$[Co(en)_2Br(OC_2O_3)]$[2] failed, and partial hydrolysis and quenching experiments on $[Co(en)_2(O_2C_2O_2]$ (OAc)[3] led to only *cis*- and *trans*-$[Co(en)_2(OH)_2]^+$ ions following ion-exchange chromatography. A more likely candidate, the pyrolysis of $[Co(en)_2(H_2O)_2]_2(C_2O_4)_3$, led to only the chelate $[Co(en)_2(O_2C_2O_2)]^+$ in significant amounts.[4] Other assorted experiments were not encouraging, so we returned to the Harris and Chan method[5] via anation of $[Co(en)_2(OH)(H_2O)]^{2+}$.

Treating *trans*-$[Co(en)_2(OH_2)(OH)](ClO_4)_2$ (0.1 mole dm^{-3}) with $Na_2C_2O_4$ (0.1 mole dm^{-3}) in aqueous solution at ambient temperatures leads to significant amounts of the intermediates following ion-exchange chromatography (Dowex AGl (NO_3^-), followed by Dowex 50W × 2 (Na^+)). Purple *trans*-$[Co(en)_2(OH)(OC_2O_3)]$ was eluted with 0.05 M morpholine (pH ~ 10) and dark red *cis*-$[Co(en)_2(OH)(OC_2O_3)]$ with 0.1 M $NaNO_3$ (some *cis* + *trans*-$[Co(en)_2(OH)_2]^+$ and $[Co(en)_2(C_2O_4)]^+$ remain adsorbed on the top of the column).[6]

Attempts to crystallize the separate isomers was only partly successful. Concentration and addition of appropriate NaX salts led to crystallization of *trans*-$[Co(en)_2(OH_2)(OC_2O_3)]X \cdot nH_2O$ (X = PF_6^-, $CF_3SO_3^-$, ClO_4^-; $n = 1,2$). A crystal structure of *trans*-$[Co(en)_2(OH_2(OC_2O_3)](CF_3SO_3) \cdot 2H_2O$, Fig. 1, confirms its geometry as well as showing some other interesting features.[6] Similar attempts

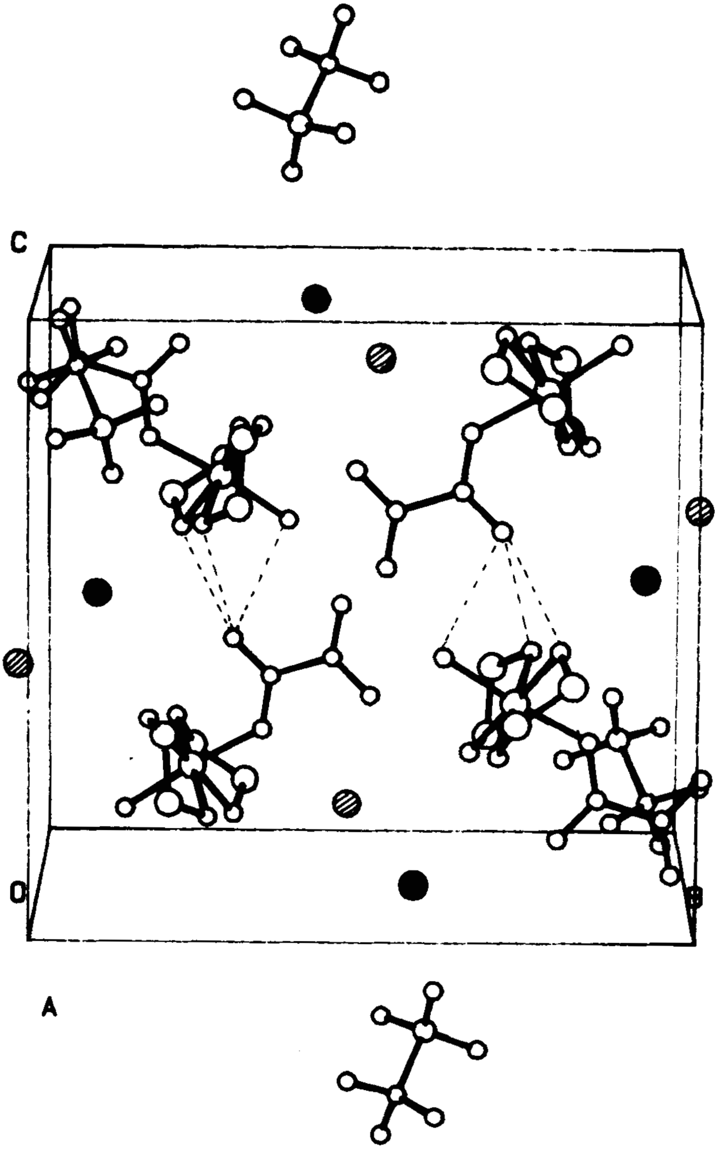


FIGURE 1 Projection of the unit cell contents of *trans*[Co(en)$_2$(C$_2$O$_4$)OH$_2$]-(CF$_3$SO$_3$).2H$_2$O down the *a* axis.

with the *cis*-eluent were, however, unsuccessful, partly because it cyclizes to the sparingly soluble chelate reasonably rapidly at room temperature at $pH < 7$ ($t_{½} \simeq 2.5$ h). Both hydroxo isomers react rapidly with acetic anhydride at $pH \sim 7$ to give different $[Co(en)_2(OCOCH_3)(OC_2O_3)]$ species and we are following up this observation.

The visible-UV spectra of the two isomers differ significantly, Fig. 2, and show pH variations in keeping with other known aqua/hydroxo *cis*- and *trans*-bis(ethylenediamine) systems. Spectrophotometric measurements at $I = 1.0$ ($NaNO_3$) and $T = 25$ °C gave the following pK_a values,

	pK_{a_1}	pK_{a_2}
cis-$[Co(en)_2(OH/H)(OC_2O_3/H)]^{2+,1+,0}$	1.76 ± 0.02	7.42 ± 0.06
trans-$[Co(en)_2(OH/H)(OC_2O_3/H)]^{2+,1+,0}$	1.66 ± 0.04	6.31 ± 0.02

and these correspond to ionization of the dangling oxalate moiety (cf. pK_{a_1} ($H_2C_2O_4$) $= 1.23$) and aqua ligand, respectively. Aqueous solutions can be stored at low temperature for long periods of time (preferably frozen) but in most instances fresh preparations were used in what follows. These, and other trial experiments, showed to us that both probable *cis* and *trans* intermediates were reasonably stable in aqueous solution, particularly under mildly alkaline conditions (pH 9–10). But what of their chemistry in acidic and more strongly alkaline solutions?

HYDROLYSIS OF *cis*- AND *trans*-$[Co(en)_2(OH)(OC_2O_3)]$

Alkaline hydrolysis of both isomers follow the rate law $k_{obs} = k_{OH}[OH^-]$ ($[OH^-] = 0.1$–1.0 mole dm^{-3}) with k^c_{OH} and k^t_{OH} values of 6.3×10^{-3} and 6.5×10^{-4} mole^{-1} dm^3 s^{-1} respectively, $I = 1.0$ ($NaClO_4$), $T = 25.0$ °C ($t_{½} = 110$ s and 18 min., respectively, in 1.0 mole dm^{-3} NaOH). Both give clean reactions, and within the accuracy of our spectrophotometric measurements *both* give *cis*-$[Co(en)_2(OH)_2]^+$ product. ^{18}O-tracer experiments using ~6 at. % $C_2^{18}O_4^{2-}$-labelled complexes showed exclusive Co–O bond fission. This is in agreement with the alkaline hydrolysis of monodentate

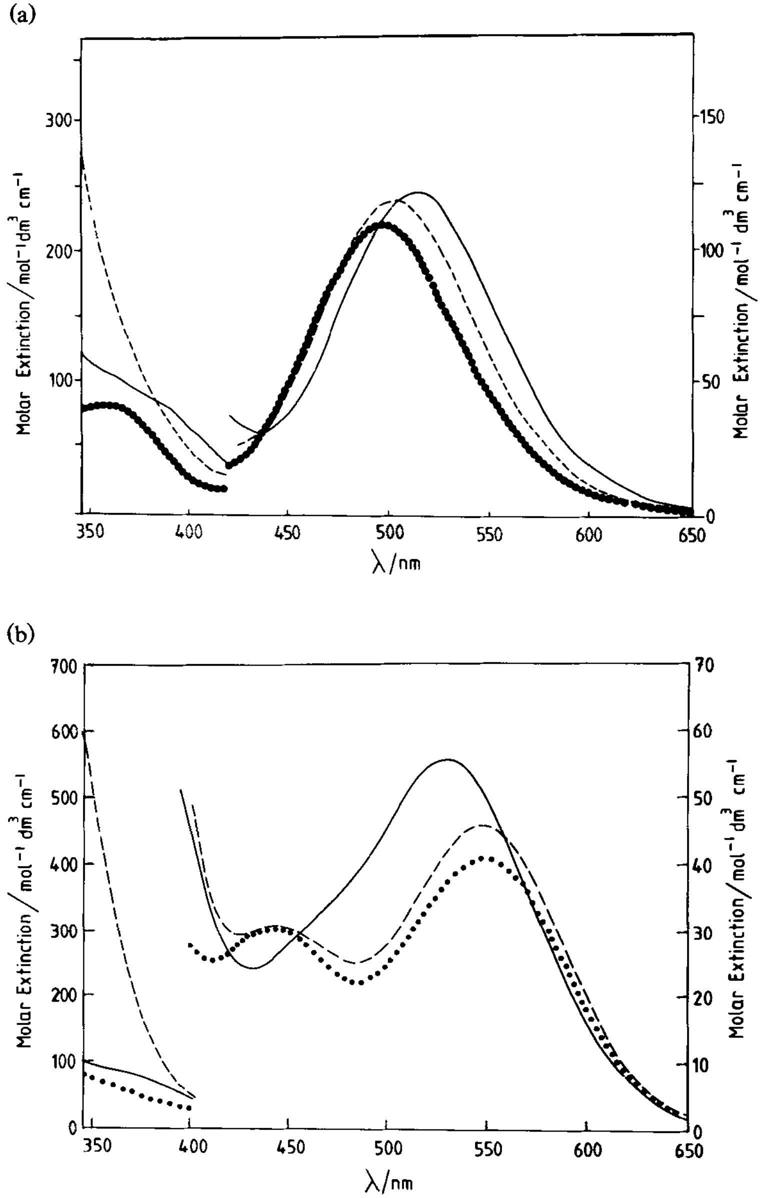
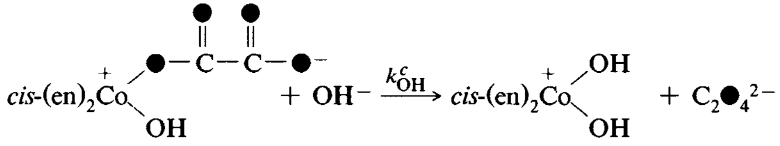
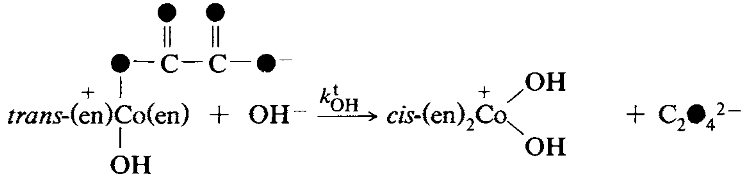


FIGURE 2 Visible spectra of *cis*-(a) and *trans*-(b) $[Co(en)_2(C_2O_4H)OH_2]^{2+}$ at *p*H 0 (···), $[Co(en)_2(C_2O_4)OH_2]^{+}$ at *p*H 4 (– – –), and $[Co(en)_2(C_2O_4)OH]$ at *p*H 9(—).

$[Co(NH_3)_5(OC_2O_3)]^+$ and other carboxylate species.[7-9] An S_N1CB mechanism is likely here.



$(k^{c}_{OH} = 6.3 \times 10^{-3}\ \text{mole}^{-1}\ \text{dm}^3\ \text{s}^{-1})$



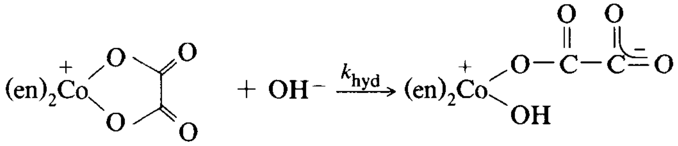
$(k^{t}_{OH} = 6.5 \times 10^{-4}\ \text{mole}^{-1}\ \text{dm}^3\ \text{s}^{-1})$

How does this fit in with the alkaline hydrolysis of the chelate as described by Andrade and Taube?

HYDROLYSIS AND OXYGEN EXCHANGE IN $[Co(en)_2(O_2C_2O_2)]^+$

It was clear at the outset that the likely sole immediate product of alkaline hydrolysis would be *cis*-$[Co(en)_2(OH)_2]^+$ and that the difficulty others have had in following this and related hydrolyses (e.g., of $[Co(en)_2(OC(O)CH_2C(O)O)]^+$) arises, at least in part, from subsequent isomerization to the *trans* isomer.[10-12] Unfortunately the isosbestic points for *cis*- and *trans*-$[Co(en)_2(OH)_2]^+$ occur at wavelengths where little change occurs during hydrolysis, and after initial trials we resorted to initial rate measurements at a fixed reactant concentration and at $\lambda = 497$ nm where a large optical density change occurs for the hydrolysis reaction and a very much smaller change for isomerization. Data were collected over the $[OH^-]$ range 1.0–0.1 mole dm^{-3} and fit the two-term rate expression $k_{hyd} = k_1^{ch}[OH^-] + k_2^{ch}[OH^-]^2$ ($k_1^{ch} = 0.9 \times 10^{-5}$ mole^{-1} dm^3 s^{-1} $k_2^{ch} =$

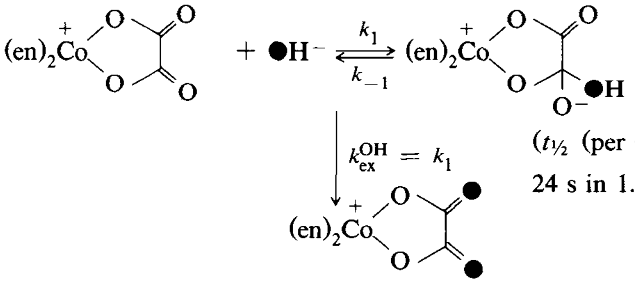
6.2×10^{-5} mole^{-2} dm^{6} s^{-1}, $I = 1.0$ ($NaNO_3$), $T = 25.0$ °C). This corresponds to a $t_{1/2} = 2.7$ h in 1.0 M OH^- so the reaction is very much slower than hydrolysis of either monodentate intermediate species. It must correspond to the ring-opening reaction. Other in-



$$k_{hyd} = k_1^{ch}[OH^-] + k_2^{ch}[OH^-]^2$$

both first- and second-order $[OH^-]$ dependencies for this, and temperature variations in the rate suggest that k_1^{ch} has the higher activation energy.[10,12]

Oxygen exchange into the chelate is very much faster. This was followed by analyzing isolated chelate after standing in $H_2{}^{18}O/{}^{18}OH^-$ solutions for varying times, and at different $[OH^-]$ (0.02 and 0.1 mole dm^{-3}). Essentially no hydrolysis occurs under these conditions, and recovery of $[Co(en)_2(O_2C_2O_2)](ClO_4)$ was effectively quantitative. Only two out of the four oxygen atoms had exchanged*, with $k_{ex} = k^{OH}[OH^-]$, k^{OH} (per O atom) $= 2.9 \times 10^{-2}$ mole^{-1} dm^{3} s^{-1} at 25.0 °C. Clearly this must occur without opening of the chelate since otherwise the monodentate species would have been detected (and they do not recyclize under the conditions anyway, as given above). Oxygen exchange must therefore be a precursor to ring opening and the mechanism given is related to the H^+-catalyzed



($t_{1/2}$ (per O) = 24 s in 1.0 M OH^-)

process examined by Andrade, Taube, and Jordan ($k_{ex}^{H} = k_1[H^+]$;

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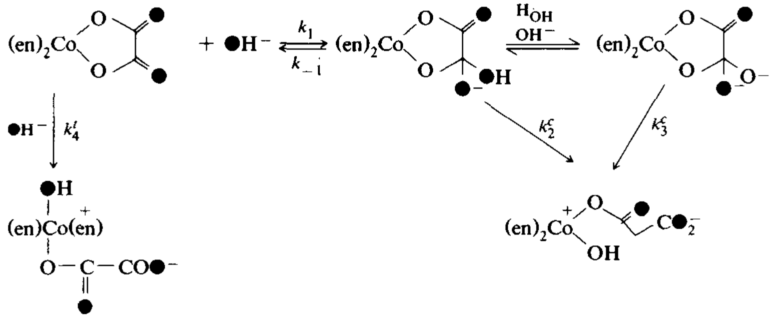
*There is some suggestion of a third exchanging oxygen, but if this is real its rate is very much slower, $< 4 \times 10^{-6}$ s^{-1} in 1.0 M NaOH.

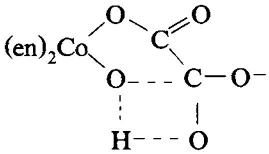
$t_{1/2} = 3 \times 10^4$ s in 1.0 M HCl).[13] Attempts to evaluate the equilibrium constant $K^{OH} = k_1/k_{-1}$ by looking for expected spectral changes in the hydrated species using rapid-mixing spectral scans in 1.0 M NaOH suggested $K^{OH} < 10^{-2}$ mole^{-1} dm^3, whence $k_{-1} > 3$ s^{-1}, at 25 °C.

^{18}O-exchange during complete hydrolysis was then re-examined by recovering $Ag_2C_2O_4$. We found 2.94 O atoms had undergone exchange in 1.0 M NaOH, and two of these are required for fast exchange into the chelate. The 0.94 remainder is consistent with the incorporation of one oxygen via the second-order in [OH^-] path since the experiment was conducted largely (approximately 87 percent) under these conditions. It will be shown below that the first order in [OH^-] path leading to *cis*-[$Co(en)_2(OC_2O_3)(OH)$] must also occur via C–O bond fission since the reverse reaction occurs in this manner, but it is possible that the difference from 1.0 results from some 50 percent of another pathway (approx. 6.3% of total in 1.0 M NaOH) and this could well result in *trans*-[$Co(en)_2(OC_2O_3)(OH)$] via the normal S_N1 CB mechanism. Experiments at lower [OH^-] where the first-order path predominates will give more precision to this result but direct detection of a *trans*-[$Co(en)_2(OC_2O_3)(OH)$] product is impossible. The Andrade and Taube experiment[1] measures the second-order path which, like the remainder of the first-order path, necessarily leads to *cis* product (Scheme I). Comparison of the first-order rates for O-exchange and hydrolysis gives a value of 3×10^3 for the k_{-1}/k_2^c ratio consistent with OH^- being a better leaving group than CoO^-

SCHEME I



from the saturated carbon center. It is very likely that CoO^- is in fact a very poor leaving group and that protonation at some early stage is required.



CYCLIZATION IN *cis*- AND *trans*-$[Co(en)_2(OH/H)(OC_2O_3/H)]^{2+,1+,0}$

We then turned our attention to the reactions of the *cis* and *trans* monodentate species under more acidic conditions. Chan and Harris[5] had observed cyclization to occur at pH 7.8–9 and also at $p\text{H} < 7$ but they assumed either that they were dealing with only the *cis* isomer, or that the *cis* and *trans* species were in rapid equilibrium. Our kinetic data at 25 °C and $I = 1.0$ ($NaClO_4$) is given in Fig. 3. Under the pH conditions the sole product is chelated $[Co(en)_2(O_2C_2O_2)]^+$. Clearly the *cis* species is more reactive than the *trans*, and shows a decided increase in rate about pK_{a_1} (protonation of the dangling carboxylate moiety).

Cyclization in the *trans*-reactant shows little pH variation and it has been shown[6] that this occurs exclusively *via the cis monodentate.* Thus the observed rate ($k_t = 8 \times 10^{-6}\ s^{-1}$) is a measure of the isomerization rate, and this most likely occurs via water exchange at the metal center (probably multiple water exchanges are *trans*-$[Co(en)_2(OH_2)(OC_2O_3)]^+ \xrightarrow{k_t}$ *cis*-$[Co(en)_2(OH_2)(OC_2O_3)]^+$ necessary for complete isomerization).

The more interesting, and more rapid, cyclization of the *cis* reactant was then examined in a number of ^{18}O-labelling experiments. Care must be taken to avoid solvent exchange into oxalate of the monodentate and chelate under acidic conditions.[13] At pH 4–5, where the reactant is entirely *cis*-$[Co(en)_2(OH_2)(OC_2O_3)]^+$, recovery of chelate showed consistently approximately 30% loss of one oxygen label to solvent. Recovered unreacted *cis*-monodentate showed full retention of label under the conditions, and the product chelate was similarly shown to be inert to exchange. The chelate must therefore be formed

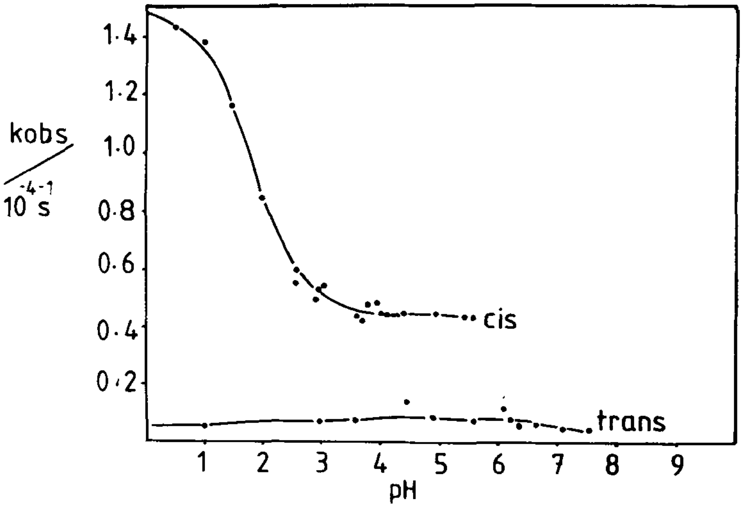
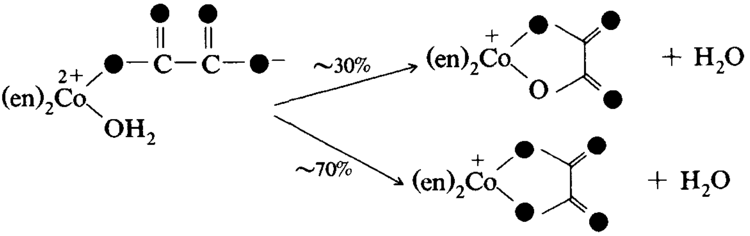
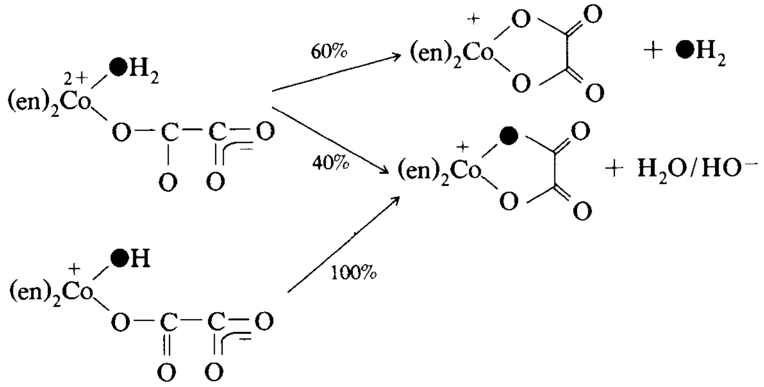


FIGURE 3 Rate *p*H profiles for cyclizations of *trans* and *cis* monodentate oxalate species (μ = 1.0(NaNO$_3$), 25.0 °C).

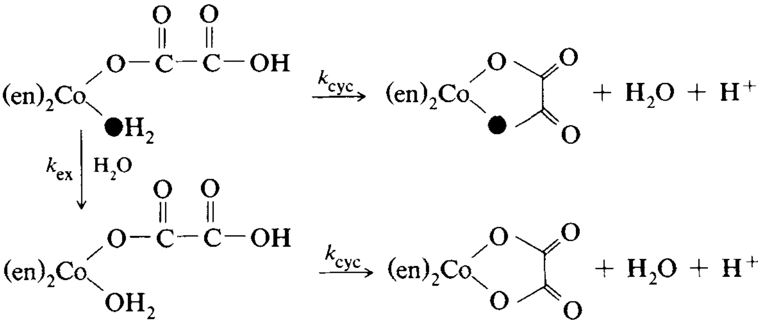
via two paths with at least 30% arising from an intramolecular process,



In another experiment at *p*H 7.5 unlabelled $Na_2C_2O_4$ was reacted with *cis* + *trans*-[Co(en)$_2$(OH)(H$_2$O)]$^{2+}$ following equilibration of *trans*-[Co(en)$_2$(OH)(H$_2$O)]$^{2+}$ with $H_2{}^{18}O$. Both the *cis* and *trans*-[Co(en)$_2$(OH)(OC$_2$O$_3$)] reactants recovered from the reaction mixture showed no incorporation of solvent label into the oxalate part, but recovered chelate gave 78% and 73% incorporation of one solvent label (duplicate experiments). Under the *p*H conditions both the aqua and hydroxo *cis* monodentates are the reactants and using the rate data this gives a 40% intramolecular cyclization in the former and 100% intramolecular cyclization in the latter. The different experiments for the aqua-intermediate are in satisfactory agreement, but the result for the hydroxo complex gives additional information.

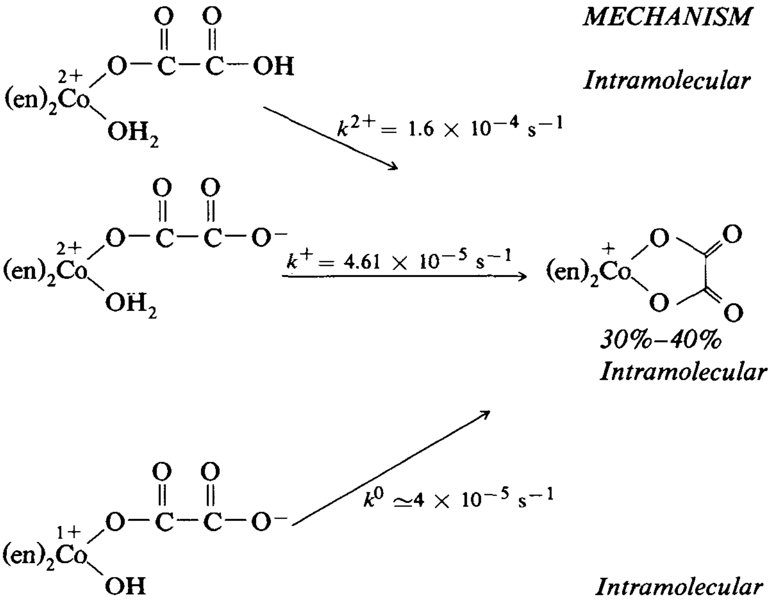


At *p*H 1 the rate for *cis* (Fig. 3) shows a substantial increase compared to *p*H 4, and this is entirely consistent with intramolecular general acid catalysis. Chloroacetic, acetic, and phosphoric acids also catalyze the reaction. This is reminiscent of chelation of monodentate glycinate in *cis*-$[Co(en)_2(OH_2)(NH_2CH_2CO_2H)]^{3+}$ where the reaction is much faster ($t_{1/2} \simeq 40$ s) and which was clearly shown to be intramolecular.[2] The problem with *cis*-$[Co(en)_2(OH_2)(OC_2O_3H)]^{2+}$ is that monodentate oxalate undergoes O-exchange at *p*H < 2, and a similar property is found with exo-O in the chelate $[Co(en)_2(O_2C_2O_2)]^+$. It was therefore necessary to again use the aqua-labelled reactant but this time in unlabelled solvent. There were obvious difficulties in carrying out this experiment, but the result was clear. Recovered chelate showed 5% and 8% incorporation of aqua-label (duplicate experiments).



Clearly there must be a route for the intramolecular reaction, and using the known cyclization rate of 1.23×10^{-4} s^{-1} the exchange result gives a k_{ex} value of $2.4–1.4 \times 10^{-3}$ s^{-1} ($t_{1/2}$-300–400 s). This does not seem an unreasonable value for water exchange in such a species.

In summary then there appears to be three paths leading to the cyclized $[Co(en)_2(O_2C_2O_2)]^+$ ion, all occurring via *cis* species.



ANATION OF *cis*- AND *trans*-$[Co(en)_2(OH)(H_2O)]^{2+}$ SPECIES BY OXALATE

This leaves the initial anation reaction to consider. Harris and coworkers[14–16] had previously studied the reaction of *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ with $H_2C_2O_4$ and $HC_2O_4^-$ in acid conditions (0.1–2.0 M HNO_3), and the process is very slow at 25 °C. Chan and Harris[5] had looked at anation at *p*H 7.3–8.1 and proposed a preassociative ion-pair mechanism, which seems perfectly reasonable.

$$\begin{tikzcd}
{[Co(en)_2(OH)(H_2O)]^{2+} + C_2O_4^{2-}} \arrow[r, shift left, "K_{ip}"] & {} \arrow[l, shift left] \\
 & {[Co(en)_2(OH)(H_2O)]^{2+} \cdot C_2O_4^{2-}} \arrow[d, "k_0"] \\
 & {[Co(en)_2(OH/H)(OC_2O_3)]^{+,2+}}
\end{tikzcd}$$

However it was unclear in this second study what the configuration of the relative species was (*cis* or *trans*) and the configuration(s) of the product monodentate(s). Our experience suggested that this would be a complex problem since the anation rate was not too different from isomerization in the reactant. But we were looking for such a problem to test the capabilities of reverse-phase ion-pair HPLC as an analytical tool. We found that all five species, *cis* and *trans* reactants, *cis* and *trans* monodentates, and the final chelate, could be easily separated.

An on-line HP-integrator allowed quantitative estimation of all species *during the reaction* and the results are summarized in Scheme II.

Scheme II

$$\begin{tikzcd}
{cis\text{-}[Co(en)_2(OH_2)(OH)]^{2+}} \arrow[r, shift left, "k_1"] \arrow[d, shift right, "C_2O_4^{2-}"'] & {trans\text{-}[Co(en)_2(OH_2)(OH)]^{2+}} \arrow[l, shift left, "k_2"] \arrow[d, shift left, "C_2O_4^{2-}"] \\
{cis\text{-}[Co(en)_2(OH_2)(OH)]^{2+} \cdot C_2O_4^{2-}} \arrow[u, shift right] \arrow[r, shift left, "k_1^1"] \arrow[d, "k_3"'] \arrow[dr, "k_4"] & {trans\text{-}[Co(en)_2(OH_2)(OH)]^{2+} \cdot C_2O_4^{2-}} \arrow[u, shift left] \arrow[l, shift left, "k_2^1"] \arrow[d, "k_6"] \arrow[dl, "k_5"'] \\
{cis\text{-}[Co(en)_2(OH/H)OC_2O_3)]^{0/1+}} \arrow[d, "k_8"'] & {trans\text{-}[Co(en)_2(OH/H)(OC_2O_3)]^{0/1+}} \arrow[l, "k_7"'] \\
{[Co(en)_2(O_2C_2O_2)]^{+}} &
\end{tikzcd}$$

Anation was followed under pseudo-first-order conditions over the *p*H range 6.5–10.0, at different $[C_2O_4^{2-}]_T$ (up to 0.3 mole dm^{-3}), and starting with either *cis* or *trans* reactant. To evaluate the data it was necessary to know the pK_a values for the *cis* and *trans* species *under the conditions* since it became apparent that these were dependent on the ionic media (as well as ionic strength). Values under different conditions are as follows:

	cis		*trans*	
	$pK^c_{a_1}$	$pK^c_{a_2}$	$pK^T_{a_1}$	$pK^T_{a_2}$
1.0 M $NaClO_4$	5.74 ± 0.04	8.10 ± 0.04	4.28 ± 0.04	7.98 ± .04
1.0 M $NaNO_3$	6.10 ± 0.04	8.38 ± 0.06	4.40 ± 0.05	8.00 ± .03
0.2 M $C_2O_4{}^{2-}$+ 0.8 M $NaClO_4$	6.52 ± .03	8.36 ± 0.03		8.30 ± .03

A large amount of data was collected and representative curves for the disappearance of reactants and the appearance of products are given in Fig. 4. Although we have not yet completed this study, several observations can be made.

First, the rate of isomerization of the *cis*- and *trans*-$[Co(en)_2(OH)\ (H_2O)]^{2+}.C_2O_4^{2-}$ species is substantially slower than that for the non-ion-paired complexes. This means that the anation rate approaches the isomerization rate at the highest $[C_2O_4^{2-}]$. Both *cis*- and *trans*-$[Co(en)_2(OH)H_2O]^{2+}.C_2O_4^{2-}$ form *cis*- and *trans*-$[Co(en)_2(OH/H)\ (OC_2O_3)]^{+,2+}$, although the *cis* isomer reacts more rapidly. At pH 7.4 and $[C_2O_4^{2-}] = 0.3$ M the rates are:

	k/min^{-1}
cis $\xrightarrow{k'_3}$ cis	0.029
cis $\xrightarrow{k'_4}$ trans	0.013
trans $\xrightarrow{k'_5}$ cis	0.01
trans $\xrightarrow{k'_6}$ trans	0.015

These rates are composites of ion-pair constants and rate constants but studies using varying $[C_2O_4^{2-}]$ are providing data which allow these to be separated.

The pK_{a_2} of *cis*-$[Co(en)_2(OH)OH_2]^{2+}$ appears to have shifted even further in 0.3 M oxalate, with a value in excess of 8.5. For the *trans* isomer $8.04 < pK_{a_2} < 8.54$. At pH > 9 the reverse reactions must also be considered, especially k_{-3} and k_{-4}.

In conclusion, the HPLC technique offers a powerful method for analyzing complicated reaction schemes and we next intend to re-

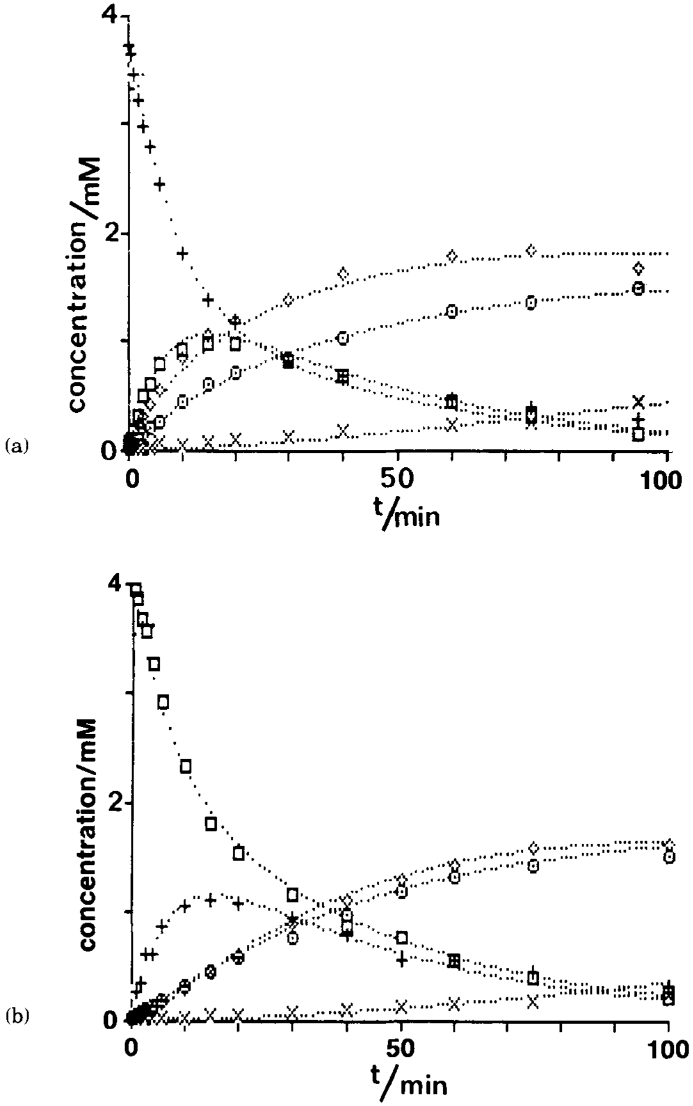


FIGURE 4 Plots of concentration vs time for all species seen in the anation by oxalate at *p*H 8.04 and $[C_2O_4^{2-}]$ = 0.3 M (μ = 1.0 ($NaClO_4$), 25.0 °C). +—*cis*-$[Co(en)_2(OH_2)OH/H]^{2+,+}$, □—*trans*-$[Co(en)_2(OH_2)OH/H]^{2+,+}$, ◇—*cis*-$[Co(en)_2(C_2O_4)OH/H]^{0,+}$, ⊙—*trans*-$[Co(en)_2(C_2O_4)OH/H]^{0,+}$, ×—$[Co(en)_2O_2C_2O_2]^+$.

examine anation with phosphate since we suspect the kinetic analysis of Lincoln and Stranks[17] is incomplete.

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References

1. C. Andrade and H. Taube, J. Am. Chem. Soc. **86**, 1328 (1964).
2. C. J. Boreham, D. A. Buckingham, D. J. Francis, A. M. Sargeson and L. G. Warner, J. Am. Chem. Soc. **103**, 1975 (1981).
3. V. Carunchio, F. Giannetta and G. Grassini Strazza, J. Inorg. Nucl. Chem. **133**, 3025 (1971).
4. This method is commonly used to prepare $[Co(NH_3)_5X]^{n+}$ species.
5. S. C. Chan and G. M. Harris, Inorg. Chem. **10**, 1317 (1971).
6. G. M. Miskelly, C. R. Clark, J. Simpson and D. A. Buckingham, Inorg. Chem. **22**, 3237 (1983).
7. N. S. Angerman and R. B. Jordan, Inorg. Chem. **6**, 379 (1967).
8. R. B. Jordan and H. Taube, J. Am. Chem. Soc. **86**, 3890 (1964).
9. N. S. Angerman and R. B. Jordan, Inorg. Chem. **6**, 1376 (1967).
10. M. E. Farago, M. A. R. Smith and I. M. Keefe, Coord. Chem. Rev. **8**, 95 (1972).
11. S. Sheel, D. T. Meloon and G. M. Harris, Inorg. Chem. **1**, 170 (1962).
12. M. E. Farago and C. F. V. Mason, J. Chem. Soc. (A) 3100 (1970).
13. C. Andrade, R. B. Jordan and H. Taube, Inorg. Chem. **9**, 711 (1970).
14. P. M. Brown and G. M. Harris, Inorg. Chem. **7**, 1872 (1968).
15. R. van Eldik and G. M. Harris, Inorg. Chem. **18**, 1997 (1979).
16. R. Van Eldik, Inorg. Chim. Acta **49**, 5 (1981), references therein.
17. S. F. Lincoln and D. R. Stranks, Aust. J. Chem. **21**, 1745 (1968).