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The Anation by Oxalate and Isomerization of *cis*- and *trans*-$[Co(en)_2(OH_2)OH]^{2+}$

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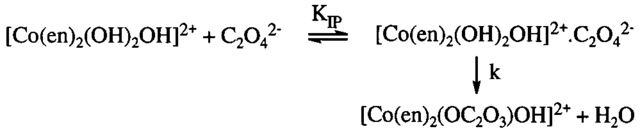
Introduction

The anation of *cis*- and *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ by $C_2O_4^{2-}$ [1−3] is much faster than the anation of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ by $HC_2O_4^-$ or $H_2C_2O_4$.[4−8] The changes in reactivity parallel changes in the rates of water exchange, with $[Co(en)_2(OH_2)OH]^{2+}$ reacting almost 10^3 times faster than $[Co(en)_2(OH_2)_2]^{3+}$ or $[Co(en)_2(OH)_2]^+$.[9−11] The three previous reports[1−3] on the anation of $[Co(en)_2(OH_2)OH]^{2+}$ by $C_2O_4^{2-}$ have interpreted spectrophotometric rate data in terms of the simple ion-pairing mechanism



$$\begin{array}{c} [Co(en)_2(OH)_2OH]^{2+} + C_2O_4^{2-} \overset{K_{IP}}{\rightleftharpoons} [Co(en)_2(OH)_2OH]^{2+}.C_2O_4^{2-} \\ \downarrow k \\ [Co(en)_2(OC_2O_3)OH]^{2+} + H_2O \end{array}$$

with $K_{IP} = 5.8\ M^{-1}$ and $k = 8.2 \times 10^{-4}\ s^{-1}$ at 25 °C ($I = 0.37$ M). However, the stereochemistry (cis or trans) of the reactants and products was not determined, and the effect of the concomitant reactant isomerization was not considered. Previous studies from this laboratory[12−14] have shown that the reaction produces both *cis*- and *trans*-$[Co(en)_2(OC_2O_3)OH]$ and that these ions do not readily isomerize under the conditions of anation ($t_{1/2}$(isom) ∼ 24 h). This suggested that it should be possible to determine the stereochemical course of the anation process provided isomerization between the cis and trans reactants is not too much faster than anation.

The present paper reports the use of reversed-phase high-performance ion-pair chromatography (RP-HPIPC) to separate and quantitate the five complexes, *cis*- and *trans*-$[Co(en)_2(OH_2)OH]^{2+}$, *cis*- and *trans*-$[Co(en)_2(OC_2O_3)OH]$, and $[Co(en)_2(O_2C_2O_2)]^+$, observed during anation in neutral to alkaline solution. This liquid chromatography technique has been demonstrated to allow rapid analysis of multiply charged complex ions,[15−23] but has seldom been used to follow the kinetics of a complicated reaction.[24]

Experimental Section

$[Co(en)_2(O_2CO)](ClO_4)$,[25] *trans*-$[Co(en)_2(OH_2)OH](ClO_4)_2$,[10] *cis*-$[Co(en)_2(OC_2O_3)OH_2](PF_6)\cdot 3H_2O$,[14] *trans*-$[Co(en)_2(OC_2O_3)OH_2](CF_3SO_3)\cdot 2H_2O$,[12] and $[Co(en)_2(O_2C_2O_2)]Cl$[26] were prepared as described in the literature. Other reagents were used as supplied.

Acid dissociation constants were determined spectrophotometrically (Cary 219) immediately after pH adjustment (either by rapid titration or mixing with buffer), Table 1, so as to minimize complications due to facile isomerization (cis−trans) in the $[Co(en)_2(OH_2)(OH)]^{2+}$ ions ($t_{1/2}$ ∼ 3 min at pH 7−8, 25 °C[9]). Details on calculation of the acid dissociation constants are provided in the Supporting Information. The values obtained in 1 M NO_3^- media (cf. Table 1) are similar to those reported earlier.[27]

The observed acid dissociation constants of *cis*-$[Co(en)_2(OH_2)_2]^{3+}$ (pK_{a1}(cis), pK_{a2}(cis); Table 1) are strongly dependent on oxalate concentration, with the apparent acidities of both the diaqua and aqua−hydroxo forms decreasing by a factor of 3−4 between 1 M ClO_4^- and 0.28 M $C_2O_4^{2-}$ media. These decreases suggest ion association constants of $K_{IP,2}^c = 10 \pm 5\ M^{-1}$ for *cis*-$[Co(en)_2(OH_2)OH]^{2+}\cdot C_2O_4^{2-}$, $K_{IP,1}^c = 20 \pm 5\ M^{-1}$ for *cis*-$[Co(en)_2(OH_2)_2]^{3+}\cdot C_2O_4^{2-}$, and the possibility of a second association to give the ion triplet *cis*-$[Co(en)_2(OH_2)_2]^{3+}\cdot 2C_2O_4^{2-}$ with $K_{IT}^c = 20 \pm 10\ M^{-1}$. The acidity of *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ is also markedly anion dependent, but the absence of significant curvature in the pK_{a2}(trans) versus $[C_2O_4^{2-}]$ plot meant that it was not possible to estimate ion association constants for the trans isomers.

Chromatographic analyses were carried out using a Varian 5000 chromatograph equipped with a U6K universal injector (Waters Assoc.), a Z-module (Waters Assoc.) containing a Radial-Pak C_{18} cartridge column (Waters Assoc.; 10 μm, 100 mm × 8 mm ID), and a UV-50 variable wavelength detector (Varian). All analyses were monitored at 250 nm. Concentrations were calculated from peak areas obtained using a Hewlett-Packard 3390A recording integrator. Isocratic RP-HPIPC analyses for the 1+ (25 mM sodium hexanesulfonate in methanol (10% v/v)−water (pH 2.8)) and 3+ (25 mM sodium hexanesulfonate in methanol (42% v/v)−water (pH 2.8)) ions were performed separately. Full details are provided in the Supporting Information.

Estimates of the rate constants were obtained from initial rate analysis of the HPIPC data followed by iterative least-squares fitting of a fourth-order Runge−Kutta simulation using the Solver module in Microsoft

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Table 1. Acid Dissociation Constants for *cis*- and *trans*-$[Co(en)_2(OH_2)(OH/H)]^{2+,3+}$, 25 °C, I = 1.0 M (in Mixed $ClO_4^-/C_2O_4^{2-}$ Media Unless Otherwise Stated)

$[C_2O_4^{2-}]$ (M)	pK_{a1}(cis)	pK_{a2}(cis)	pK_{a1}(trans)	pK_{a2}(trans)
0.0[a]	6.04(6)	8.26(6)	4.40(6)	8.00(6)
0.0[b]	6.06	8.19	4.45	7.94
0.0	5.73(4)	7.97(6)	4.28(6)	8.00(4)
0.05	5.99(5)	8.23(5)		
0.10	6.26(10)	8.32(5)		8.12(4)
0.20	6.45(5)	8.30(10)		8.27(4)
0.284	6.74(4)	8.69(9)		
0.30				8.48(4)

[a] Measured in 1 M NO_3^- media, this work. [b] Measured in 1 M NO_3^- media, ref 27. Standard deviations in parentheses.

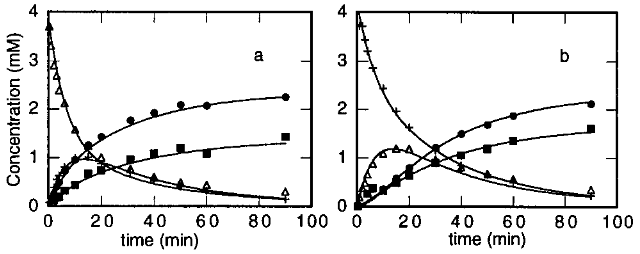
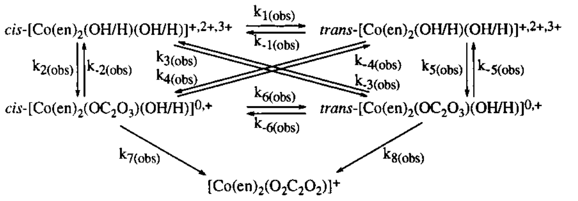


Figure 1. Plots of measured concentrations of cobalt complexes as a function of time during the anation by oxalate. Smooth curves are least-squares fits of fourth-order Runge−Kutta simulations to the data. △ represents *cis*-$[Co(en)_2(OH/H)OH/H]^{+,2+,3+}$, + represents *trans*-$[Co(en)_2(OH/H)OH/H]^{+,2+,3+}$, ● represents *cis*-$[Co(en)_2(OC_2O_3)OH/H]^{+,2+}$ + $[Co(en)_2(O_2C_2O_2)]^+$, and ■ represents *trans*-$[Co(en)_2(OC_2O_3)OH/H]^{+,2+}$. (a) 3.8 mM *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ + 0.3 M $C_2O_4^{2-}$ at pH 7.40. (b) 3.9 mM *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ + 0.3 M $C_2O_4^{2-}$ at pH 7.42. Buffer: 0.10 M HEPES, $T = 25.0$ °C.

Scheme 1



Excel 5. Experiments starting with *cis*- and *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ at the same pH were refined simultaneously to give a consistent set of rate constants. Least-squares minimization was not suitable for the runs at pH 9.91 (rates too dissimilar) or for experiments starting with *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ at low pH (solubility problems); here the rate constants reported are those obtained from initial rate analysis.

Results

The stereochemical description of anation of $[Co(en)_2(OH_2)(OH/H)]^{2+,3+}$ by oxalate required the reaction mixture to be analyzed for five components: *cis*- and *trans*-$[Co(en)_2(OH_2)_2]^{3+}$, *cis*- and *trans*-$[Co(en)_2(OC_2O_3)OH_2]^+$, and $[Co(en)_2(O_2C_2O_2)]^+$. This was achieved by sampling the reaction solution periodically, quenching in acid, and obtaining the Co(III) complex distribution as a function of time by RP-HPIPC using acidic (pH ca. 3) eluents. Data were obtained at $[C_2O_4^{2-}] = 0.10$ M (pH 7.41), 0.20 M (pH 7.41), and 0.30 M (pH 6.84, 7.41, 8.04, 8.54, 8.92, and 9.91). Representative concentration−time plots derived from such chromatograms ($[C_2O_4^{2-}] = 0.3$ M, pH = 7.41) are given in Figure 1, together with fits obtained by simulation on the basis that the kinetically important processes are those shown in Scheme 1.

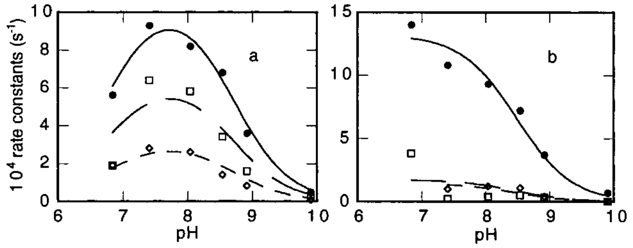


Figure 2. (a) Plots of observed pseudo-first-order rate constants for ● isomerization of *cis*-$[Co(en)_2(OH/H)(OH/H)]^{+,2+,3+}$, □ anation to form *cis*-$[Co(en)_2(OC_2O_3)OH/H]^{0,+}$, and ◇ anation to form *trans*-$[Co(en)_2(OC_2O_3)OH/H]^{0,+}$ as a function of pH. Smooth curves are calculated as described in text, assuming that *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ is the most reactive form of the reactant complex. (b) Plots of observed pseudo-first-order rate constants for ● isomerization of *trans*-$[Co(en)_2(OH/H)(OH/H)]^{+,2+,3+}$, □ anation to form *cis*-$[Co(en)_2(OC_2O_3)OH/H]^{0,+}$, and ◇ anation to form *trans*-$[Co(en)_2(OC_2O_3)OH/H]^{0,+}$ as a function of pH. Smooth curves are calculated as described in text, assuming that *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ is the most reactive form of the reactant complex.

The derived rate constants for anation and isomerization ($k_{1(obs)}$, $k_{-1(obs)}$, $k_{2(obs)}$, $k_{3(obs)}$, $k_{4(obs)}$, and $k_{5(obs)}$) obtained using various conditions of $C_2O_4^{2-}$ concentration (0−0.30 M) and pH (6.84−9.91) are listed in Table S1 (Supporting Information). Data fitting was facilitated by the fact that $k_{-2(obs)}$, $k_{-3(obs)}$, $k_{-6(obs)}$, and $k_{7(obs)}$ were able to be calculated using data obtained previously[12−14] while k_{-6} (5.8×10^{-6} s^{-1}) and k_8 (3.2×10^{-6} s^{-1}) were obtained separately during the course of this study. Hydrolysis of *cis*- and *trans*-$[Co(en)_2(OC_2O_3)OH]$ to give *trans*-$[Co(en)_2(OH/H)OH]^{+,2+}$ (k_{-4} and k_{-5}) occurs at less than half the rate of hydrolysis to give *cis*-$[Co(en)_2(OH/H)OH]^{+,2+}$. More detailed analysis of these paths was not possible due to isomerisation of *cis*- and *trans*-$[Co(en)_2(OH/H)OH]^{+,2+}$. In the simulation, hydrolysis of *cis*- and *trans*-$[Co(en)_2(OC_2O_3)OH]$ was set to occur only via *cis*-$[Co(en)_2(OH/H)OH]^{+,2+}$. This does not affect the conclusions reached about the anation kinetics.

Discussion

The $k_{i(obs)}$ values for anation and isomerization of *cis*-$[Co(en)_2(OH/H)OH/H]^{3+,2+,+}$ vary with pH and show maxima at around neutral pH (Figure 2, Table S1). It is in this region that the mole fraction (f) present as *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ reaches its maximum value. For 1 M $LiClO_4$ solution this maximum concentration occurs at pH 6.85 ($f = 0.87$), whereas it occurs at increasingly higher pH as the $C_2O_4^{2-}$ concentration increases. For 0.28 M $C_2O_4^{2-}$ this is at pH 7.7 ($f = 0.82$). The pH dependence of $k_{i(obs)}$ implies that *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ is the only reactive entity, both for isomerization and anation. This is in accord with previous studies on anation, water exchange, and isomerization in $[Co(en)_2(OH/H)OH/H]^{+,2+,3+}$ and similar systems.[1,9−11,28,29] Thus, the pH dependence of the first-order rate constants for both isomerization and anation may be accommodated using the expression $k_i = k_{i(obs)}/f$, where k_i represents the rate constant for isomerization ($i = 1$) or anation ($i = 2, 3$) in *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ and f is appropriate to the composition of the medium. Similar treatment of the $k_{i(obs)}$ data obtained for the trans isomer gives the first-order rate constants for isomerization (k_{-1}) and anation by oxalate (k_4, k_5) in *trans*-$[Co(en)_2(OH_2)OH]^{2+}$. Table S2 (Supporting Information) lists these rate constants, and the correspondence between observed and calculated values as a function of pH is shown in Figure 2.

At pH 7.4 the anation processes are much faster than hydrolyses of the oxalato complexes and isomerization and anation by oxalate of *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ at this pH could be interpreted in terms of an ion-pair mechanism. Accordingly, the variation in the derived first-order rate constants k_1, and k_2 and k_3, is described by eqs 1 and 2, respectively, where $k_{1(IP)}$, $k_{2(IP)}$, and $k_{3(IP)}$ are the rate constants for the ion pair *cis*-$[Co(en)_2(OH_2)OH]^{2+}\cdot C_2O_4^{2-}$ reacting to form *trans*-$[Co(en)_2(OH_2)OH]^{2+}\cdot C_2O_4^{2-}$, *cis*-$[Co(en)_2(OC_2O_3)OH/H]^{0,+}$, and *trans*-$[Co(en)_2(OC_2O_3)OH/H]^{0,+}$, respectively. The value

$$k_1 = (k_1' + k_{1(IP)}K_{IP,2}{}^{c}[C_2O_4{}^{2-}])/(1 + K_{IP,2}{}^{c}[C_2O_4{}^{2-}]) \quad (1)$$

$$k_{2(3)} = k_{2(IP)(3(IP))}K_{IP,2}{}^{c}[C_2O_4{}^{2-}]/(1 + K_{IP,2}{}^{c}[C_2O_4{}^{2-}]) \quad (2)$$

of the rate constant for isomerization of free *cis*-$[Co(en)_2(OH_2)OH]^{2+}$ (k_1') was fixed at 2.0×10^{-3} s^{-1}. This corresponds to the value obtained in 1.0 mol dm^{-3} $LiClO_4$ (cf. Table S2) and is in agreement with that observed for 1.0 mol dm^{-3} $NaClO_4$ media.[10,29] Least-squares fitting gives $k_{1(IP)} = (7 \pm 1) \times 10^{-4}$ s^{-1}, $k_{2(IP)} = (6.9 \pm 0.6) \times 10^{-4}$ s^{-1}, and $k_{3(IP)} = (3.2 \pm 0.6) \times 10^{-4}$ s^{-1} for $K_{IP,2}{}^{c} = 15$ M^{-1} (cf. $K_{IP,2}{}^{c} = 10 \pm 5$ M^{-1} from the direct spectrophotometric measurement). Thus isomerization in *cis*-$[Co(en)_2(OH_2)OH]^{2+}\cdot C_2O_4^{2-}$ is some 3-fold slower than in free *cis*-$[Co(en)_2(OH_2)OH]^{2+}$.

The k_i vs $[C_2O_4^{2-}]$ data for the reactions of *trans*-$[Co(en)_2(OH_2)OH]^{2+}$ ($i = -1, 4, 5$) do not show the curvature characteristic of ion-pair saturation. However, there is obviously a substantial interaction with $C_2O_4^{2-}$ in this system since the isomerization rate constant, k_{-1}, decreases from 3×10^{-3} s^{-1} in 1 M $LiClO_4$ to 1×10^{-3} s^{-1} in 0.28 M $Li_2C_2O_4$ and both k_4 and k_5 increase under the same conditions (Table S2). The values of K_{IP} (5.8 M^{-1}) and k (8.2×10^{-4} s^{-1}) obtained in the simple spectrophotometric kinetic studies[1-3] are clearly composites of separate ion association constants and isomerization and anation rates. In this system all the rates are sufficiently similar that common kinetic simplifications are not appropriate.

In conclusion these results show that the title reaction is much more involved than had been proposed by earlier authors, and the spectrophotometric constants cannot be directly related to any of the individual processes. Both the *cis*- and *trans*-$[Co(en)_2(OH_2)OH]^{2+}\cdot C_2O_4^{2-}$ ion pairs give rise to both *cis*- and *trans*-$[Co(en)_2(OC_2O_3)OH_2]^+$ products. The results for the trans ion pair suggest that oxalate incorporation is equally likely to occur with isomerization as with retention, while anation in the cis ion pair is twice as likely to occur with retention rather than isomerization. Also, the sum of the rate constants for isomerization and anation within the ion pair is similar to the rate constant for isomerization in the absence of oxalate suggesting that release of coordinated H_2O is rate-limiting, with competitive entry of H_2O or $C_2O_4^{2-}$ occurring as a fast subsequent step.

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Supporting Information Available: Tables S1 and S2, giving rate constants for the anation and isomerization, and experimental details of the acid dissociation constant and chromatographic measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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