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# Ethylenediaminediacetate Complexes of Cobalt(III). Part III. The Aquation of $\alpha$-*cis* and $\beta$-*cis*-$[Co(CO_3)(edda)]^-$ Complexes

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*The aquation of both the $\alpha$-cis and $\beta$-cis isomers of $[Co(CO_3)(edda)]^-$ has been studied over a range of temperatures. The data are consistent with a duality of mechanism in which aquation occurs through both water and acid attack.*

*The rate constants for the aquation of the $\alpha$-cis- and $\beta$-cis-$[Co(CO_3)(edda)]^-$ complexes are more than ten times greater than those of the analogous $[Co(CO_3)(trien)]^+$ isomers. These increased rates arise from more favourable activation entropies and are interpreted in terms of charge and solvation effects.*

## Introduction

In our first paper in this series[1] we reported the preparation and characterisation of a series of ethylenediaminediacetate (edda) complexes of cobalt(III). The aim of that study was to prepare a series of anionic complexes whose kinetics could be compared with the data already available for cationic cobalt(III) complexes. We recently reported[2] the aquation of the $\alpha$-*cis*- and $\beta$-*cis*-$[CoCl_2(edda)]^-$ and $[CoCl(edda)(OH_2)]$ complexes. In this paper the aquation of the $\alpha$-*cis*- and $\beta$-*cis*-$[Co(CO_3)(edda)]^-$ complexes are reported and compared with the results available for analogous cationic carbonate complexes.[3–13]

Initial investigations on the aquation of $[Co(CO_3)(NH_3)_4]^+$ led Pederson[9] to propose a duality of mechanisms in which aquation occurred through both water and acid attack. Oxygen-18 tracer studies by Posey and Taube[12] were interpreted in terms of a rate-determining acid-catalysed ring opening (consisting of Co–O bond fission) followed by a fast decarboxylation. These observations were confirmed by Scheidegger and Schwarzenbach.[13] A thorough series of investigations by Harris *et al.*[3–6, 14] has established unequivocally that in bidentate carbonate complexes aquation is rate-determined by water and acid catalysed ring opening followed by rapid decarboxylation.

This study was undertaken to investigate what effect a change in charge from + 1 to – 1 had on the rate and activation parameters of the aquation process. Favourable sites exist for hydrogen-bonding in edda complexes[2] and a further objective of this work was to determine the effect of a highly structured solvent environment on the aquation process.

## Experimental

The isolation and identification of all reactants and products have been described.[1]

Rates were measured using a Durrum–Gibson stopped-flow spectrophotometer and a repetitive-scan Perkin–Elmer 450 spectrophotometer. Rate constants were evaluated from $\log(D-D_\infty)$ versus time plots using values of D at 540 nm. For runs in which $[H^+] \geqq 0.02\ dm^{-3}$ mol the acid was provided as $HClO_4$. For lower acidity runs McIlvaine[15] phosphate–citric acid buffers were used. The ionic strength was maintained at 1 *M* using $NaClO_4$. The contribution of the McIlvaine buffers to the ionic strength was determined from the data of Elving, Markowitz and Rosenthal.[16]

## Results and Discussion

The aquation of $\alpha$-*cis*- and $\beta$-*cis*-$[Co(CO_3)(edda)]^-$ were studied in the range $1 \leqq pH \leqq 5$ over a range of temperature*. Pseudo-first-order rate constants are recorded in Tables I and II. For both isomers the rate data fits rate laws of the form

$$k_{obs} = k_o + k_1[H^+] \qquad (1)$$

Rate constants for the acid catalysed path, $k_1$, were determined from the slopes of plots of $k_{obs}$ versus $[H^+]$ for runs at $pH \leqq 3$, where the acid catalysed path makes the dominant contribution to the aquation. The intercepts of similar plots at lower acidities gave rate constants, $k_o$, for the water catalysed path. Values of $k_o$ and $k_1$ at various temperatures and activation parameters are presented in Table III.

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* The $\beta$-*cis* isomer is the (SR, RS) racemate.[1]

TABLE I. Pseudo-first-order rate constants for the aquation of α-*cis*-$[Co(CO_3)(edda)]^-$.

| $[H^+]$(*M*) | $k_{obs}^{30.3°}$ ($s^{-1}$) | $k_{obs}^{25°}$ ($s^{-1}$) | $k_{obs}^{20°}$ ($s^{-1}$) |
|---|---|---|---|
| 0.10 | 13.5 | 0.2 | 5.02 |
| 0.05 | 6.9 | 4.18 | 2.47 |
| 0.02 | 2.60 | 1.72 | 1.04 |
| 0.01 | 1.21 | 0.81 | 0.476 |
| 0.0032 | 0.380 | 0.239 | 0.155 |
| 0.001 | 0.136 | 0.075 | 0.052 |
| 0.0001 | 0.0164 | 0.0109 | 0.0056 |
| 0.000032 | 0.0077 | 0.00462 | 0.00261 |
| 0.00001 | 0.0053 | 0.00326 | 0.00154 |

TABLE II. Pseudo-first-order rate constants for the aquation of β-*cis*-$[Co(CO_3)(edda)]^-$.

| $[H^+]$(*M*) | $k_{obs}^{30.3°}$ ($s^{-1}$) | $k_{obs}^{25°}$ ($s^{-1}$) | $k_{obs}^{20°}$ ($s^{-1}$) |
|---|---|---|---|
| 0.10 | 0.531 | 0.309 | 0.182 |
| 0.05 | 0.228 | 0.145 | 0.089 |
| 0.02 | 0.097 | 0.067 | 0.0359 |
| 0.01 | 0.053 | 0.0360 | 0.0174 |
| 0.0032 | 0.0146 | 0.0094 | 0.0060 |
| 0.001 | 0.0055 | 0.00370 | 0.00177 |
| 0.0004 | 0.00269 | 0.00158 | 0.00089 |
| 0.0002 | 0.00162 | 0.00102 | 0.000600 |
| 0.0001 | 0.00123 | 0.00066 | 0.000339 |

The mechanism of aquation of the α-*cis*- and β-*cis*-$[Co(CO_3)(edda)]^-$ isomers is thought to be identical with that postulated for cationic carbonate complexes,[3–6] viz:

$$[Co(CO_3)(edda)]^- + H_2O \xrightarrow{k_o} [Co(OH)(CO_3H)(edda)]^- \quad (2)$$

$$[Co(CO_3)(edda)]^- + H_3O^+ \xrightarrow{k_1} [Co(CO_3H)(edda)(OH_2)] \quad (3)$$

$$[Co(CO_3H)(edda)(OH_2)] + H_2O \xrightarrow{K_1} [Co(OH)(CO_3H)(edda)]^- + H_3O^+ \quad (4)$$

$$[Co(CO_3H)(edda)(OH_2)] \xrightarrow{k_2} [Co(OH)(edda)(OH_2)] + CO_2 \quad (5)$$

$$[Co(edda)(OH_2)_2]^+ + H_2O \xrightarrow{K_2} [Co(OH)(edda)(OH_2)] + H_3O^+ \quad (6)$$

Rate-determining carbonate ring opening occurs through both water and acid attack, reactions (2) and (3), followed by a rapid decarboxylation, reaction (5). Reactions (4) and (6) are rapid proton transfer reactions.

A comparison of the data obtained here with that reported for various cationic carbonate complexes is made in Table IV. For both α-*cis*- and β-*cis*-$[Co(CO_3)(edda)]^-$ the rate constants for the acid and water catalysed paths are at least ten times greater than for the analogous $[Co(CO_3)(trien)]^+$ isomers. The rate constants for the aquation of α-*cis*-$[Co(CO_3)(edda)]^-$ are almost ten times greater than has been found for any other bidentate carbonate complex.

For the water catalysed path ($k_0$) the enhanced rate found for the $[Co(CO_3)(edda)]^-$ isomers results from a more favourable entropy of activation. Similarly for the acid catalysed path ($k_1$) the activation enthalpies are not greatly different from those found for the cationic complexes but the activation entropies are clearly more favourable. The more positive entropies of activation may result from a higher degree of solvent orientation around the reactant complex. The enhanced opportunity for hydrogen-bonding in edda complexes has been discussed.[2] Dasgupta and Harris[4] have pointed out that the transition state for the water catalysed path must include a very specifically orientated water molecule. This was thought to be the reason for the relatively unfavourable activation entropy for this path compared with the acid catalysed path, where proton addition to the chelated carbonate might only be necessary to form the transition state. It seems reasonable that a water molecule hydrogen-bonded to adjacent carbonate and acetate oxygen atoms (Figure 1) may provide a situation similar to that Dasgupta and Harris consider necessary to enable simultaneous displacement of the oxygen atom of the carbonate group and proton transfer to

TABLE III. Rate constants and activation parameters[a] for the aquation of the α-*cis*- and β-*cis*-$[Co(CO_3)(edda)]^-$ ions.

| Temp. °C | α-*cis* $10^4k_o$ ($s^{-1}$) | $k_1$($M^{-1}s^{-1}$) | β-*cis* $10^4k_o$ ($s^{-1}$) | $k_1$($M^{-1}s^{-1}$) |
|---|---|---|---|---|
| 20 | 11.3 | 50.1 | 1.92 | 1.82 |
| 25 | 21.7 | 82.6 | 3.80 | 3.04 |
| 30.3 | 39.4 | 136 | 6.90 | 5.23 |
| | $\Delta H_o^* = 87 \pm 13$ | $\Delta H_1^* = 69 \pm 4$ | $\Delta H_o^* = 89 \pm 13$ | $\Delta H_1^* = 73 \pm 4$ |
| | $\Delta S_o^* = 0 \pm 50$ | $\Delta S_1^* = 23 \pm 13$ | $\Delta S_o^* = 10 \pm 50$ | $\Delta S_1^* = 10 \pm 13$ |

[a] The enthalpy of activation, $\Delta H^*$, is given in kJ $mol^{-1}$; the entropy of activation, $\Delta S^*$, in $JK^{-1}$ $mol^{-1}$.

TABLE IV. Rate parameters for the aquation reactions of various cobalt(III) carbonate complexes at 25°.[a]

| Complex | $10^4 k_o$ ($s^{-1}$) | $\Delta H_o^*$ (kJ $mol^{-1}$) | $\Delta S_o^*$ ($JK^{-1}$ $mol^{-1}$) | $k_1$ ($M^{-1}$ $s^{-1}$) | $\Delta H_1^*$ (kJ $mol^{-1}$) | ($JK^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|---|---|
| $[Co(CO_3)(NH_3)_4]^+$ | 1.3 | 50 | –155 | 1.5 | 64 | –26 |
| $[Co(CO_3)(en)_2]^+$ | 1.2 | 75 | –63 | 0.6 | 58 | –31 |
| $[Co(CO_3)(pn)_2]^+$ | 1.0 | 75 | –63 | 0.5 | 59 | –55 |
| $[Co(CO_3)(tn)_2]^+$ | 0.8 | 67 | –88 | 0.8 | 50 | –80 |
| $[Co(CO_3)(tren)]^+$ | 1.7 | 63 | –105 | 2.0 | 46 | –84 |
| *cis*-$[Co(CO_3)(NH_3)_2(en)]^+$ | 0.3 | 71 | –101 | 0.9 | 67 | –17 |
| *trans*-$[Co(CO_3)(NH_3)_2(en)]^+$ | 1.1 | 80 | –59 | 8.9 | 42 | –84 |
| α-*cis*-$[Co(CO_3)(trien)]^+$ | 1.5 | 84 | –29 | 5.2 | 63 | –21 |
| β-*cis*-$[Co(CO_3)(trien)]^+$ | 0.1 | 71 | –97 | 0.2 | 71 | –21 |
| α-*cis*-$[Co(CO_3)(edda)]^-$ | 22 | 87 | –4 | 83 | 69 | +23 |
| β-*cis*-$[Co(CO_3)(edda)]^-$ | 3.8 | 89 | –11 | 3.0 | 73 | +10 |

[a] All values except those for the edda complexes were taken from reference 6.

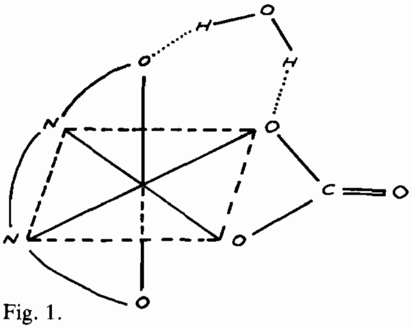

Fig. 1.

that oxygen atom. The presence of this specifically orientated water molecule attached to the reactant complex would reduce the amount of ordering required in the formation of the transition state and would lead to a more positive activation entropy, as was observed.

The acid catalysed path for the cationic complexes is a reaction between two unipositive ions and many of these complexes have activation entropies of the order of –20 to –40 $JK^{-1}$ $mol^{-1}$. This is of the order predicted for a reaction between unipositive ions on the basis of electrostatic theory.[4,17] In the acid catalysed aquation of the $[Co(CO_3)(edda)]^-$ isomers the reaction is between unipositive and uninegative ions. For reactions in which ions come together in the transition state with a neutralisation of charge solvent molecules are released and the entropy of activation becomes more positive.[18] On the basis of the electrostatic theory[17] one would predict an entropy of activation of between +20 and +40 $JK^{-1}$ $mol^{-1}$ and the observed values are in fact positive, being respectively 23 and 10 $JK^{-1}$ $mol^{-1}$ for the α-*cris* and β-*cis* isomers.

Dasgupta and Harris[6] observed that complexes in which an amine bridge was diagonal to the carbonate chelate aquated less rapidly than isomeric forms in which the amine bridge was coplanar with the carbonate group. This was attributed to a lessening of the strain of the O–Co–O linkage for which the bond angle is of the order of 70° compared with the normal angle in octahedral structures of 90°.[3] α-*cis*-$[Co(CO_3)(trien)]^+$, with an amine bridge coplanar with the carbonate group, was found to aquate about 26 times faster than the β-*cis* analogue in which the amine bridge was situated diagonally to the carbonate group. For the $[Co(CO_3)(edda)]^-$ isomers the α-*cis* aquates about 27 times faster than the β-*cis* but the increased rate appears to be due to a combination of enthalpy and entropy factors.

Harris *et al.*[4–6] have postulated that decarboxylation occurs only through the decomposition of the dicarbonatoaqua complex according to reaction (5). The pK for the reaction

$$cis\text{-}[Co(CO_3H)(OH_2)N_4]^{2+} + H_2O \overset{K_1}{\rightleftharpoons} cis\text{-}[Co(OH)(CO_3H)N_4]^+ + H_3O^+ \quad (7)$$

is of the order of 6[3,4] for bipositive ions and it is therefore reasonable to consider that under the experimental conditions investigated (i.e. pH < 5) decarboxylation occurs only through the $[Co(CO_3H)(OH_2)N_4]^{2+}$ species. For the edda complexes the pK is likely to be even larger owing to a reduction of two units of charge on the complex. Thus in these systems decarboxylation should again occur only *via* the bicarbonatoaqua species, reaction (5). The resultant hydroxoaqua product will quickly pick up a proton to form the diaqua complex, reaction (6).

The decarboxylation of the $[Co(CO_3H)(NH_3)_5]^{2+}$ ion was found to occur[14] with a rate constant of 1.25 $s^{-1}$ at 25° and an estimate[3] of 2 $s^{-1}$ has been made for the rate constant of decarboxylation of *cis*-$[Co(CO_3H)(OH_2)(en)_2]^{2+}$. For α-*cis*-$[Co(CO_3)(edda)]^-$ the second order rate constant governing ring opening at 25° is 83$M^{-1}$ $s^{-1}$. If the rate of decarboxylation is similar here to that found for cationic complexes, a two stage process should be observable over much of the acid range investigated. At low pH's ($[H^+] > 0.02M$) the decarboxylation would be rate-determining whereas at higher pH's ($[H^+] < 0.02M$) ring opening would be rate determining. As the data could be accounted for in terms of a single rate-determining process it is postulated that decarboxylation in this complex (and possibly also in the *β-cis* isomer) is much faster than was observed for the cationic complexes. Dasgupta and Harris[14] have proposed a mechanism of decarboxylation in which the transition state is of the form shown in Figure 2. The hydrogen of the monodentate bicarbonate is hydrogen-bonded to the oxygen attached to the cobalt, causing a weakening of the O*–C bond and facilitating O*–C bond rupture. i.e. decarboxylation. In the $[Co(CO_3H)(edda)(OH_2)]$ isomers there is an increased negative charge on the central cobalt atom (arising from the edda ligand). This would lead to a weakening of the Co–O* bond and an increase in the basicity of the oxygen atom (O*) attached to the cobalt atom. This more basic oxygen atom would facilitate hydrogen-bonding from the bicarbonate hydrogen and by weakening the O*–C– bond would enhance the rate of decarboxylation. The much faster rate of decarboxylation of the anion $[Co(CO_3)(NTA)]^{2-}$ (NTA = nitrilotriacetate) $(k^{20^\circ} = 34.5\ s^{-1})$[19] than for various cationic species provides some evidence in support of this argument.

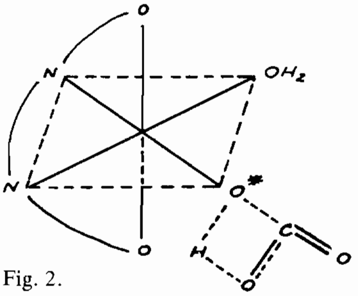

Fig. 2.

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