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Ethylenediaminediacetate Complexes of Cobalt(III). Part II. The Aquation of α-*cis*- and β-*cis*-$[CoCl_2(edda)]^-$ and α-*cis*- and β-*cis*-$[CoCl(edda)(OH_2)]$

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The aquation of both the α-cis and β-cis isomers of $[CoCl_2(edda)]^-$ *have been studied over a range of temperatures. The reactions occur with total retention and the rates are independent of acid concentration. The rates are surprisingly little different from the aquation of the stereochemically similar cationic isomers of* $[CoCl_2(trien)]^+$.

The aquation of the $[CoCl(edda)(OH_2)]$ *isomers are base catalysed through reactions of the hydroxochloro species and are also stereoretentive. The pK values of the chloroaqua species have been determined and the activation parameters found for the reactions through the aquation and base catalysed paths.*

All reaction features are consistent with a dissociative mode of reaction.

Introduction

We have recently published the preparation and stereochemical identification of a series of ethylenediaminediacetate complexes of cobalt(III).[1] The aim of that study was to prepare a series of anionic complexes whose kinetics could be studied for comparison with the wealth of data already available for cationic cobalt(III) complexes.[2–8] In particular the results of this work will be compared with those on the stereochemically similar isomers of $[CoCl_2(trien)]^+$.[9]

Based on classical arguments[3] it has been concluded that anionic complexes would favour a dissociative mode of reaction and that the rates of reaction should be appreciably faster than similar cationic cobalt(III) compounds. The most studied anionic complexes of cobalt(III) have cyanate and dimethylglyoximate ligands. These show a strong tendency to the dissociative mode and react significantly faster than the amine complexes.[10]

Adamson[11] postulated specific solvation effects which he considered facilitated a front side displacement aquation reaction in the *cis*-$[CoCl(NO_2)(en)_2]^+$ ion. Special sites for hydrogen-bonding solvation interactions exist between chloro and aqua ligands *cis* to the carboxyl group of the edda ligand. These interactions must contribute to differences between the reactions of the edda complexes and the analogous cationic complexes.

Experimental

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

The rates were measured using a Perkin Elmer 450 Spectrophotometer on repetitive scan. Rate constants were determined from $\log(D-D_\infty)$ versus time plots using wavelengths which corresponded to the isosbestic points in the spectra of primary and secondary reaction products, and were thus for reactant removal. Solutions were acidified with $HClO_4$ and ionic strength was maintained at 1.0 dm^{-3}mol using recrystallised $NaClO_4$.

Acid dissociation constants were determined by potentiometric titration of solutions of complex with standard, carbonatefree sodium hydroxide under a nitrogen atmosphere and were calculated by the method of Noyes.[12]

Results and Discussion

The rates of the aquation reactions:

$$[CoCl_2(edda)]^- + H_2O \rightarrow [CoCl(edda)(OH_2)] + Cl^- \quad (1)$$

were determined spectrophotometrically over the acidity range $10^{-3} \leqq [H^+] \leqq 1$ dm^{-3}mol for both the α-*cis* and β-*cis* isomers.* Aquation of both isomers give 100% loss of the first chloride under these conditions and the rates are independent of $[H^+]$. (Tables I and II.) Rotatory dispersion curves of solutions (10^{-2} dm^{-3}mol $HClO_4$, 1 dm^{-3}mol $NaClO_4$) of the Λ-α-*cis* and Λ-β-

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* The β-*cis* isomer is thought to be the (*SR,RS*) racemate.[1]

TABLE I. First-order rate constants (k_{obs}) for the aquation of α-*cis*-$[CoCl_2(edda)]^-$.[a]

Temperature (° C)	$[H^+]$ (dm^{-3} mol)	$10^3\ k_{obs}$ (s^{-1})
24.5	1.0	0.212
24.5	0.10	0.210
24.5	0.01	0.208
24.5	0.001	0.206
29.4	0.10	0.389
34.1	0.10	0.705
37.1	0.10	1.00

[a] From Kα-*cis*-$[CoCl_2(edda)]\cdot H_2O$.

TABLE II. First-order rate constants (k_{obs}) for the aquation of β-*cis*-$[CoCl_2(edda)]^-$.[a]

Temperature (° C)	$[H^+]$ (dm^{-3} mol)	$10^3\ k_{obs}$ (s^{-1})
25.3	1.0	1.79
25.3	0.10	1.79
25.3	0.01	1.76
25.3	0.001	1.80
20.5	0.10	0.914
16.0	0.10	0.555
28.9	0.10	2.76

[a] From Kβ-*cis*-$[CoCl_2(edda)]\cdot H_2O$.

cis isomers show that both reactions occurred with retention of absolute configuration.[1]

The rate parameters for the stereoretentive aquation of several *cis* dichloro cobalt(III) complexes are presented in Table III. A dissociative mechanism has been proposed[3,4,7,8] for the aquation of complexes of the form *cis*-$[CoCl_2N_4]^+$ and it is postulated that the α-*cis*- and β-*cis*-$[CoCl_2(edda)]^-$ isomers aquate by the same mechanism.

In the α-*cis* complex the two positions occupied by chloride ions are equivalent. This is not so in the β-*cis* isomer and the rate constant could have been a composite one, resulting from the unequal rates of dissociation of chloride from the two non-equivalent positions. However the visible spectra and R.D. curves show no evidence for the formation of two β-*cis*-$[CoCl(edda)(OH_2)]$ species and it is therefore apparent that one chloride aquates much more readily than the other. This was also true for β-*cis*-$[CoCl_2(trien)]^+$ where the chloride *trans* to the "planar" *sec*-N aquates about twenty times faster than the chloride *trans* to the terminal amine of the R ring.[9]

A comparison of the rate parameters for the trien system[9] with those of the edda complexes (Table III) indicates several similarities. In the edda system the β-*cis* isomer aquates about eight times as fast as the α-*cis*. This compared with a factor of about nine for the trien complexes. Surprisingly, the edda complexes aquate at rates which are very similar to those observed for the trien system. The α-*cis* edda isomer aquates about 50% faster than the trien analogue and the β-*cis* edda complex aquates about 20% faster than the trien complex.

In the trien complexes the difference in rates between the α-*cis* and β-*cis* isomers is due to differences in both ΔH^* and ΔS^* but in the edda system the difference is due mainly to a lower ΔH^* for the β-*cis* isomer. It is possible that the smaller ΔH^* results from the formation of a slightly distorted incipient tetragonal pyramidal intermediate, allowing the release of some strain associated with the G ring glycinate arm.

The similarity in rates for the trien and edda systems is surprising. From classical considerations,[3] it was thought that the change in charge from +1 to −1 would produce a marked enhancement in the aquation rates. Furthermore the edda ligand coordinates through two carboxylate oxygen atoms which are capable of electron pair donation through π-bonding to the cobalt atom. The presence of potential π-donors results in an enhancement of aquation rates for complexes of the type $[CoXA(en)_2]^+$.[3,13,14] Neither of these effects appear to be significant, or rather, if they are significant they are counteracted by solvation effects.

TABLE III. Rate parameters for the aquation of several *cis* dichloro Cobalt(III) complexes.

Complex	10^3 k s^{-1} (at 25° C)	ΔH^* ($kJ\ mol^{-1}$)	ΔS^* ($JK^{-1}\ mol^{-1}$)
$[CoCl_2(en)_2]^+$	0.2[a]	90	−21
$[CoCl_2(tren)]^+$	2.96[b]	75	−42
$[CoCl_2(cyclam)]^+$	16.0[c]	77	−25
β-*cis*-(*RR*, *SS*)-$[CoCl_2(2,3,2\text{-}tet)]^+$	1.1[d]	93	8
α-*cis*-$[CoCl_2(trien)]^+$	0.156[e]	88	−25
β-*cis*-(*RR*, *SS*)-$[CoCl_2(trien)]^+$	1.45[e]	85	−13
α-*cis*-$[CoCl_2(edda)]^-$	0.225[f]	96 ± 5	−3 ± 15
β-*cis*-$[CoCl_2(edda)]^-$	1.73[f]	89 ± 5	1 ± 15

[a] ref. 4,16. [b] ref. 17. [c] ref. 4,18. [d] ref. 19. [e] ref. 9. [f] this work.

Favourable sites certainly exist in anionic $[CoCl_2(edda)]^-$ complexes for hydrogen-bonding to solvent water molecules but it is difficult to predict whether such structure will accelerate or inhibit reaction through the postulated dissociative process. Strong solvation with specific solvent ordering about a reactant can lead to slow aquation rates, if the increase in enthalpy required for desolvation is not compensated by an increase in entropy derived from the loss of order during activation.

The results in Table III show that the edda complexes have higher activation enthalpies and more favourable activation entropies than their trien analogues. These high activation enthalpies can be accounted for if the dissociation of a chloride ion requires more energy to disrupt the highly structured solvation shell of the edda system. The more favourable activation entropies can be interpreted on the basis of charge and solvation effects. The formation of the transition state for the edda complexes requires at least the partial development of a chloride ion and a neutral species from a large uninegative ion. In the trien complexes a large bipositive ion and a chloride ion are developing from a unipositive ion. There is therefore likely to be a greater increase in solvent orientation accompanying the formation of the transition state in the trien complexes than the edda complexes. This of course would produce a more positive ΔS^* for the edda complexes, as we observed. Further it can be argued that the dissociation of a chloride ion from an edda complex destructures a highly organised complex environment provided the chloride is not free enough at the transition state to develop its own separate order. This would also result in a relatively more positive ΔS^* for the edda complexes.

The Hg^{2+} induced aquations of the *α-cis-* and *β-cis-* $[CoCl_2(edda)]^-$ isomers also occur with retention of configuration. Although it is envisaged that both the spontaneous and induced aquations occur via a dissociative mechanism it is unlikely that the five-coordinate intermediate is as fully developed in the spontaneous aquation. It seems likely that in the spontaneous reaction, the dissociation of a chloride is accompanied by the concomitant interchange of a water molecule from the intimately connected solvation sphere.

The rates of the reactions:

$$[CoCl(edda)(OH_2)] + H_2O \rightarrow [Co(edda)(OH_2)_2]^+ + Cl^-$$

were determined for the *α-cis* and *β-cis* isomers over the acidity ranges $10^{-4} < [H^+] < 10^{-1}$ dm^{-3}mol and $5 \times 10^{-3} < [H^+] < 1$ dm^{-3}mol respectively. Both isomers aquate with 100% loss of chloride under the conditions investigated. R.D. curves of solutions (10^{-2} dm^{-3}mol $HClO_4$, 1 dm^{-3}mol $NaClO_4$) of the *Λ-α-cis* and *Λ-β-cis* isomers (obtained by allowing optically pure samples of the dichloro complexes to aquate spontaneously) showed that both reactions occurred with retention of absolute configuration.[1] Summaries of kinetic runs for the two isomers are presented in Tables IV and V. The kinetic data fits rate laws of the form:

$$k_{obs} = k_1 + k_2/[H^+] \quad (3)$$

Plots of k_{obs} versus $1/[H^+]$ at the various temperature (Figures 1 and 2) give straight lines from which k_1 (intercept) and k_2 (slope) can be evaluated. Values of k_1 and k_2 and activation parameters based on the

TABLE IV. Pseudo-first-order rate constants (k_{obs}) for the aquation of *α-cis*-$[CoCl(edda)(OH_2)]$.[a]

Temperature (° C)	$[H^+]$ (dm^{-3} mol)	10^3 k_{obs} (s–1)
44.5	0.100	0.140
44.5	0.0100	0.146
44.5	0.00100	0.176
44.5	0.00050	0.212
44.5	0.000100	0.486
50.8	0.100	0.284
50.8	0.0100	0.291
50.8	0.00100	0.360
53.6	0.100	0.387
53.6	0.0100	0.412
53.6	0.00100	0.549
57.8	0.100	0.609
57.8	0.0100	0.637
57.8	0.00100	0.823

[a] From *α-cis*-$[CoCl(edda)(OH_2)]\cdot H_2O$.

TABLE V. Pseudo-first-order rate constants (k_{obs}) for the aquation of *β-cis*-$[CoCl(edda)(OH_2)]$.[a]

Temperature (° C)	$[H^+]$ (dm^{-3} mol)	10^3 k_{obs} (s^{-1})
54.0	1.00	0.233
54.0	0.200	0.284
54.0	0.100	0.345
54.0	0.0500	0.464
54.0	0.0200	0.815
54.0	0.010	1.34
54.0	0.0050	2.41
49.4	1.00	0.132
49.4	0.100	0.197
49.4	0.0100	0.788
49.4	0.0050	1.39
44.5	1.00	0.074
44.5	0.100	0.120
44.5	0.0100	0.513
44.5	0.0050	0.931
40.7	1.00	0.0420
40.7	0.100	0.0700
40.7	0.0100	0.333
40.7	0.0050	0.576

[a] From *β-cis*-$[CoCl(edda)(OH_2)]\cdot 2H_2O$.

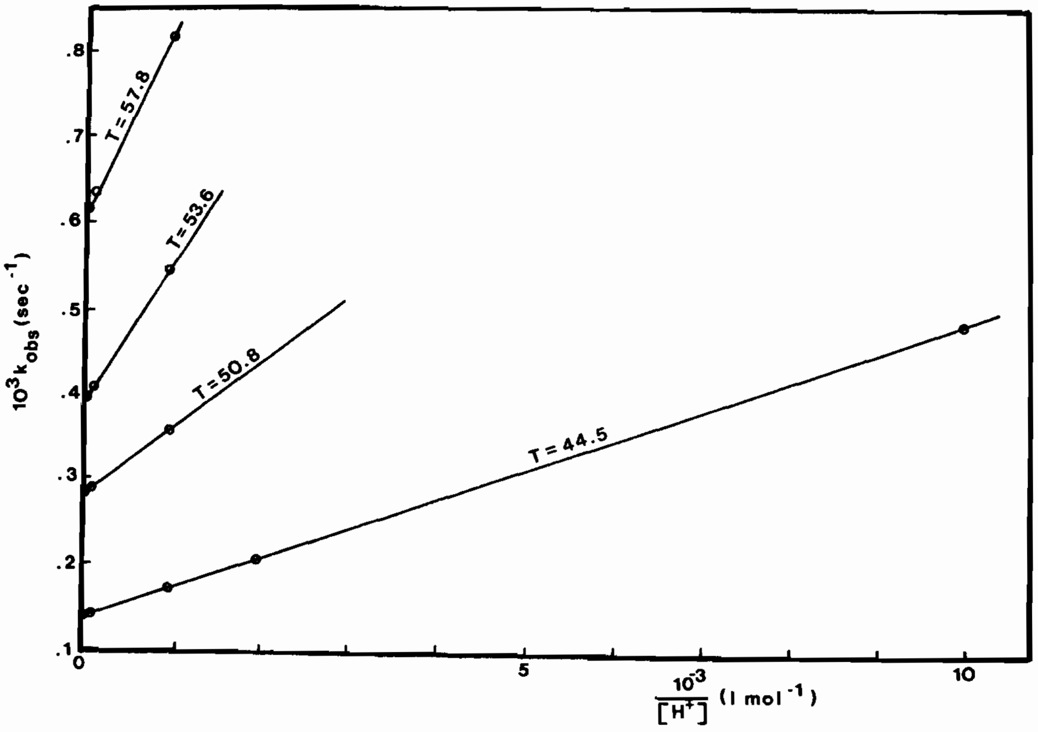

Figure 1. Plots of k_{obs} against $^1/_{[H^+]}$ at various temperatures for aquation of α-*cis*-[CoCl(edda)(OH_2)].

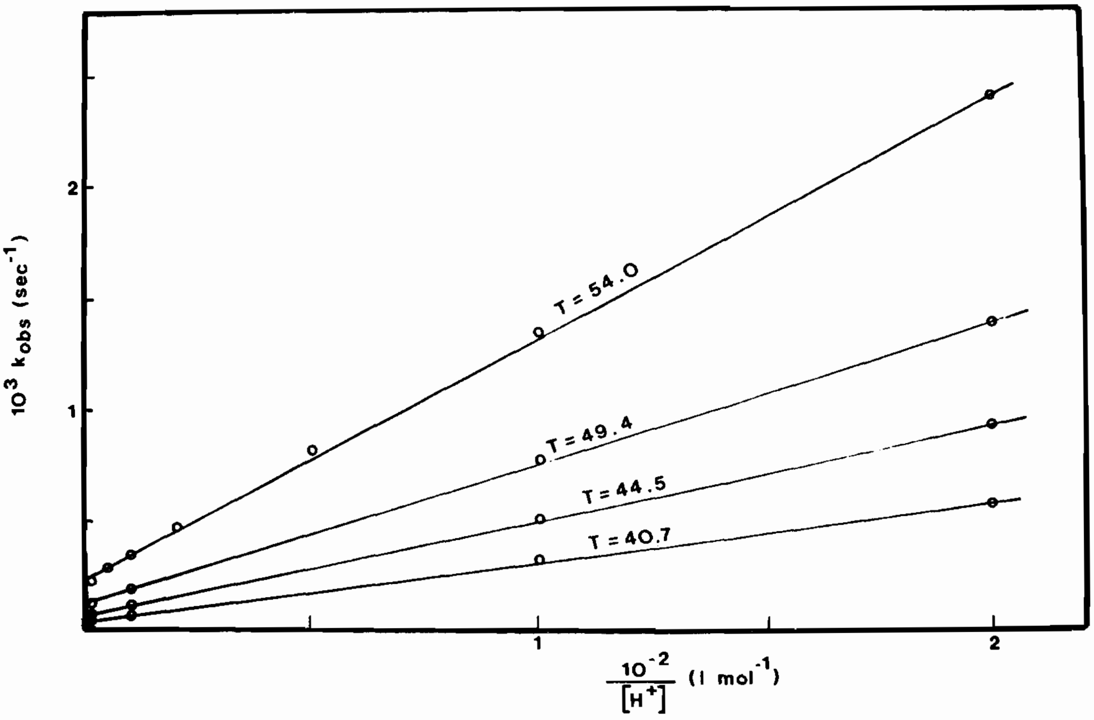

Figure 2. Plots of k_{obs} against $^1/_{[H^+]}$ at various temperatures for aquation of β-*cis*-[CoCl(edda)(OH_2)].

temperature dependence of k_1 and k_2 are recorded for the *α-cis* and *β-cis* isomers in Table VI.

The acid dependence of the observed rate constants is the result of pH dependent pre-equilibria. These equilibria are between the chloroaqua and hydroxochloro species, viz:

$$[\mathrm{CoCl(edda)(OH_2)}] + \mathrm{H_2O} \xrightleftharpoons{\mathrm{K_a}} [\mathrm{Co(OH)Cl(edda)}]^- + \mathrm{H_3O^+} \quad (4)$$

These two species react to produce diaqua complexes which in turn are involved in acid–conjugate base equilibria according to the reaction sequence:

$$\begin{array}{l} [\mathrm{CoCl(edda)(OH_2)}] + 2\mathrm{H_2O} \xrightleftharpoons{\mathrm{K_a}} \\ \qquad \downarrow \mathrm{k_3} \quad [\mathrm{Co(OH)Cl(edda)}]^- + \mathrm{H_3O^+} + \mathrm{H_2O} \\ [\mathrm{Co(edda)(OH_2)_2}]^+ + \mathrm{H_2O} + \mathrm{Cl^-} \xrightleftharpoons{\mathrm{K_{a1}}} \ \downarrow \mathrm{k_4} \qquad (5) \\ \qquad\qquad [\mathrm{Co(OH)(edda)(OH_2)}] + \mathrm{H_3O^+} + \mathrm{Cl^-} \end{array}$$

K_a and K_{a1} are the acid dissociation constants of the chloroaqua and diaqua complexes respectively. This mechanism gives a rate law of the form:

$$k_{obs} = \frac{k_3 + k_4K_a/[\mathrm{H^+}]}{1 + K_a/[\mathrm{H^+}]} \qquad (6)$$

Under the acidity conditions investigated $K_a/[\mathrm{H^+}] \ll 1$ and the rate law simplifies to:

$$k_{obs} = k_3 + k_4K_a/[\mathrm{H^+}] \qquad (7)$$

This is of the same form as the experimentally derived expression (3) and thus the rate constant k_1 relates to the rate of aquation of the chloroaqua complex and k_2 (= k_4K_a) determines the rate of aquation of the hydroxochloro species.

The acid dissociation constants (pK_a) for *α-cis*-[CoCl(edda)(OH$_2$)] are 8.5 ± 0.1 and 8.2 ± 0.1 at 10° and 20° respectively, while the values at the same temperatures for the *β-cis* isomer are 6.5 ± 0.1 and 6.2 ± 0.1.

It is characteristic of chloroaqua complexes of cobalt(III) to aquate via two paths.[9,15] The extent to which each path contributes to the overall rate at a particular acidity is dependent on the pK_a of the chloroaqua species. The lower pK_a of the *β-cis* isomer is consistent with the greater contribution made to the rate by the *β-cis*-[Co(OH)Cl(edda)]$^-$ species. The pK_a's of the edda complexes are higher than for the trien analogues. For the *α-cis* isomers $pK_a^{20°}$ for the edda complex is 8.2 (7.1 for the trien complex) while for the *β-cis* isomer the $pK_a^{20°}$ is 6.2 (5.9 for the trien analogue). The lower pK_a's for the trien complexes is consistent with the increase of +2 in charge.

The rate parameters for aquation of the chloroaqua species at 40° are presented for the edda and trien complexes in Table VII. The edda complexes aquate at faster rates than the trien complexes. The lower values of ΔH^* for the edda complexes may result from easier dissociation of a chloride ion from a developing unipositive ion, compared with a tripositive ion for the trien complex. Charge separation was not the dominant feature in the dichloro complexes as the edda complexes had higher activation enthalpies than the trien

TABLE VII. Rate constants at 40° and activation enthalpies for the aquation of some edda[a] and trien[b] complexes of cobalt(III).

Complex	k s^{-1}	ΔH^* kJ mol^{-1}
α-cis-[CoCl(edda)(OH$_2$)]	7.9 × 10^{-5}	94 ± 5
α-cis-[CoCl(OH$_2$)(trien)]$^{2+}$	0.377 × 10^{-5}	101
β-cis-[CoCl(edda)(OH$_2$)]	4.1 × 10^{-5}	103 ± 5
β-cis-[CoCl(OH$_2$)(trien)]$^{2+}$	1.8 × 10^{-5}	113
α-cis-[Co(OH)Cl(edda)]$^-$	80 × 10^{-2}	70 ± 20
α-cis-[Co(OH)Cl(trien)]$^+$	1.6 × 10^{-2}	80
β-cis-[Co(OH)Cl(edda)]$^-$	140 × 10^{-2}	40 ± 20
β-cis-[Co(OH)Cl(trien)]$^+$	32 × 10^{-2}	80

[a] This work. [b] Ref. 9.

TABLE VI. Rate constants and activation parameters for the aquation of the *cis*-[CoCl(edda)(OH$_2$)] isomers.

Isomer	Temperature (°C)	$10^3 k_1$[c] (s^{-1})	$10^7 k_2$[c] (dm^3 mol^{-1} s^{-1})	ΔH_1^*	ΔH_2^*[d]	ΔS_1^*	ΔS_2^*[d]
				(kJ mol^{-1})		(JK^{-1} mol^{-1})	
α-cis[a]	44.5	0.140	0.364	94 ± 5	70 ± 20	–23 ± 15	–30 ± 60
	50.8	0.283	0.767				
	53.6	0.391	1.59				
	57.8	0.611	2.12				
β-cis[b]	40.7	0.046	27.0	103 ± 5	40 ± 20	0 ± 15	–110 ± 60
	44.5	0.075	43.0				
	49.4	0.135	63,3				
	54.0	0.240	109				

[a] From *α-cis*-[CoCl(edda)(OH$_2$)]·H$_2$O. [b] From *β-cis*-[CoCl(edda)(OH$_2$)]·2H$_2$O. [c] Defined by Equation 3. [d] Activation parameters corrected for temperature dependence of K_a's.

complexes. However the dichloro complexes may offer unique sites for hydrogen-bonding with solvent water molecules. Apart from the presence of the *cis* chlorine and oxygen atoms, the overall negative charge on the dichloro complexes may enhance the hydrogen-bonding interaction with solvent water molecules.

It is interesting that the β-*cis* chloroaqua complex aquates more slowly than the α-*cis* isomer, while the β-*cis* dichloro and hydroxochloro complexes aquate more rapidly than the α-*cis* analogues. The higher ΔH^* responsible for the decreased rate seems to result from a more highly structured solvent environment of the β-*cis* complex, which also correlates with the more positive ΔS^* for this isomer.

The rate parameters for aquation of the hydroxochloro complexes at 40° are also tabulated for the edda and trien systems in Table VII. The large uncertainty in the activation parameters arises from error in the K_a measurements.

Again the edda complexes react faster than their trien analogues. A detailed consideration of the activation parameters is scarcely warranted in view of the uncertainty in their measurement. However it seems that the edda complexes have lower activation enthalpies than the trien complexes and charge factors again appear to offer a logical explanation.

It seems that the aquations of the chloroaqua and hydroxochloro complexes of edda proceed via dissociative mechanisms similar to the dichloro complexes. The greatly enhanced rate of the hydroxochloro compared with the chloroaqua complex ($\sim 10^4$ for the α-*cis* and $\sim 3 \times 10^4$ for the β-*cis* isomer) is typical of cobalt(III) complexes.[9, 15] It is thought to be a consequence of π-donation from a filled oxygen p orbital to the d^2sp^3 cobalt orbital vacated by chloride dissociation, leading to enhanced stability of the transition state.[3]

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