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The Base Hydrolysis of the Malonatobis(ethylenediamine)cobalt(III) Cation

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The base hydrolysis of the $[Coen_2mal]^+$ *cation has been studied. In solutions of low hydroxide concentration, the reaction is one stage and the product is a mixture of the cis and trans*$[Coen_2(OH)_2]^+$ *ions. Spectrophotometric and polarimetric second order rate constants measured under the same conditions are identical. In solutions of ionic strength near 3.7 mol* dm^{-3}*, there is a pre-equilibrium, which is medium dependent; and an apparent limiting rate is reached when the hydroxide concentration is more than about 2 mol* dm^{-3}*. The mechanisms of the reaction are discussed.*

Introduction

In previous papers,[1a,2] we have described work on the base hydrolysis of some carboxylato-bis(ethylenediamine)cobalt(III) cations, and have recently described some of the problems encountered in assigning a mechanism to such a reaction.[3] This paper presents the results of the study of the alkaline hydrolysis of the malonato bis(ethylenediamine)cobalt(III) ions.

Experimental and Results

Preparation of the Complexes

Malonatobis(ethylenediamine)cobalt(III) bromide was prepared by the method of Price and Duff[4], and resolved by means of the optically active[5] K[CoEDTA]. The method of resolution was similar to that used by Dwyer[6] for the resolution of $[Coen_2C_2O_4]^+$. The iodide salt used in this work had $[M]_{597nm} = +2.400$.

Kinetics

(a) Solutions of ionic strength 0.1 mol dm^{-3}. The complex solution, sodium hydroxide solution, and sodium perchlorate to maintain ionic strength, were placed in a thermostatted vessel. At known time intervals samples were withdrawn and run into a known volume of perchloric acid cooled in ice. The spectra of the samples (then containing unreacted $[Coen_2mal]^+$ and $[Coen_2(OH_2)_2]^{3+}$ as product, since the reaction is one-stage) were measured using a Unicam SP 500 spectrophotometer. Rate constants k_2, Table I, were obtained from the slopes of the graphs of $\log_{10}a(b-2x)/b(a-x)$ against time, where a and b represent the initial concentrations of the complex and hydroxide, and x was calculated from the known spectra of the $[Coen_2mal]^+$ ion and of the equilibrium mixture[7] of the $[Coen_2(OH)_2]^+$ ions measured in acid solution, where appropriate (see Table I).

(b) Solutions of ionic strength ~1.0 mol dm^{-3} or 3.7 mol dm^{-3}. A known volume of standard complex solution was added to standard sodium hydroxide together with sodium perchlorate or sodium chloride solution in a thermostatted cell in a Unicam SP 700 recording spectrophotometer. The change in absorbance at 20,000 cm^{-1} was recorded as a function of time. Semi-log plots of $\log_{10}(A_t-A_\infty)$ *versus* time, where A_t is the absorbance at time t and A_∞ is the absorbance at 'infinity', gave pseudo first order rate constants. (k_1, Tables III, V), which were divided by $[OH^-]$ to give second order rate constant, k_2. Spectra were scanned at known time intervals using a Unican SP 800 recording spectrophotometer fitted with a repeat scan attachment.

TABLE I. Spectrophotometric Rate Constants for the Base Hydrolysis of the $[Coen_2mal]^+$ Ion[a] (perchlorate media).

Temp °C	[Complex] mmol dm^{-3}	[NaOH] mol dm^{-3}	μ mol dm^{-3}	k_2 $mol^{-1}\ dm^3\ s^{-1}$
38.0	10.0	0.040	0.100	2.26×10^{-3}
38.0	10.0	0.060	0.100	2.39×10^{-3}
38.0	10.0	0.090	0.100	2.26×10^{-3} [b]
45.0	10.0	0.040	0.100	6.58×10^{-3}
45.0	10.0	0.090	0.100	6.40×10^{-3} [b]
55.0	10.0	0.040	0.100	2.59×10^{-2}
55.0	10.0	0.060	0.100	2.56×10^{-2}
62.0	5.0	0.044	0.104	4.83×10^{-2}
62.0	5.0	0.066	0.104	4.81×10^{-2}
45.0	10.0	0.040	0.050	8.00×10^{-3}
45.0	10.0	0.040	0.070	7.29×10^{-3}
45.0	10.0	0.040	0.139	6.24×10^{-3}

[a] Solutions acidified before measurement. [b] Product is *cis* $[Coen_2(OH_2)_2]^{3+}$.

TABLE II. Rate Constants for the Loss of Optical Activity from the [Coen$_2$mal]$^+$ Ion. [Complex] = 1.25 mmol dm^{-3}. μ = 0.0997 mol dm^{-3} (perchlorate media).

Temp °C	NaOH mol dm^{-3}	k$_2$ mol^{-1} dm^3 s^{-1}
37.3	0.0656	1.96×10^{-3}
37.3	0.0985	2.27×10^{-3}
43.0	0.0438	4.75×10^{-3}
43.0	0.0656	4.70×10^{-3}
43.0	0.0985	5.11×10^{-3}
52.0	0.0438	1.82×10^{-2}
52.0	0.0656	1.90×10^{-2}
52.0	0.0985	1.95×10^{-2}

TABLE III. Rate Constants for the Base Hydrolysis of the [Coen$_2$mal]$^+$ Ion. Temp. = 37.5° C (perchlorate media).

[Complex] mmol dm^{-3}	[NaOH] mol dm^{-3}	μ mol dm^{-3}	10^{3}k$_1$ s^{-1}	10^{3}k$_2$ mol^{-1} dm^{-3} s^{-1}	A∞[a]
10.0	1.00	1.010	1.54	1.54	83
6.9	1.03	1.037	1.54	1.54	82
6.9	1.00	1.007	1.53	1.53	80
6.9	0.620	1.007	1.04	1.70	80
6.9	0.100	1.007	0.154	1.54	66[b]

[a] Molar absorbance of final solution measured at 20,000 cm^{-1} in alkaline conditions. [b] *cis/trans* equilibrium of [Coen$_2$(OH)$_2$]$^+$ Ions.

TABLE IV. Rate Constants for the Loss of Optical Activity from the [Coen$_2$mal]$^+$ Ion. μ = ∿1.0 mol dm^{-3} (perchlorate media). Temp. = 37.5° C.

[Complex] mmol dm^{-3}	[NaOH] mol dm^{-3}	10^{4}k$_1$ s^{-1}
1.40	1.00	8.25
0.905	1.00	8.50
6.25[a]	1.00	8.80
0.75	1.00	9.00

[a] Rotation measured on acidified samples.

TABLE V. Spectrophotometric Rate Constants for the Base Hydrolysis of the [Coen$_2$mal]$^+$ Ion. Temp. = 37.5° C, (perchlorate media, except where shown).

[Complex] mmol dm^{-3}	[NaOH] mol dm^{-3}	μ mol dm^{-3}	k$_1$ s^{-1}	k$_2$ mol^{-1} dm^3 s^{-1}
6.9	0.414	3.717	3.58×10^{-4}	8.64×10^{-4}
6.9	0.552	3.717	4.60×10^{-4}	8.34×10^{-4}
6.9	0.852	3.717	6.86×10^{-4}	8.32×10^{-4}
8.7	0.945	3.680	8.05×10^{-4}	8.53×10^{-4}
9.6[a]	0.945	3.679	5.70×10^{-4}	6.0×10^{-4}
6.9	1.030	3.717	9.00×10^{-4}	8.75×10^{-4}
6.9	1.380	3.717	1.13×10^{-3}	8.24×10^{-4}
8.7	1.630	3.679	1.34×10^{-3}	8.22×10^{-4}
9.6[a]	1.630	3.680	1.02×10^{-3}	6.35×10^{-4}
10.0	2.00	3.720	1.63×10^{-3}	8.15×10^{-4}
8.7	2.03	3.679	1.69×10^{-3}	8.30×10^{-4}
8.7[a]	2.03	3.679	1.34×10^{-3}	6.60×10^{-4}
9.6[a]	2.03	3.680	1.24×10^{-3}	6.10×10^{-4}
8.7	2.30	3.679	1.69×10^{-3}	7.32×10^{-4}
6.9	2.34	3.717	1.65×10^{-3}	7.10×10^{-4}
9.6[a]	2.70	3.680	1.37×10^{-3}	5.05×10^{-4}
6.9	2.75	3.717	1.58×10^{-3}	5.76×10^{-4}
6.9	3.03	3.717	1.62×10^{-3}	5.33×10^{-4}
6.9	3.44	3.717	1.53×10^{-3}	4.45×10^{-4}
8.7	3.67	3.679	1.53×10^{-3}	4.17×10^{-4}
6.9	3.71	3.717	1.45×10^{-3}	3.90×10^{-4}

[a] Chloride medium.

TABLE VI. Rate Constants for the Loss of Optical Activity from the [Coen$_2$mal]$^+$ Ion. μ = ∿3.6 mol dm^{-3}. Temp. = 37.5° C (perchlorate media).

[Complex] mmol dm^{-3}	[NaOH] mol dm^{-3}	10^{3}k$_1$ s^{-1}
1.40	2.0	0.90
1.38	2.8	1.17
1.38	3.6	1.17
1.55	3.6	1.15
3.77	3.6	1.15

Polarimetry

(a) The optically active malonato complex, [Coen$_2$mal]$^+$ together with standard sodium hydroxide and sodium perchlorate solutions were placed in a jacketted 10 cm polarimeter tube. The rotation was measured on a Hilger standard polarimeter at the mercury yellow line over a period of time. Pseudo first order rate constants (k$_1$, Tables IV, VI) were evaluated graphically and divided by the initial hydroxide concentration to give second order constants.

(b) The complex solution, sodium hydroxide and sodium perchlorate media were placed in a thermostatted vessel. At known time intervals samples were withdrawn and run into a known volume of hydrochloric acid cooled in ice. The rotation at the mercury yellow line was measured. Alternatively, the O.R.D. curves were measured using a Bendix–Ericson recording spectropolarimeter.

For all kinetic runs a graph was plotted of rotation against time and a smooth curve was drawn through the points. Rotations at known time intervals were read off the curve and were used to obtain semi-log plots.

Results of Kinetic Studies of the Hydrolysis of the [*Coen*$_2$*mal*]$^+$ *Ion*

Solutions of ionic strength ~ *0.1 mol dm*$^{-3}$*.*

The results of the spectrophotometric studies are shown in Table I. Under these conditions the product of reaction is the equilibrium mixture[7] of the *cis* and *trans* [Coen$_2$(OH)$_2$]$^+$ions, except where [OH$^-$] was 0.9*M*. ΔH^+ is 28.7 ± 1 Kcal mol^{-1} and ΔS^+ is +20 ± 2 cal K^{-1} mol^{-1}.
The rate is seen to decrease with increasing ionic strength.

The results of the polarimetric studies are shown in Table II.

Solutions of ionic strength approximately 1.0 mol dm^{-3}*.*

The results of the spectrophotometric studies are shown in Table III.

Polarimetric rate constants are shown in Table IV.

Solutions of ionic strength ~ *3.7 mol dm*$^{-3}$*.*

Spectrophotometric rate constants are shown in Table V.

The results of the polarimetric studies are shown in Table VI.

Scanning Experiments

It became evident from single wavelength studies that the initial spectrum varied with the hydroxide concentration, and that the ionic medium had an effect on the reaction. The initial spectra of reaction mixtures containing the complex with various concentrations of sodium hydroxide, both in perchlorate and in chloride media, were scanned over the range 15,000–30,000 cm^{-1} at 18.6° C. At this temperature changes in the spectra in the time taken for measurement were negligible. In some cases the mixture was acidified with hydrochloric acid and the spectrum was found to have reverted to that of the malonato complex.

A series of experiments was carried out in which the spectrum was scanned during the course of the reaction. The spectrophotometric changes and isosbestic points were dependent upon the initial spectrum. The initial and final spectra for two different conditions are shown in Figure 1. Pseudo first order rate constants were calculated from the changes in absorbance at 21,000 cm^{-1} (where the molar absorbances of the initial spectra vary little) and at 27,000 cm^{-1}. The constants were in agreement with those in Table V.

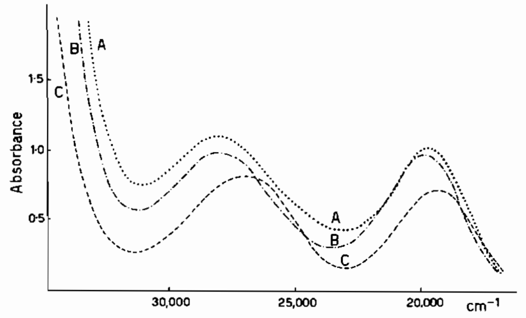


Figure 1. Spectra measured at the beginning (A and B) and at the end (C) of the base hydrolysis of the [Coen$_2$mal]$^+$ ion. [Complex] = 8.7 mmol dm^{-3}. Temp. = 37.5° C. μ = 3.7 mol dm^{-3} (perchlorate). A, initial spectrum, [NaOH] = 3.7 mol dm^{-3}; B, initial spectrum, [NaOH] = 2.03 mol dm^{-3}; C, final spectrum under both conditions.

In solutions where μ = ~ 0.1 mol dm^{-3}, the hydrolysis is slower than the equilibration of the dihydroxo-products, and their equilibrium mixture is obtained. However, for the runs in Table V in perchlorate media, where the isomerisation should be negligible, the final molar absorbance at 20,000 cm^{-1}, measured in alkaline solution, varies between 80 and 83, which corresponds to 70–75% of *cis*[Coen$_2$(OH)$_2$]$^+$ as product. In chloride media the spectra approximate to the *cis* isomer. Some results are given in Table VII. There is no indication of the presence of the intermediate [Coen$_2$ malOH]^0 since the value of the absorbance at 30,000 cm^{-1} approximates to that of *cis*[Coen$_2$(OH)$_2$]$^+$.

A series of experiments was carried out in which the hydroxide concentration was 1.63 mol dm^{-3} and the ionic strength was 3.6 mol dm^{-3} (perchlorate) at 37.5° C. Samples were scanned during the base hydrolysis for various known times, the mixtures were then acidified with a known volume of acid, and the spectra were measured again. In acidic media the *final* spectra approximated to a mixture of *cis* and *trans*[Coen$_2$ (OH$_2$)$_2$]$^{3+}$ which are formed from the [Coen$_2$(OH)$_2$]$^+$ ions on acidification, without isomerization. The results are shown graphically in Figure 2. The line AB indicates the expected molar absorbance at 27,000 cm^{-1} for a

TABLE VII. Average Final Molar Absorptions Measured in Alkaline Solution for the Base Hydrolysis of [Coen$_2$ mal]$^+$, in Perchlorate (I), and in Chloride (II), Media.

	A 19.2 kK	% *cis*	A 20.0 kK	% *cis*	A 27.0 kK	% *cis*	A 30.0 kK
I	88	82	83	74	93	78	43
II	91	92	85	98	100	92	43
[Coen$_2$(OH)$_2$]$^+$	93	100	86	100	104	100	41

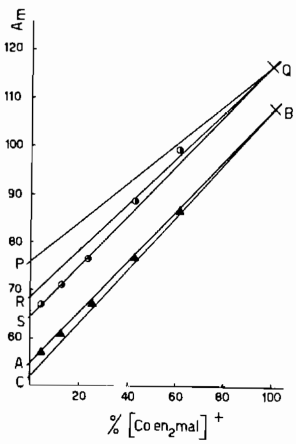


Figure 2. Molar absorbances measured at various times during the base hydrolysis of the $[Coen_2mal]^+$ ion (acidified samples). ABC, A_m values at 27,000 cm^{-1}. AB, calculated values for mixture of $[Coen_2mal]^+$ and *cis* $[Coen_2(OH_2)_2]^{3+}$; BC, calculated values for $[Coen_2mal]^+$ and *cis* and *trans* $[Coen_2(OH_2)_2]^{3+}$ in 3 : 1 ratio; ▲ experimental values. PQS, A_m values at 20,100 cm^{-1}. PQ, calculated for $[Coen_2mal]^+$ and *cis*$[Coen_2(OH_2)_2]^{3+}$; RQ, calculated for $[Coen_2mal]^+$ and *cis* and *trans*$[Coen_2(OH_2)_2]^{3+}$ in a 4 : 1 ratio; SQ, calculated for $[Coen_2mal]^+$ and *cis* and *trans*$[Coen_2(OH_2)_2]^{3+}$ in a 3 : 1 ratio; ◑ experimental values.

mixture containing $[Coen_2mal]^+$ and *cis*$[Coen_2(OH_2)_2]^{3+}$. The line CB shows the values for $[Coen_2mal]^+$ together with *cis* and *trans*$[Coen_2(OH_2)_2]^{3+}$ in a 3 : 1 isomer ratio. At this wavenumber the molar absorbances are largely independent of the isomeric ratio of the products. The envelope PQS shows the molar absorbances at 20,100 cm^{-1}; PQ is $[Coen_2mal]^+$ and *cis*$[Coen_2(OH_2)_2]^{3+}$; RQ is $[Coen_2mal]^+$ and $[Coen_2(OH_2)_2]^{3+}$ in a *cis* to *trans* ratio 4 : 1; SQ is $[Coen_2mal]^+$ and $[Coen_2(OH_2)_2]^{3+}$ in a *cis* to *trans* ratio of 3 : 1. The experimental results are not able to show with certainty the isomeric ratio of the initial product.

Discussion

Unlike the base hydrolysis[8, 9] of the oxalato[2] and the carbonato[1] analogues, the reaction is one stage; and yet it is evident from the scanning experiments that some kind of pre-equilibrium is present.[10] Two possible reaction sequences are as follows:

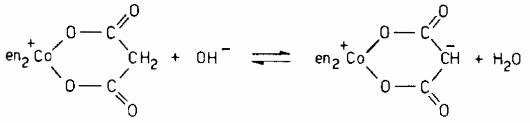
(i) The rate determining step is ring opening and this is followed by fast release of the malonate ion:

$$[Coen_2mal]^+ + OH^- \xrightarrow{\text{slow}} [Coen_2malOH]^0 \qquad (1)$$

$$[Coen_2malOH]^0 + OH^- \xrightarrow{\text{fast}} [Coen_2(OH)_2]^+ + mal^{2-} \qquad (2)$$

$$cis[Coen_2(OH)_2]^+ \rightleftharpoons trans[Coen_2(OH)_2]^+ \qquad (3)$$

At the same time a fast equilibrium exists in which a proton is removed from the malonato ring. This produces a non-reactive resonance stabilized ring, which effectively removes the complex from participation in the reaction (2) as shown in (4):



The observations are consistent with this reaction sequence. When the concentration of base is low, reactions (2 and 3) are faster than reaction (1) and the conjugate base produced in reaction (4) is in very low concentration. Thus the reaction is second order and ionic strength dependent, and the conjugate base cannot be detected spectrophotometrically. In concentrated base the conjugate base becomes detectable, and a limiting first order rate constant is observed.

If this mechanism operates then the pre-equilibrium involves the abstraction of a proton from the malonato ring (reaction (4)). The protons from this group are labile in acid media and exchange with solvent[11], which would indicate that this mechanism is feasible. If it were operating then the initial spectrum observed in 3.7 mol dm^{-3} NaOH solution should approximate to that of the deprotonated species, and the fact that the spectrum returns to that of the malonato complex on acidification is readily understood.

(ii) Another possible mechanism involves a pre-equilibrium between the chelated and dechelated forms of the malonato complex:

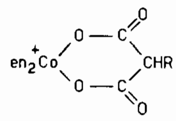
$$OH^- + [Coen_2mal]^+ \overset{\text{fast}}{\rightleftharpoons} [Coen_2malOH]^0 \qquad (5)$$

The malonate is then released from the hydroxomalonato complex at a rate which is independent of the concentration of hydroxide:

$$[Coen_2malOH]^0 \xrightarrow{\text{slow}} [Coen_2OH]^{2+} + mal^{2-} \qquad (6)$$

$$[Coen_2OH]^{2+} + OH^- \rightarrow [Coen_2(OH)_2]^+ \qquad (7)$$

If mechanism (ii) operates (equation (5)) then the spectrum in 3.7 mol dm^{-3} sodium hydroxide solution should approximate to that of the dechelated species, $[Coen_2malOH]^0$. The spectra of the analogous complexes containing unidentiate substituted malonato ligands are very much like this spectrum, *e.g.* that of[1, 12] $[Coen_2CO_3OH]^0$ and of[1, 2] $[Coen_2C_2O_4OH]^0$. Further studies have been made of the base hydrolysis of the $[Coen_2Rmal]^+$ ions,[13] containing the C-substituted malonato chelate group, where R is ethyl or benzyl:



For both C-substituted complexes the base hydrolysis was found to proceed in two stages. The first, by analogy[2] with $[Coen_2C_2O_4]^+$ is ascribed to the ring opening reaction and the second to ligand loss. The spectal profile of the second stage is very similar to that shown by $[Coen_2mal]^+$ during hydrolysis in 3.7 mol dm^{-3} base; there are no isosbestic points and there is a large drop in absorbance around 30,000 cm^{-1}. The addition of acid to the alkaline solution of the $[Coen_2mal]^+$ thus brings about fast ring-closure

$$[Coen_2mal]^+ \underset{H_3O^+}{\overset{OH^-}{\rightleftharpoons}} [Coen_2malOH]^0 \qquad (8)$$

Table IV shows that the rate of loss of optical activity in alkaline solution calculated using samples "killed" with acid is the same as that measured directly in alkaline solution. If the reactions in equation (8) take place, then they must do so with complete retention of configuration, indicating that cobalt–oxygen bond fission is not involved.

The simple malonato complex, $[Coen_2mal]^+$ is not susceptible to acid hydrolysis even in concentrated perchloric acid above 80° C, whereas the substituted malonato complexes react readily in acid solution in two stages. Between pH 2 and pH 3, at about 40° C the first stage is complete in about 20 minutes, and the second, to give $[Coen_2(OH_2)_2]^{3+}$, in approximately 4 hours.[13] Thus the stability of the simple malonato chelate ring in acid is probably due to the fast ring closure reaction. Acid ring-closure thus exhibits steric retardation, indicating a bimolecular reaction, involving a water molecule. Further work on this point is in progress.

In order to explain the fact that the loss of optical activity is faster than that of ligand loss, the back reaction in equation (5), *i.e.* ring closure in alkaline solution could take place with change in configuration. This would imply that racemization would take place with exchange of oxygen with the solvent in the $[Coen_2 malOH]^0$ species. Alternatively a twisting mechanism like that proposed for $[Coen_2(OH)_2]^+$ could be envisaged.[7]

In mechanism (ii) the equilibrium (5) is between an uncharged species and two ions. This means that a more polar solvent would tend to favour the formation of ions and a less polar solvent would tend to favour the neutral species. This effect was demonstrated by the use of water/methanol as solvent. The results indicate that perchlorate medium tends to produce more of the non-ionic form than goes chloride medium. Thus in mixed NaOH/NaCl solutions where the same stiochiometric ionic strengths are involved, it may be that the effective ionic strengths are different.

A further medium effect is shown in Table V, where as the medium contains less and less perchlorate, (*e.g.* the last run in this table contains no perchlorate) the observed first order rate constant falls slightly.

Table VII indicates that in the presence of chloride ions the *cis*$[Coen_2(OH)_2]^+$ ion is the product, whereas in the presence of perchlorate or of no added anion, about 25% of the *trans* isomer is produced. Since the *cis/trans* isomerisation of the $[Coen_2(OH)_2]^+$ ions is not affected by these anions[7], the *trans* isomer must be produced in the step where malonate is replaced by hydroxide attacking at cobalt. This will apply to either of the mechanisms discussed above. The results for the malonato complex and the oxalato analogue[2] indicate that the species surrounding the complex in the transition state (and this must include the leaving group) have an influence on the steric course of the reaction. At the high ionic strengths involved, outer sphere co-ordination must be important, and it is possible that a slight change in the members of the sphere could tip the balance between one intermediate and another[2] as well as influencing the position of the incoming group. Further work on the hydrolysis of dicarboxylic acid complexes is in progress.

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