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Isotope Exchange at the Active Methylene Groups in Coordinated Malonate in the $[Coenmal_2]^-$ Ion

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Each malonato ligand has two protons in the methylene group; one in the H_B position, between the malonato rings, and the other in the H_A position, near to the ethylenediamine group. In D_2O/D_2SO_4 mixtures these undergo exchange with deuterium. The protons in the H_B positions are replaced first, $\Delta H^{+} = 26.4$ kcal mol^{-1}, $\Delta S^{+} = +26$ e.u. The protons in the H_A positions are replaced more slowly, $\Delta H^{+} = 26.4$ kcal mol^{-1}, $\Delta S^{+} = +22$ e.u. There is only a small degree of stereospecificity, which is discussed in terms of the conformational mobility of the malonato ring, the proximity of the neighbouring groups, solvation effects, and of the possibility of a non stereospecific reaction path.

Introduction

The $[Coenmal_2]^-$ ion in aqueous acid gives a pmr spectrum showing an AB pattern.[1] Sargeson and coworkers[1b] suggested that one pair of protons, H_A, lies adjacent to the amino groups, while the other, H_B, lies between the malonato groups (Figure 1). When deuteration of this ion proceeds at an experimental pD of 2.8 the AB pattern diminishes generally. The H_B (low field) pair of resonances disappeare due to deuteration of the R_B positions. The spin–spin coupling with H_A is thus removed and the H_A pair of resonances disappears, giving way to a broad band at 1.835 ppm, which gradually increases in intensity. The second, subsequent stage of the reaction is the decrease of the signal at 1.835 ppm while the R_A positions undergo deuteration.

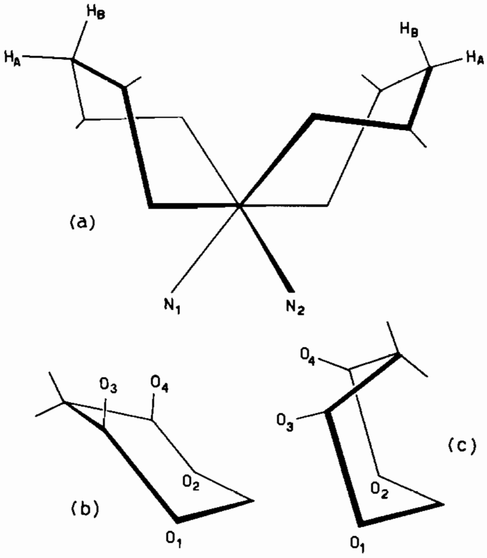

Figure 1. Conformations of coordinated malonate: (a) two skew boats showing H_A and H_B protons; (b) chair; (c) boat.

Experimental

Preparation of Potassium Ethylenediaminebis (malonato)cobaltate(III) Hydrate

$K[Coenmal_2]H_2O$ was prepared by Dwyer's method.[2] Calc. for $C_8H_{12}N_2CoKO_8$: C, 25.3; H, 3.2; K, 10.3; N, 7.3. Found: C, 25.2; H, 3.8; K, 10.3; N, 6.9%.

Pmr Spectra

All spectra were measured on a Varian HA 60 spectrometer. Samples were dissolved in D_2O/D_2SO_4 mixtures and the pD of the solution was calculated from the pH value measured on a Pye Dynacap pH meter. Chemical shifts were relative to freshly distilled *t*-butanol or to HOD, on a sweep width of 500Hz at a scan rate of 1Hz.

Results

The Pmr Spectrum of the $[Coenmal_2]^-$ ion

The spectrum shows a broad signal at 1.47 ppm (half width 12Hz) which is assigned to the methylene groups of the ethylenediamine. Addition of deutero base causes a rapid sharpening to a half width of 2Hz and the disappearence of the broad peak at 3.75ppm. This last signal is assigned to the two equivalent NH_2groups. The AB pattern centered at 2.11ppm is assigned to the malonato protons.[1]

In order to understand the stereospecificity of isotopic exchange at these methylene groups, the conformation and relative motion of the two malonato rings must be considered.

Sargeson and coworkers[1b] have suggested that the chair conformer (Figure 1) is unlikely because of the eclipsed lone pairs and lone pair interactions; whereas the lone pair interactions are much less in the case of the boat and intermediate skew boat structures. However, in the extreme boat conformers, interference will still be expected (a) between the NH_2 group of the ethylenediamine and the H_A protons; and (b) between the two H_B protons. Which is the greater of these interactions will determine the intermediate skew boat time-averaged conformer "seen" by the spectrometer. If, for example, the malonate–malonate repulsion is the greater, the time-averaged environment will contain the H_A protons displaced toward the NH_2 groups and surrounded by more valence electrons than the H_B protons. It is thus possible to assign the high field resonance to the H_A protons. If the chair form is disregarded (or given a set contribution) then the rings move from boat through skew boat and back again in two ways (Figure 1). Figures 2a and 2b show a symmetric movement of the two rings, and figures 2c and 2d show an antisymmetric movement. Competing repulsion terms in the symmetric movement are the H_A–N interactions, and the H_B–oxygen lone pair interactions. In the antisymmetric movement, the interactions would again include the H_A–N, and a large repulsion in the form of atom–lone pair interactions: H_{B2}–O_{11}, H_{B1}–O_{12}, H_{A1}–O_{32}, and H_{A2}–O_{31}. Since the repulsive effects of the eclipsed lone pairs are considered more significant than the eclipsed bonding pairs[1b] the conformers having H_A and nitrogen atoms adjacent are probably more stable. Thus it seems likely that the protons in the H_A positions are sheltered by the ethylenediamine groups thus introducing stereospecificity. The spectrum of the $[Coenmal_2]^-$ ion is given in Table I.

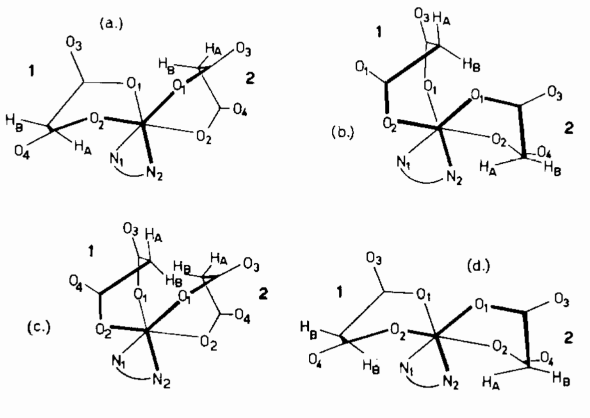

Figure 2. Mobile conformers of coordinated malonate in $[Coenmal_2]^-$: (a) and (b) symmetric movement; (c) and (d) antisymmetric movement.

Kinetics Results

Let the complex ion $[Coenmal_2]^-$ be represented as $CoXH_AH_B$, indicating that it contains a pair of protons H_A adjacent to the amine groups, and another, H_B, between the malonate rings. Let the protons between the malonate rings be replaced by deuterium to give the complex $CoXH_AD_B$. Rate constants for this stage of the reaction were calculated from plots of $\ln(I/I_2 - I_\infty/I_{2\infty})$ against time, where I is the H_B peak integral and I_2 is the ethylenediamine peak integral, which is not subject to deuteration. The slope of the straight line obtained gave the first order rate constants, k_1^B, at each acid concentration.

The order of the reaction was 1.13 (least squares) in D_3O^+ it thus appears to be second order, although no attempt was made to keep the ionic strength constant.

During the second stage of the reaction the H_A protons are replaced by deuterium to give the deuterated complex $CoXD_AD_B$. The rate constants for this part of the reaction, k_1^A, were obtained from the monitoring of the collapse of the singlet at 1.835 ppm, and were calculated in a similar way. The derived rate constants are shown in Table II.

TABLE I. 60 MHz Pmr Spectrum of the $[Coenmal_2]^-$ Ion (ppm *vs.* t-butanol).

Signal		
H_A	−1.84	
H_B	−2.36	J_{AB} = 18Hz
CH_2 (en)	−1.47	
NH_2 (en)	−3.75	

TABLE II. Rate Constants for the Deuteration of the Active Methylene Groups in the $[Coenmal_2]^-$ Ion in D_2O Solution.

Temp. °C	D_3O^+ m*M*	$10^4k_1^B$ s^{-1}	k_2^B $M^{-1}s^{-1}$	$10^4k_1^A$ s^{-1}	k_2^A $M^{-1}s^{-1}$
37	0.76	6.58	0.88	0.97	0.13
	0.91	7.52	0.84	1.12	0.12
	1.18	10.1	0.86	1.56	0.13
	1.60	13.3	0.83	2.00	0.13
44	0.76	19.7	2.59	3.15	0.42
	0.91	25.0	2.74	3.83	0.42
	1.18	27.0	2.74	4.24	0.37
	1.60	35.2	2.20	5.44	0.34
25	1.18	1.80	0.15	0.26	0.022

TABLE III. Stereospecificity Data for the Deuteration of the [Coenmal$_2$]$^-$ Ion.

Temp. °C	Mean k_2^B $M^{-1}s^{-1}$	Mean k_2^A $M^{-1}s^{-1}$	k_2^B/k_2^A Stereospecificity
25	0.15 ± 0.013	0.022 ± 0.005	6.85 ± 0.90
37	0.85 ± 0.04	0.128 ± 0.02	6.65 ± 0.75
44	2.43 ± 0.2	0.383 ± 0.055	6.36 ± 0.75
		Mean	6.60 ± 0.8

TABLE IV. Activation Parameters for the Deuteration of Some Coordinated Malonato Groups.

Complex [Coenmal$_2$]$^-$	ΔH^{+} kcal mol^{-1}	ΔS^{+} cal K^{-1} mol^{-1}
H_B	26.4 ± 3	+ 26.0 ± 10
H_A	26.4 ± 3	+ 22.0 ± 5
[Coen$_2$mal]$^+$ [a]	27.4 ± 3	+ 27.0 ± 6
[Cobipy$_2$mal]$^+$ [a]	18.4 ± 4	− 1.0 ± 5

[a] From ref. 4.

The ratio of the second order rate constants, k_2^B/k_2^A, gives the degree of stereospecificity which is found to be 6.6 ± 0.8, compared with the value of 10 for the cobalt(III) EDDA complex[3]. Stereospecificity data are shown in Table III. Activity parameters are shown in Table IV.

Discussion

The general mechanism for the exchange in acidic solution of the hydrogens at the α-carbon atom of the coordinated malonato ligand has been discussed.[4] Isotopic exchanges in such systems have been found to be stereospecific.[3,5]

In the case of the [Coenmal$_2$]$^-$ ion, the positions H_B are exchanged first. The protons in the H_A positions are replaced more slowly. The most likely averaged conformation of the malonato group in [Coenmal$_2$]$^-$ appears to be that displaced from the skew boat position, so that H_A and the amine groups are in close proximity. At first sight it might appear that there would be steric hindrance to the lengthening of the α-C–H_A bond on going to or from the activated complex. Table III, however, shows that the activation energies for isotopic exchange in both H_A and H_B positions are the same, and that the differences in rate are entropy controlled.

In the *trans*-[CoEDDAen]$^+$ complex ion the sheltering of the H_B proton from the solvent has been ascribed to the "backbone" of the aminocarboxylate ligand.[3] Molecular models were used to show that H_B is 1.5 A from the octahedral edge spanned by the "backbone" and is held in sheltered position because of conformational rigidity.

In comparison, the malonato ring is not rigid. However, the H_B position is more susceptible to solvation and to exchange. Isotopic exchange at the H_B position would therefore release more solvent molecules from the solvation layer, than would exchange at H_A. This entropy effect is just enough to make the H_B position slightly more reactive.

Ring opening in the [CoEDDAen]$^+$ ion was proposed[3] to account for the low specificity of isotopic exchange. It is possible that ring opening could provide a reaction path for isotopic exchange in the [Coenmal$_2$]$^-$ ion. Then a complete scheme would involve the keto-enol intermediate described before for the mono-malonato system,[4] with the addition of a non-stereospecific pathway involving dechelation.

Acknowledgement

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References

1 a) H. Yoneda and Y. Morimoto, *Inorg. Chim. Acta, 1,* 413 (1967); b) D.A. Buckingham, L. Durham and A.M. Sargeson, *Aust. J. Chem, 20,* 257 (1967).

2 F.P. Dwyer, *J. Am. Chem. Soc., 83,* 1285 (1961).

3 J.L. Sudmeir and G. Occupati, *Inorg. Chem., 7,* 2524 (1968).

4 M.E. Farago and M.A.R. Smith, *J.C.S. Dalton,* 2120 (1972).

5 J.L. Legg and D.W. Cooke, *Inorg. Chem., 4,* 1576 (1964); D.H. Williams and D.H. Busch, *J. Am. Chem. Soc., 87,* 4644 (1965).