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^{1}H and ^{13}C NMR Studies on Malonic and Ethylmalonic Acids and their Cobalt(III) Complexes

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Magnetic resonance studies on malonic and ethyl malonic acids show that the α-protons exchange with deuterium from solvent in both acid and basic D_2O solution. In basic solution the $[Coen_2mal]^+$ ion undergoes a fast ring opening with hydroxide. At the same time the α-protons exchange with deuterium from the solvent. ^{13}C n.m.r. studies show that the methylene carbon in $[Comal_3]^{3-}$ is deshielded with respect to those in $[Coen_2mal]^+$, free malonic acid or the free anion. The ^{13}C n.m.r. shieldings for ethylmalonic acid and $[Coen_2Etmal]^+$ are reported.

Introduction

There has been recent interest in the malonate group: crystallographic work has shown that the conformation of the six membered malonato-chelate ring is greatly dependent on its environment in the solid state *e.g.* [1–5]; malonate has been shown to be an important C_2 biosynthetic unit [6] and the acidity of the α-protons in the malonate ligand has been demonstrated [7–10].

In this and subsequent papers we describe further investigations of the malonato group coordinated to metal ions, and present a study of malonic and of C-substituted ethylmalonic acids and their derived complexes in solution by both ^{1}H and ^{13}C n.m.r. spectroscopy. There have been several investigations of malonato complexes using ^{1}H n.m.r. particularly those of cobalt(III) [7, 10], and some reports of the application of ^{13}C n.m.r. spectroscopy to the study of cobalt(III) complexes, including those of aminopolycarboxylates [11–13], and of amino acids [14], and of diamines [15].

The aim of this research is three-fold: firstly, the assignment of chemical shifts to malonic acids and their complexes of cobalt and of other metals; secondly, the investigation of the stereochemistry of complexes containing more than one malonate ring each of which carry a C-substituent [10] and thirdly, the elucidation of the first step in the reaction of the metal-malonato ring with hydroxide ions. The kinetic results of this last reaction, in the case of $[Coen_2mal]^+$ are explicable either in terms of a ring opening reaction or of a proton extraction from the malonato methylene group [16].

Experimental

^{1}H n.m.r. spectra were measured with a Perkin Elmer 60 MHz continuous wave spectrometer at 35 °C, or with a Jeol Inc., JNM PS 100 Fourier transform 100 MHz spectrometer in the ^{1}H mode. Chemical shifts were relative to tertiary butanol as internal standard, or to external TMS. ^{13}C n.m.r. spectra were measured using the Jeol Fourier transform instrument in the ^{13}C mode. Most spectra were obtained using D_2O lock, 8000 data points, repetition times between 3 and 10 seconds, and up to 6000 scans depending on the concentration of the sample. Concentrations were normally about 0.2 g cm^{-3}. Either tertiary butanol or *p*-dioxane were used at internal standards. Most ^{13}C spectra were carried out at Rothamsted (some were measured by P.C.M.U., Harwell, where T.S.P. was used as internal standard, and some by U.L.I.R.S., King's College, London). ^{1}H n.m.r. spectra were measured at Bedford College.

Preparation of Cobalt Complexes

$[Coen_2mal]Br$ and $K[Coenmal_2]H_2O$ were prepared as before [10, 16]. $K_3[Comal_3]3H_2O$ was prepared by both the methods of Lohmiller and Wendlandt, and Al-Obodie and Sharpe [17], and gave satisfactory elemental analyses. $[Coen_2Etmal]Br\cdot$

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H_2O was prepared as follows: 10 g of $[Coen_2CO_3]Cl$ prepared by Dwyer's method [18], was treated with the Ag_2O freshly precipitated from 11 g silver nitrate. The silver chloride and the excess of silver oxide was filtered off and ethylmalonic acid (5 g) was added. The mixture was shaken until the evolution of CO_2 had ceased. The volume of the solution was reduced to 40 cm^3 on a rotary evaporator and KBr (8 g) was added to the hot solution. The carmine-red leaf crystals were filtered off from the ice-cold solution, washed with ice-cold methanol, cold ether and dried *in vac.* The crude product was recrystallised from warm water and dried as before.

Anal. Calc. for $C_9H_{24}N_4CoBrO_5$: C, 26.6; H, 5.9; N, 13.8; Co, 14.4. Found: C, 26.6; H, 5.7; N, 14.0; Co, 14.4%.

Results

Uncomplexed Acids

Malonic acid

The ^1H n.m.r. spectrum of malonic acid in D_2SO_4 solution shows the methylene group signal split into a triplet (2.1 ppm *vs.* *t*-butanol J ~ 7.3 Hz) indicating the presence of the CHD group, where its signal is superimposed on the singlet from the CH_2 group. The intensities of these signals decrease with time as CD_2 is produced.

In NaOD/D_2O solutions a similar trend is noticed: *viz.* the appearance of the triplet, the intensity of which decreases with time. In solution in D_2O and neutralised with Na_2CO_3, malonic acid shows only a singlet from the CH_2 group (1.91 ppm *vs.* *t*-butanol) which remained unchanged for several hours. A singlet for the methylene signal is also reported for a malonic acid solution in polysol-d [19a].

The ^{13}C n.m.r. spectrum of malonic acid in D_2O shows a signal of 171.57 ppm for the carbonyl shielding and a split signal at 42.4 ppm for the CH_2 resonance confirming the presence of CH_2, CHD and CD_2. The carbonyl resonance compares with a value of 170.4 ppm for a saturated solution in methanol [20]. In NaOH solution the carbonyl peak shifts to 178.37 ppm, and the methylene signal is split (Table III). When malonic acid is neutralised in H_2O with Na_2CO_3, then evaporated to dryness and redissolved in D_2O, the proton decoupled spectrum shows a singlet for the CH_2 resonance which persists for several hours. If neutralisation is carried out in D_2O, some exchange occurs during neutralisation, but the spectrum is then 'frozen' for several hours and shows the peaks required for CH_2, CHD and CD_2 species.

Ethylmalonic acid

In D_2O solution ethylmalonic acid gives signals in the ^1H n.m.r. spectrum from the CH_3 group, –0.28 ppm (triplet J ~ 7.5 Hz); CH_2 group, 0.65 ppm (quintet, J ~ 7.6 Hz); CH, 2.19 ppm (triplet J ~ 7.24 Hz). The spectrum is similar to that reported in trifluoroacetic acid solution [19b]. On standing the CH signal decreases and the CH_2 quintet broadens. Finally the CH triplet disappears and the CH_2 signal sharpens to a quartet. Similar effects are noticed when the acid is neutralised with Na_2CO_3 (Table I). With an excess of NaOD the CH signal has almost disappeared and the CH_2 signal is a quartet when the first measurement is taken in the fresh solution.

TABLE I. Splitting of CH_2 Signal in Ethylmalonic Acid in D_2O/Na_2CO_3 Solution as α-H Exchanges with D from Solvent.

Intensity	Splitting of CH_2 Signals	Time
$CH:CH_2:CH_3$		
1:2:3	quintet	fresh solution
0.75:2:2	broad quintet	after two days
0.45:2:3	7 or 8 bands	after seven days
0:2:3	quartet	in excess of NaOD (fresh solution)

The ^{13}C n.m.r. spectrum of ethylmalonic acid in fresh D_2O solution exhibits a singlet for the CH resonance; this rapidly collapses to a complex triplet. When ethyl malonic acid is neutralised in H_2O, evaporated to dryness and dissolved in D_2O a singlet results for the CH resonance (doublet in ORD spectrum), which persists for several hours. No resonance is observed for the CH carbon in NaOH solution, indicating fast exchange. The ^{13}C n.m.r. spectrum of ethyl malonic acid is given in Table II.

TABLE II. ^{13}C N.m.r. Spectrum (ppm *vs.* TMS) of CH_3CH_2-$CH(CO_2H)_2$.

	CO_2H	CH	CH_2	CH_3
D_2O solution	174.28	54.05	22.80	11.73
D_2O/NaOD	180.88	–	24.40	13.00
D_2O/Na_2CO_3	180.86	61.4	24.38	13.04

Cobalt(III) Complexes of Malonic Acid

The 60 MHz ^1H n.m.r. spectrum of $[Coen_2mal]Br$ has been reported [9]. Relative to t-butanol the spectrum (in ppm) was reported as follows: NH_2 (*cis* to O), 3.13; NH_2 (*trans* to O), 4.14; CH_2(mal), 2.11; CH_2(en), 1.47. The present work using 100 MHz shows the CH_2(mal) signal at 2.17 ppm and the methylene groups from the ethylenediamine show the expected splitting: giving signals at 1.57 and 1.47 ppm. On the addition of base the CH_2(mal) signal broadens and then splits into a triplet, showing that

TABLE III. ^{13}C N.m.r. Signals from Malonate Group (ppm *vs.* TMS).

	Carboxyl	Methylene		
Malonic acid/D_2O	171.57	42.23	41.43	40.64
Malonate ion/NaOH	178.49	49.44	48.73	47.92
Malonate ion/neutral	178.37	48.9		
$[Coen_2mal]^+$	179.5	~42		
$[Coenmal_2]^-$	180.22, 179.93	–		
$[Comal_3]^{3-}$	182.81	46.21		
uns$[CoTMDDAmal]^-$ [a]	178.66, 179.31	43.52		

[a]From ref. 13.

deuterium substitution has occurred as in the free malonate anion. The CH_2 signal then disappears with time as in the case of the $[Coen_2mal]^+$ ion with D_2SO_4 [9].

The ^{13}C n.m.r. spectrum (ppm *vs.* TMS) of the $[Coen_2mal]^+$ ion is as follows: carboxyl, 179.5; CH_2-(en), 45.87, 44.25; CH_2(mal), ~42. On addition of base to $[Coen_2mal]^+$ in D_2O solution the methylene-(mal) signals are no longer visible, but changes are noticed in the signals from the ethylenediamine methylenes.

The ^{13}C n.m.r. spectrum of the $[Comal]^{3-}$ ion shows the carboxyl carbon at 182.81 and the malonato methylene at 46.21 ppm (see Table III).

Cobalt(III) Complex of Ethylmalonic Acid $[Coen_2Etmal]^+$

The ^1H n.m.r. spectrum (ppm *vs.* t-butanol) of the $[Coen_2Etmal]^+$ ion has been reported [9]. C–H(mal), 1.90 (triplet); CH_2, 0.72 (quintuplet), CH_3, –0.40 (triplet). The ^{13}C n.m.r. spectrum (ppm *vs.* TMS) shows signals at 183.72 (carboxyl); 56.22 (CH); 47.44, 46.34 (CH_2, en); 26.26 (CH_2); 14.23 (CH_3).

Discussion

Free Acids and Anions

The ^1H n.m.r. spectra show that the $>CH_2$ protons of malonic acid exchange with deuterium from the solvent in both acidic and basic solution. In neutral solution, however, this exchange is very slow (confirmed by ^{13}C spectrum).

With ethylmalonic acid a similar trend is observed, the reactions are, however, faster than for the unsubstituted compound, in basic solution. Table I shows that initially the CH_2 signal is a quintet, with splitting from neighbouring CH and CH_3 groups. When the exchange of D for H in the CH group is complete, with excess NaOH for example, the coupling of the $>CH_2$ groups is now only with the methyl group giving a quartet. As the exchange takes place the $>CH_2$ signal becomes complicated as it arises from the quintet of the $>CHCH_2CH_3$ group superimposed on the quartet of the $>CDCH_2CH_3$ group. When half exchange has taken place this gives rise to seven or eight bands.

The ^{13}C n.m.r. spectra give expected values for the shieldings in both acids. The results in Tables II and III show that on formation of the anion [21] the carboxylate carbon signal shifts to a lower field with a shift of +6.60 ppm for ethylmalonic acid and a similar shift of +6.92 ppm for malonic acid.

For ethylmalonic acid there is a downfield shift for both methylene and methyl carbons in basic media.

Complexes of Malonic Acid and Ethylmalonic Acid

The ^{13}C n.m.r. spectrum of $[Coen_2mal]^+$ shows that the malonato group is chelated in neutral solution since there are two signals from the ethylene diamine carbons. A monodentate malonato group should give rise to more signals [15].

On the addition of base (saturated NaOH in D_2O) to a solution of $[Coen_2mal]^+$ the changes in ^{13}C n.m.r. spectrum shown in the Figure arise.

Figure 1(a) shows the methylene signals from the two non equivalent methylene groups of ethylenediamine in $[Coen_2mal]^+$. These are at 45.87 and 44.29 ppm. The first measurement after the addition of saturated $NaOH/D_2O$ Figure 1(b) shows three signals at 45.60, 45.12 and 44.20 ppm. At this stage in the reaction it has been suggested that in strongly basic solution the $[Coen_2mal]^+$ ion exists either as the monodentate malonato species $[Coen_2malOH]^0$ or as the species in which a proton has been removed from the malonato methylene group in the chelate ring [16]. The three signals observed are consistent with the presence of the monodentate malonato group, three signals from the ethylenediamine methylene groups are expected for a complex of the type $[Coen_2XY]$. The results are not consistent with the deprotonated species $[Coen_2mal(-H)]^0$, since two methylene signals are still expected, nor with a mixture of $[Coen_2mal]^+$ and the deprotonated species. After 24 hours three signals appear at 45.13, 44.68 and 44.20 ppm. After 48 hours the mixture was acidified. The malonato carboxyl peak now

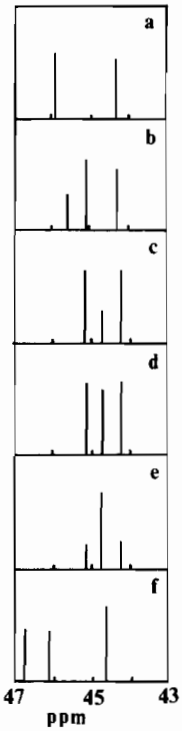

Figure. Changes in the ethylenediamine CH_2 signals when $[Coen_2mal]^+$ is treated with NaOH solution. (a) $[Coen_2mal]^+$ in D_2O. (b) Scans begun immediately after addition of NaOH solution. (c) Scans begun 1 hour after addition of NaOH. (d) After 24 hours. (e) After 48 hours. (f) Final solution acidified with conc. HCl.

appears at 172.8 ppm instead of 179.52 in the complex showing the presence of free malonic acid. The three ethylenediamine methylene signals at 46.72, 46.09 and 44.59 result from the equilibrium mixture of *cis* and *trans* $[Coen_2(OH_2)_2]^{3+}$.

Thus in neutral solution the coordinated malonate group is stable in $[Coen_2mal]^+$. It does not become dechelated, nor do the methylene group protons exchange with deuterium from the solvent. In basic media the malonato group is dechelated and at the same time exchange takes place between the methylene protons and the deuterium of the solvent.

The results in Table III show that the carboxyl carbons are deshielded on coordination with respect to the free acid, but are more shielded than the free anion. In addition the methylene carbon in $[Comal_3]^{3-}$ is deshielded with respect to the other species in Table III.

Complexes of Ethylmalonic Acid

The ^{13}C n.m.r. shieldings of ethylmalonic acid species are shown in Table IV.

The carbon signals show a successive downfield shift in the series ethylmalonic acid < ethylmalonate anion < $[Coen_2Etmal]^+$.

TABLE IV. ^{13}C N.m.r. Signals (ppm *vs.* TMS) of Ethylmalonic Acid Species.

	Carboxyl	CH	CH_2	CH_3
Acid/D_2O solution	174.28	54.05	22.80	11.73
NaOD/D_2O	180.88	–	24.4	13.00
$[Coen_2Etmal]^+$	183.72	56.22	26.26	14.23

The ethylenediamine methylene resonances in neutral solution are 45.87 and 44.78 ppm compared with those in $[Coen_2CO_3]^+$ at 45.82 and 44.78 ppm. Thus there is no evidence of strain in the two bidentate ethylenediamine ligands on changing the ring size of the third chelate in contrast to the results of Douglas and co-workers for the quadridentate ligand TMDDA [13]. However the CH_2(en) resonances in $[Coen_2(Etmal)]^+$ are at 47.44 and 46.34 ppm slightly deshielded with respect to the simple malonato or the carbonato complex.

^{13}C studies on organic compounds show that shifts to greater shielding are associated with carbons which are sterically perturbed – the steric compression shift [20 (b)].

It appears that the ethylenediamine methylene groups in the simple malonato complex are more sterically strained than in the ethyl malonato compound. A possible explanation is that the presence of the ethyl substituent gives rise to a flat boat conformation of the malonato ring. Thus the malonato ring and the ethyl substituent would be further away from the ethylenediamine groups than the skew boat confomations.

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