Proton Magnetic Resonance Studies of the Active Methylene Group in Some Cobalt(III) Malonato-cations

By **M. E. Farago** * and **M. A. R. Smith,** Chemistry Department, Bedford College, Regents Park, London NW1 4NS

The protons of the methylene group of co-ordinated malonate in the complexes [Co(en)$_2$(mal)]$^+$ and [Co(bipy)$_2$(mal)]$^+$ have been shown to exchange with deuterium in D_2SO_4–D_2O solutions. The rates are of the first order in D_3O^+ concentration. For the ethylenediamine complex $\Delta H^\ddagger$ is 27·4 kcal mol^{-1} and $\Delta S^\ddagger$ is +27 cal mol^{-1} K^{-1} and for the bipyridyl complex $\Delta H^\ddagger$ = 18·4 kcal mol^{-1} and $\Delta S^\ddagger$ is −1·0 cal mol^{-1} K^{-1}.

THE tendency of the central metal atom to increase the acidity of active methylene groups is well known, and in this paper we demonstrate this effect for the simple malonato-chelate group.

EXPERIMENTAL

Malonatobis(ethylenediamine)cobalt(III) bromide, [Co(en)$_2$(mal)]Br was prepared by the method of Price and Duff.[1] Malonatobis(bipyridyl)cobalt(III) bromide hydrate was prepared from [Co(bipy)$_2$Cl$_2$]$^+$ by a method similar to that used by Ablov and Palade [2] to prepare [Co(phen)$_2$(mal)]$^+$ from [Co(phen)$_2$Cl$_2$]$^+$.

Cobalt chloride hexahydrate (5 g) and 2,2′-bipyridyl (6·55 g) were warmed together in water (6 ml). The mixture was cooled in ice and chlorine was passed into the cooled solution for 75 min. The crude grey-green [Co(bipy)$_2$Cl$_2$]Cl was filtered off, washed with ice-water and ether, and dried at the pump. The crude product was recrystallized from 50 ml of water–hydrochloric acid (4 : 1). The recrystallized [Co(bipy)$_2$Cl$_2$]Cl (0·6 g) in water (5 ml) was ground with silver oxide, freshly precipitated from silver nitrate (0·95 g). The excess of Ag_2O and the AgCl were filtered off and the boiling filtrate was treated with malonic acid (0·25 g). Boiling was continued for 5 min, then potassium bromide (1 g) was added and the mixture was placed in ice. The deep red *crystals* of [Co(bipy)$_2$(mal)]Br,H_2O were filtered off, washed with ice-water, ethanol, and ether, and air dried. After recrystallization from the minimum of boiling water, the product was washed and dried as before (Found: C, 48·8; N, 9·8; H, 3·8. $C_{23}H_{20}BrCoN_4O_5$ requires C, 48·4; N, 9·8; H, 3·5%); $\varepsilon_{max.}$ 81·4 at 20,100 cm^{-1} (aqueous solution, SP 800 spectrophotometer).

[Co(en)$_2$(Etmal)]Br,H_2O was prepared as described elsewhere.[3]

^{1}H N.m.r. spectra were recorded on a Varian HA60 60 MHz n.m.r. spectrometer fitted with a Varian variable-temperature accessory. Thermostatting was to ±1 °C and activation parameters are subject to considerable error. Temperatures were calibrated by shift differences of methanol and ethylene glycol. Chemical shifts were relative to t-butyl alcohol or HOD as internal standards.

The acid-catalysed deuterium exchange rates were determined in deuteriosulphuric acid solutions. The stock acid solution and the n.m.r. tube containing a weighed amount of complex were brought to the required temperature. After addition of the acid, the tube was rapidly transferred to the thermostatted cavity of the spectrometer and peak areas were continuously monitored. In the ethylenediamine complex the $-CH_2{\cdot}CH_2-$ signal was included in the integral. Since this is not subject to deuteriation the malonato-α-hydrogen was expressed as a fraction of it. Plots of $\ln (I_1/I_2 - I_1/I_2)$ against time were constructed, where I_1 is the proton peak integral and I_2 is the ethylenediamine $-CH_2$ peak integral. Values of k_D', the pseudo-first-order rate constants, were obtained from the slopes, these being divided by the acid concentration to give the second-order rate constants, k_D.

RESULTS

(*a*) [Co(en)$_2$mal]$^+$.—The ^{1}H n.m.r. spectrum of this complex has been reported.[4,5] There is non-equivalence of the amino-protons. One pair is *cis* to the oxygen donor atoms of the malonate and the other *trans*. This results in

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[1] T. S. Price and J. C. Duff, *J. Chem. Soc.*, 1920, 1076.

[2] A. V. Ablov and D. M. Palade, *Russ. J. Inorg. Chem.*, 1961, **6**, 159; 1962, **7**, 1304.

[3] M. E. Farago and M. A. R. Smith, submitted to *J.C.S. Dalton*.

[4] H. Yoneda and Y. Morimoto, *Inorg. Chim. Acta*, 1967, **1**, 413.

[5] D. A. Buckingham, L. Durham, and A. M. Sargeson, *Austral. J. Chem.*, 1967, **20**, 257.

two broad bands at $-3{\cdot}13$ p.p.m. and $-4{\cdot}14$ p.p.m., which disappear in deuterio-base. The ethylenediamine protons of the $-(CH_2)_2-$ group give a broad unresolved band at $-1{\cdot}47$ p.p.m., which on deuteriation of the amine groups sharpens by some 4—5 Hz to a half-width of 7·5 Hz. The change in conformation in solution of both ethylenediamine rings would produce two separate second-order spin–spin coupling patterns, which would explain the broadness of this band in comparison with the monoethylenediamine complex,[5,6] $[Co(en)(mal)_2]^+$. At 80 °C the ethylenediamine methylene signal sharpens to a half-width of 6 Hz, showing that the rate of conformational interchange is increased.

There is a twofold axis of symmetry through the α-carbon atom and the cobalt atoms,[5] and therefore when the malonate ring is in either of the ' skew boat ' positions (Figure 1) the α-protons are equivalent. The singlet at $-2{\cdot}11$ p.p.m. arises as a result of rapid interchange between these conformers.[5] The spectrum in p.p.m. of $[Co(en)_2(mal)]^+$ at 33 °C from t-butyl alcohol is as follows: NH_2(*cis* to O), $-3{\cdot}13$; NH_2(*trans* to O), $-4{\cdot}14$; CH_2(mal), $-2{\cdot}11$; and CH_2(en), $-1{\cdot}47$.

The rate constants for the replacement of the malonato-methylene group protons by deuterium were obtained by monitoring the $-2{\cdot}11$ p.p.m. signal. The results are in Table 1. Activation energies obtained from an Arrhenius plot (Figure 2) for 25 °C are $\Delta H^{\ddagger} = 27{\cdot}4 \pm 3$ kcal mol^{-1} and $\Delta S^{\ddagger} = +27{\cdot}0 \pm 6$ cal mol^{-1} K^{-1}.

TABLE 1

Rate constants for the deuteriation of the active methylene group in $[Co(en)_2(mal)]^+$ in acidic D_2O

t/°C	$10^3[D_3O]^+$/M	$10^4k_D'$/s^{-1}	k_D/l mol^{-1} s^{-1}
37 ± 0·5	1·35	4·1	0·304
	2·1	6·4	0·305
	3·4	10·75	0·316
	4·3	13·4	0·312
35 ± 0·5	1·35	3·3	0·246
	2·1	5·3	0·252
27 ± 1	2·4	1·9	0·079
	2·7	1·8	0·067
	3·6	2·5	0·070
	9·1	6·4	0·070
20 ± 1	9·1	2·2	0·024

TABLE 2

Rate constants for the deuteriation of the active methylene group in $[Co(bipy)_2(mal)]^+$ in acidic D_2O

t/°C	$10^3[D_3O^+]$/M	$10^4k_D'$/s^{-1}	k_D/l mol^{-1} s^{-1}
37 ± 0·5	1·65	9·1	0·511
	2·0	11·1	0·554
	2·4	13·3	0·554
	2·8	14·3	0·587
34·5 ± 0·5	2·0	9·75	0·475
	2·8	12·3	0·440
27·5 ± 1	1·65	19·3	0·212
	3·4	7·4	0·200
	3·7	5·6	0·232
	9·1	4·8	0·28
20 ± 1	9·1	9·5	0·105

(*b*) $[Co(bipy)_2(mal)]^+$.—The ^1H n.m.r. spectrum of this complex is shown in Figure 3. Since the twofold axis of symmetry exists as in the ethylenediamine analogue, there is again one signal from the malonato methylene group at $-2{\cdot}11$ p.p.m. The rate constants for deuteriation, obtained from the monitoring of this signal, are in Table 2.

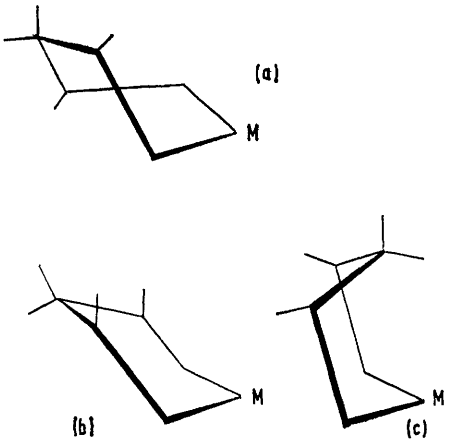

FIGURE 1 Conformations of the malonato-ring: (a) skew boat; (b) chair; (c) boat

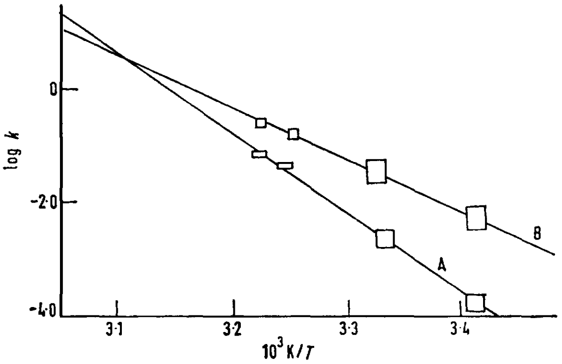

FIGURE 2 Arrhenius plots for the deuteriation of the methylene group in A, $[Co(en)_2(mal)]^+$; and (B), $[Co(bipy)_2(mal)]^+$

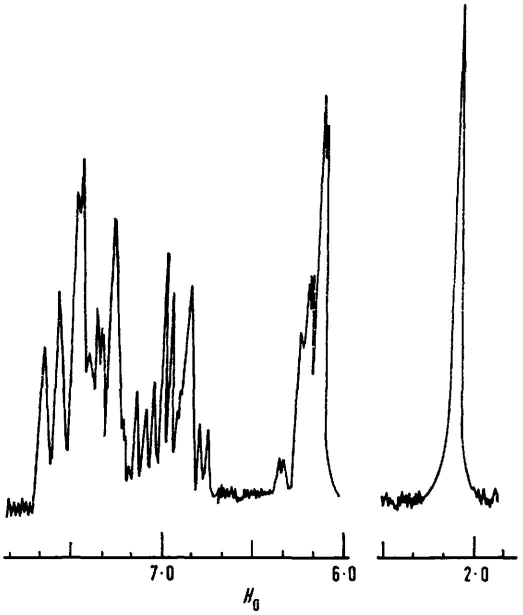

FIGURE 3 60 MHz ^1H n.m.r. spectrum of the $[Co(bipy)_2(mal)]^+$ ion in 0·002M-D_2SO_4 solution

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[6] M. E. Farago and M. A. R. Smith, to be published.

The Arrhenius plots (Figure 2) give $\Delta H^{\ddagger} = 18{\cdot}4 \pm 4$ kcal mol^{-1} and $\Delta S^{\ddagger} - 1{\cdot}0 \pm 5$ cal mol^{-1} K^{-1}.

(*c*) $[Co(en)_2(Etmal)]^+$.—The spectrum of this complex cation in weakly acidic D_2O is shown in Table 3. Shifts were measured upfield of HOD which occurs 3·50 p.p.m. downfield of t-butyl alcohol at 60 MHz. The α-ethyl group gives a first-order A_3M_2X pattern, and conformational interchange of the malonato-group is assumed to be fast. The broadening of the centre peak is due to the inequality of J_{AM} (7 Hz) and J_{AX} (6 Hz). The broad peak at 1·48 p.p.m. is assigned to the ethylenediamine methylene groups. The complex was found to undergo acid hydrolysis,[6] unlike the simple malonato-complexes, and no data were obtained on rates of exchange.

TABLE 3

^{1}H N.m.r. spectral assignments (p.p.m. *vs.* t-butyl alcohol) for the $[Co(en)_2Etmal]^+$ ion

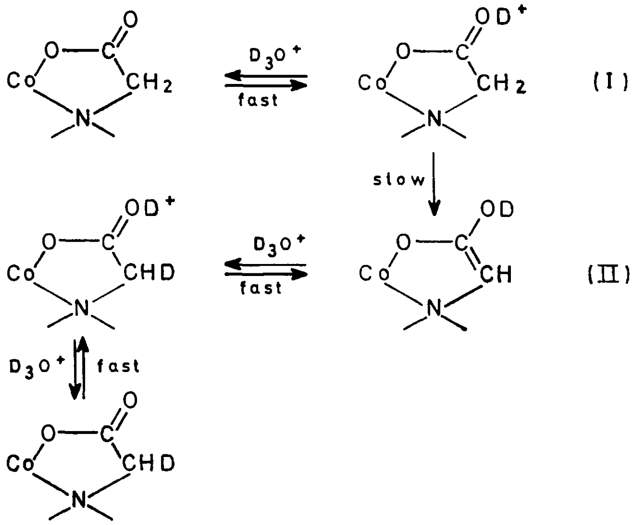
Signal	δ	
$-NH_2$(*cis* to O)	−3·13	
NH (*trans* to O)	−4·14	
$-(CH_2)_2-$(en)	−1·48	
−C−H (malonate)	−1·90 (triplet)	
$-CH_2$	−0·72 (quintuplet)	J_{MX} 6 Hz
$-CH_3$	+0·04 (triplet)	J_{AM} 7 Hz

DISCUSSION

The isotopic exchange of the methylene groups of polyaminecarboxylic acids complexed to cobalt(III) has been studied by ^{1}H n.m.r. spectroscopy. The mechanisms of the reactions have been discussed in terms of an enolization mechanism path[7,8] which requires, in both acidic and basic media, that the rate-determining step be rupture of a C–H bond (Scheme 1). Sudmeir *et al.*[9] have shown by ^{1}H n.m.r. studies of such compounds in 'super acid' ($FSO_3H-SbF_5-SO_2$) at −80 °C that the carbonyl groups can become protonated to give intermediates of type (I), thus providing evidence for such a mechanism.

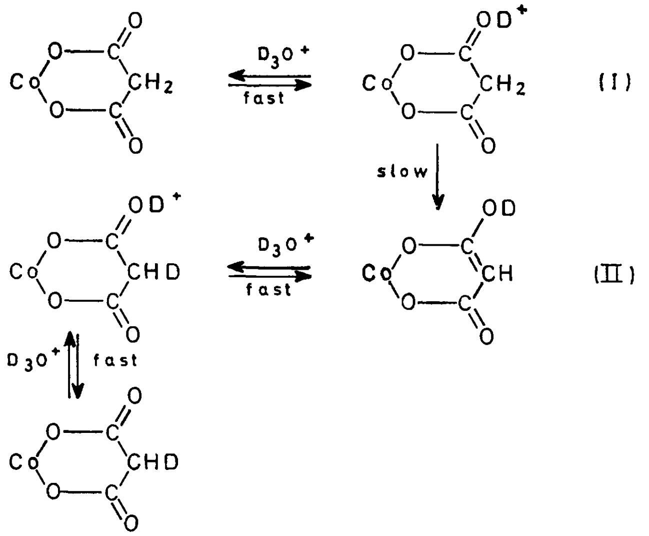
The stereochemistry of the edta complex $[Co(edta)]^-$ has been elucidated by Weakliem and Hoard.[10] The ion contains two different kinds of glycinate ring: rings (R) which are out-of-plane, strain-free, and planar; and rings (G) which are in-plane, strained, and bent. The out-of-plane ring, type (R), undergoes isotopic exchange, whereas the (G) ring does not. Terrill and Reilley[8] suggest that the strain-free ring is able to undergo enolization easily and so isotopic exchange takes place.

Both intermediates (I) and (II) in the enol mechanism (Scheme 1) can exist in various canonical forms and the resonance structure of (II) will contain a planar ring with the α-carbon trigonally hybridised. This is facilitated in the flat (R) ring where the formation of the various intermediates can take place with very little change in structure. The carbonyl group of the (G) ring in the $[Co(edta)]^-$ ion does take up a proton (at least in the 'super acid'),[9] but fails to undergo electron rearrangement and formation of (II) with its concomitant atomic movement. If the formation of a resonance-stabilized planar ring is a prerequisite for isotopic exchange, then it can be understood why $[Cu(L\text{-}ala)_2]$ becomes deuteriated, whereas neither methylene group of the β-alanine complexes undergoes isotopic exchange.[11]



SCHEME 1

The enolization mechanism is equally applicable to the malonatocobalt(III) ring (Scheme 2) which, although bent,[5] is less strained[12] than the glycinate rings in the $[(edta)]^-$ ion. The intermediates can also be resonance-stabilized giving structures which would be planar and similar to the acetylacetonato-ring. An



SCHEME 2

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[9] (*a*) J. L. Sudmeir, K. E. Schwartz, and A. J. Senzel, *Inorg. Chem.*, 1969, **8**, 215; (*b*) J. L. Sudmeir and K. E. Schwartz, *Chem. Comm.*, 1968, 1646.

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[12] C. W. Van Saun and B. E. Douglas, *Inorg. Chem.*, 1969, **8**, 1145.

example of the effect of electron-withdrawing power on the rate of exchange is given by the ion $[Co(bipy)_2(mal)]^+$, where the electron-withdrawing power of the aromatic group [13] results in faster exchange than in the ethylenediamine analogue.

The lower value of the activation entropy for the bipyridyl compound may well reflect the low affinity of the complex for water of hydration. The rigidity of the substrate is also likely to produce a highly ordered transition state.

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