Kinetic Studies in Aqueous Solutions of Iron(II)-Glycinate, -Ethylenediamine, and -Malonate Complexes†

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The kinetic properties of the complexes formed in aqueous solutions of the Fe^{2+}–glycinate (glyO), -ethylenediamine (en) and -malonate (mal) systems have been investigated by measuring the paramagnetic relaxation rate and shift of the CH_2 protons of the ligands over a wide range of complex formation. The formation rate constants (k^f) of the parent complexes are as follows: glycinate, $k_1 = 5.4 \times 10^6$, $k_2 = 5.0 \times 10^6$, and $k_3 = 1.9 \times 10^6$; ethylenediamine, $k_1 = 7.1 \times 10^7$, $k_2 = 1.8 \times 10^7$, and $k_3 = 2.1 \times 10^6$; malonate, $k_1 = 6.8 \times 10^7$ and $k_2 = 1.3 \times 10^7$ $dm^3\ mol^{-1}\ s^{-1}$. Kinetic evidence for the formation of $[Fe(gly)]^{2+}$, $[Fe(Hen)]^{3+}$, and $[Fe(Hmal)]^+$ complexes is provided. A 'carboxyl-displacement' mechanism is suggested for the interaction between $[Fe(glyO)_3]^-$ and free $glyO^-$ ligand.

The equilibrium properties of some iron(II) complexes were reported in our earlier paper.[1] The stability constants of complexes of Fe^{2+} and Co^{2+} were compared and the similarities and differences in the co-ordination properties discussed. These data gave us a good possibility to study the equilibrium dynamics of iron(II) complexes. This seems to be timely because the formation kinetics of these complexes has been studied only occasionally. Mostly the specific interactions between Fe^{2+} and different aromatic ligands [2,2′-bipyridine (bipy), 1,10-phenanthroline (phen),[2] 2,2′:6′,2″-terpyridine (terpy),[3] or 2,4,6-tripyridyl-s-triazine (tptz)[4]] were investigated. The ligand-exchange reaction between $[Fe(glyO)_2]$ and the free glycinate ($glyO^-$) was studied by Pearson and Lanier[5] using a n.m.r. relaxation method. The value of the published ligand-exchange rate constant is questionable because the formation of $[Fe(glyO)_3]^-$ having considerable stability was not considered.

However, no systematic measurements have been made to reveal the fundamental kinetic properties and the complex-formation mechanism of the iron(II) complexes. Therefore n.m.r. relaxation measurements have been carried out to study the complex-formation kinetics in the Fe^{2+}–glyO, –ethylenediamine (en), and –malonate (mal) systems.

Experimental

The experimental conditions for the preparation of the $FeCl_2$ stock solution and the iron(II) complexes were described in our earlier paper.[1] The formation constants of the complexes formed in the Fe^{2+}–glycinate ($\log \beta_1 = 3.73$, $\log \beta_2 = 6.65$, and $\log \beta_3 = 8.87$), –ethylenediamine ($\log \beta_1 = 4.26$, $\log \beta_2 = 7.73$, and $\log \beta_3 = 10.17$), and –malonate ($\log \beta_1 = 2.24$ and $\log \beta_2 = 3.86$) systems were determined.[1] The n.m.r. relaxation measurements required relatively high ligand concentrations. In pH-metry the Fe^{2+}–glycinate system could be studied at relatively high ligand excess because the complex formation occurs in the pH range where protonation of the ligand does not have a significant buffer effect.[6] This was not possible in the case of the Fe^{2+}–ethylenediamine and –malonate systems and commensurable ligand–metal concentration ratios had to be used to get reliable equilibrium data. Unfortunately, no spectrophotometry can be used to investigate the high ligand excess state because the complexes have very low absorbances.

The n.m.r. spectra of the H_2O and CH_2 protons were recorded on a Bruker WP SY FT spectrometer (operating at 200 MHz). Experimental T_2 values were calculated from the half-widths of the n.m.r. signals. The chemical shifts were referenced to 3-(trimethylsilyl)propanesulphonic acid sodium salt.

For the n.m.r. relaxation measurements, an oxygen-free titration method was elaborated. The samples (5.00 cm^3) were prepared in the n.m.r. tube (diameter 1 cm, length 20 cm) and deoxygenated with argon gas. The tube was closed with a special n.m.r. pressure cap ensuring a small overpressure of inert gas. The KOH solution was injected by an automatic burette fitted with a syringe piercing the pressure cap.

The measurements were carried out at 25 ± 1 °C unless otherwise stated. The ionic strength during the titration was adjusted to $I = 1.0$ mol dm^{-3}. Before the titrations the ionic strength of the samples was calculated (because of the high concentration of the charged species in the samples and the variable dilution) and a suitable quantity of KCl was added to the sample and to the KOH solution.

The measured linewidths and shifts were corrected for the diamagnetism (measured in the absence of Fe^{2+}) of the protons according to equations (1) and (2) where T_{2P}^{-1} and $\Delta\omega_p$ are the

$$T_{2P}^{-1} = \Pi(\Delta\nu_{\frac{1}{2}m} - \Delta\nu_{\frac{1}{2}d}) \quad (1)$$

$$\Delta\omega_p = 2\Pi(\Delta\omega_m - \Delta\omega_d) \quad (2)$$

paramagnetic contributions to the relaxation rate (s^{-1}) and shift (rad s^{-1}), $\Delta\nu_{\frac{1}{2}m}$ and $\Delta\omega_m$ are the measured linewidth at half-height and the measured resonance frequency (Hz) for a solution of the iron(II) complexes and $\Delta\nu_{\frac{1}{2}d}$ and $\Delta\omega_d$ are the measured linewidth and the measured resonance frequency (Hz) in the absence of Fe^{2+}. The experimental data measured in the absence of Fe^{2+} (the temperature and pH dependences of the resonances of the H_2O and CH_2 protons) were used for evaluation of the metal-complex systems.

The concentration distributions of the species were calculated using the program PSEQUAD.[7] For the calculation of the kinetic parameters the generalized Swift–Connick equations (see SUP 56772) were used with which the relaxation data

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† *Supplementary data available* (No. SUP 56772, 5 pp.): generalization of the Swift-Connick equations. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

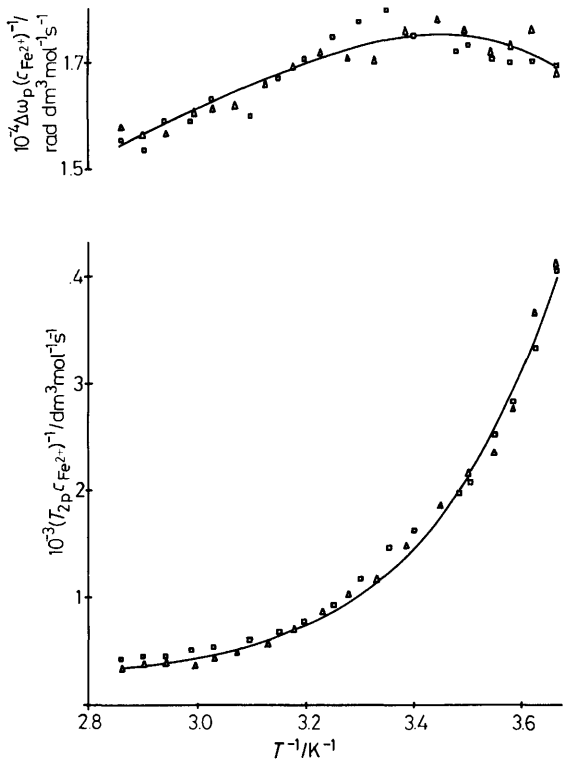

Figure 1. Temperature dependence of the paramagnetic relaxation rate and the shift in aqueous solutions of Fe^{2+} from the behaviour of the water protons, normalized for the total metal-ion concentrations [P_{Fe} = 5.817 × 10^{-3} (Δ) or 8.726 × 10^{-3}(□)]

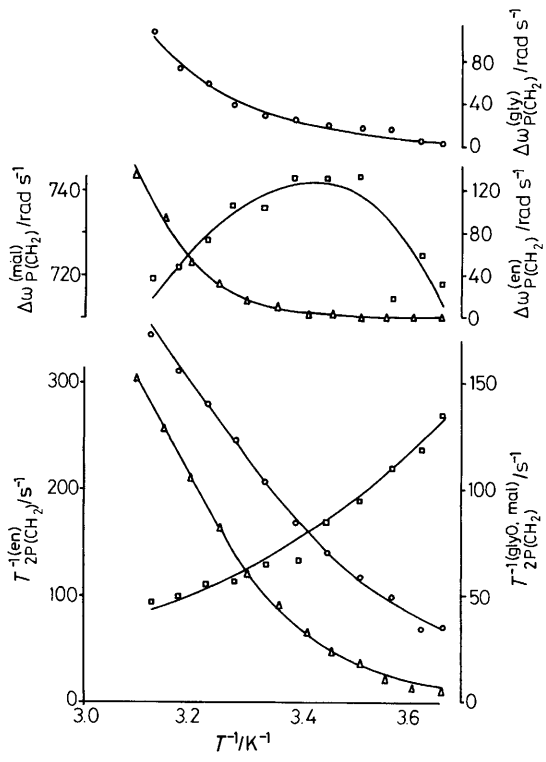

Figure 2. Temperature dependence of the paramagnetic relaxation rate and shift of the $[Fe(glyO)_3]^-$ (○), $[Fe(en)_3]^{2+}$ (△) and $[Fe(mal)_2]^{2-}$ (□) complexes from the CH_2 signals of the ligand. $P[Fe(en)_3^{2+}]$ = 9.917 × 10^{-3}, $P[Fe(mal)_2^{2-}]$ = 6.291 × 10^{-2}, and $P[Fe(glyO)_3^-]$ = 5.924 × 10^{-3}

measured in solutions containing several paramagnetic species can be evaluated.

Results and Discussion

Relaxation Mechanism of the Nucleus in the Co-ordination Sphere of Fe^{2+}.—The correct interpretation of the relaxation data required knowledge of the relaxation mechanism of the water and CH_2 protons of the ligands in the co-ordination sphere of the Fe^{2+}. Temperature-dependent measurements were carried out to separate the kinetic (average lifetime τ_M) and relaxation [paramagnetic shift ($\Delta\omega_M$) paramagnetic relaxation time (T_{2M})] parameters.

Paramagnetic relaxation of the water protons. The water-exchange rate constant of $[Fe(H_2O)_6]^{2+}$ was determined by Swift and Connick[8] using ^{17}O n.m.r. relaxation.

The temperature dependence of the paramagnetic relaxation rate and shift of the water protons was measured in solutions using different concentrations of Fe^{2+} (see Figure 1). For the simultaneous evaluation of the relaxation rate and shift data the temperature dependences of the Swift–Connick equations were used [$\tau_M = (h/kT)\ \exp\ (\Delta H^{\ddagger}/RT - \Delta S^{\ddagger}/R)$ $\Delta\omega_M/\omega_0 = \alpha/T$, and $T_{2M} = B\exp(C/RT)$; see ref. 8] and the best fit was reached when $T_{2M}^{-1} \ll \Delta\omega_M$, equations (3) and (4) where P_M is a molar

$$T_{2P}^{-1} = \frac{P_M\tau_M^{-1}\Delta\omega_M^2}{\tau_M^{-2} + \Delta\omega_M^2} = P_M r_{T2} \quad (3)$$

$$\Delta\omega_P = \frac{P_M\tau_M^{-2}\Delta\omega_M}{\tau_M^{-2} + \Delta\omega_M^2} = P_M r_\omega \quad (4)$$

ratio of the co-ordinated nucleus {$P_{FeL_i} = i[FeL_i]/c_L$; i is the co-ordination number of the ligand (or water); c_L is the total ligand (or water) concentration}, r_{T2} and r_ω are the appropriate relaxation contributions of the paramagnetic species. The effect of the outer sphere [r_{os} = (2.8 ± 0.7) × 10^3 s^{-1}] was taken into account with the only concentration-dependent parameter [equation (5)].

$$T_{2P}^{-1}(T) = P_{Fe}[r_{T2}(T) + r_{os}] \quad (5)$$

The conclusion of the investigation was that the paramagnetic relaxation in aqueous solutions of Fe^{2+} detected from the behaviour of the water protons can be attributed to the change in the resonance frequency ('Δω' mechanism). The proton and water exchange rate constants determined from the ^1H and ^{17}O nuclei [k^{Fe-H_2O} = (3.1 ± 0.2) × 10^6 s^{-1}, $\Delta H^{\ddagger}$ = 28.2 ± 2 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −28 ± 2 J K^{-1} mol^{-1}, α = (6.22 ± 0.03) × 10^{-2} K (this work); k^{Fe-H_2O} = 3.2 × 10^6 s^{-1} (ref. 8)] are the same, *i.e.* the proton exchange rate is controlled by the exchange of the water molecules in the aqueous solution of Fe^{2+}.

Paramagnetic relaxation of the CH_2 *protons.* The paramagnetic relaxation mechanism for the CH_2 protons studied may be different from that of the water protons. Therefore, the temperature dependences of the paramagnetic relaxation rates and shifts in solutions of $[Fe(glyO)_3]^-$, $[Fe(en)_3]^{2+}$, and $[Fe(mal)_2]^{2-}$ were determined (see Figure 2) in a concentration range where only one paramagnetic complex is dominant. The evaluation of the data showed that the relation $T_{2M}^{-1} \ll \Delta\omega_M$ also applies to these protons ('Δω' mechanism). The calculated activation and n.m.r. parameters for $[Fe(glyO)_3]^-$, $[Fe(en)_3]^{2+}$, and $[Fe(mal)_2]^{2-}$ are as follows: $\Delta H^{\ddagger}$ = 27 ± 1, 43 ± 1, and 14 ± 5 kJ mol^{-1}; $\Delta S^{\ddagger}$ = −73 ± 3, −25 ± 4, and −101 ± 18 J K^{-1} mol^{-1}; 10^3 α = 16.2 ± 0.6, 21.5 ± 1.6, and 2.76 ± 0.03 K. The relaxation processes of $[Fe(glyO)_3]^-$ and $[Fe(en)_3]^{2+}$ (at room temperature) are controlled by the chemical exchange, that of $[Fe(mal)_2]^{2-}$ by the paramagnetic relaxation.

Table 1. Kinetic and n.m.r. parameters of the iron(II) complexes

Kinetic process	$10^{-3}r_{T2}$/ s^{-1}	$10^{-4}r_{\omega}$/ rad s^{-1}	$10^{-3}k_d$/ s^{-1}	$10^{-4}\Delta\omega_M$/ rad s^{-1}
Fe^{2+} + gly		0.53 ± 0.01*		
$[Fe(glyO)]^+ \rightleftharpoons Fe^{2+} + glyO^-$	1.0 ± 0.3		1.0	
$[Fe(glyO)_2] \rightleftharpoons [Fe(glyO)]^+ + glyO^-$	6.0 ± 0.4		6.0	
$[Fe(glyO)_3]^- \rightleftharpoons [Fe(glyO)_2] + glyO^-$	11.4 ± 0.6		11.4	
$[Fe(glyO)_3]^- + glyO^-$	36 ± 3*	2.0 ± 0.2*	47*	10.1*
Fe^{2+} + Hen^+	15 ± 6*		15*	
$[Fe(en)]^{2+} \rightleftharpoons Fe^{2+} + en$	3.9 ± 0.8		3.9	
$[Fe(en)_2]^{2+} \rightleftharpoons [Fe(en)]^{2+} + en$	6.2 ± 0.5		6.2	
$[Fe(en)_3]^{2+} \rightleftharpoons [Fe(en)_2]^{2+} + en$	7.8 ± 0.3		7.8	
Fe^{2+} + $Hmal^-$	0.95 ± 0.14*	2.0 ± 0.2*	420*	2.0*
$[Fe(mal)] \rightleftharpoons Fe^{2+} + mal^{2-}$	0.43 ± 0.07	1.3 ± 0.1	390	1.3
$[Fe(mal)_2]^{2-} \rightleftharpoons [Fe(mal)] + mal^{2-}$	0.75 ± 0.04	1.5 ± 0.1	300	1.5

* Second-order rate constants and n.m.r. parameters, because the equilibrium data are not known; only the kinetics data indicate complex formation.

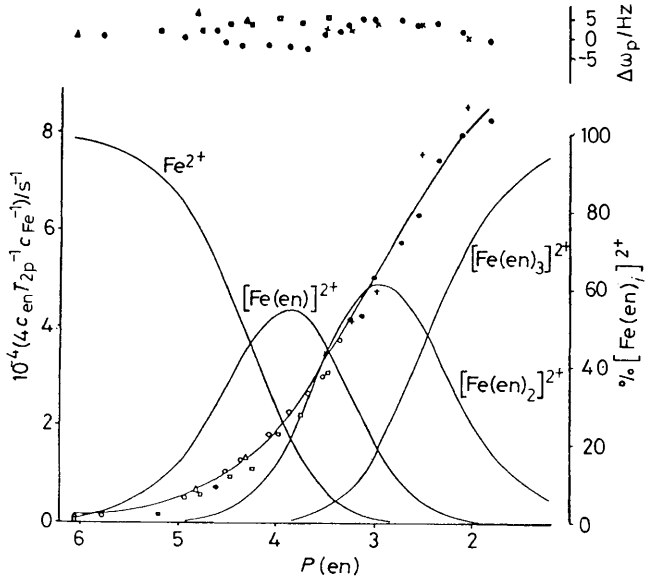

Figure 3. Normalized paramagnetic relaxation rate data for the Fe^{2+}–ethylenediamine system from the CH_2 protons of the ligand, together with the concentration distribution. c_H^0 = 1,1266; c_{en}^0 = 4.888 × 10^{-1}, c_{Fe}^0 = 9.028 × 10^{-3} (△) or 1.806 × 10^{-2} (○); c_{en}^0 = 5.089 × 10^{-1}, c_{Fe}^0 = 2.714 × 10^{-3} (×) or 4.511 × 10^{-3} (●); c_{en}^0 = 5.460 × 10^{-1}, c_{Fe}^0 = 9.028 × 10^{-3} (□) mol dm^{-3}

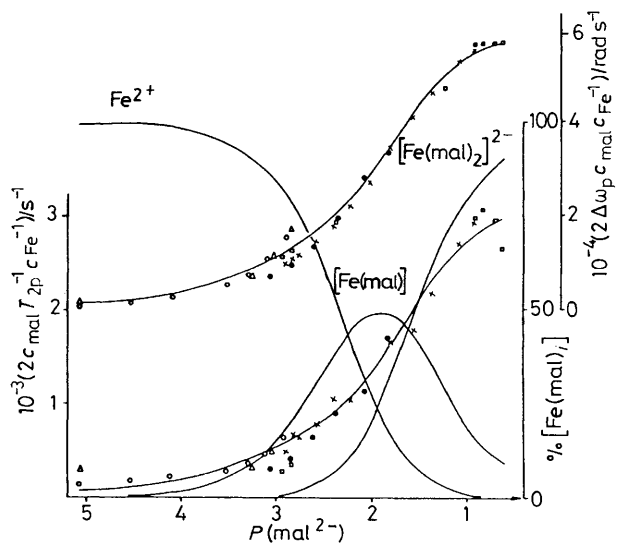

Figure 4. Normalized paramagnetic relaxation rate and shift data for the Fe^{2+}–malonate system from the CH_2 protons of the ligand, together with the concentration distribution. c_H^0 = 8.000 × 10^{-1}, c_{mal}^0 = 4.000 × 10^{-1}, c_{Fe}^0 = 3.122 × 10^{-2} (Δ) or 6.244 × 10^{-2} (○); c_H^0 = 5.671 × 10^{-1}, c_{mal}^0 = 4.000 × 10^{-1}, c_{Fe}^0 = 9.028 × 10^{-3} (□) or 1.806 × 10^{-2} (×); c_H^0 = 3.674 × 10^{-1}, c_{mal}^0 = 2.667 × 10^{-1}, c_{Fe}^0 = 2.709 × 10^{-2} (●) mol dm^{-3}

Kinetic Studies of the Iron(II) *Complexes.*—The paramagnetic relaxation data measured for the CH_2 protons of the ligands in the Fe^{2+}–ethylenediamine, –malonate, and –glycinate systems normalized for the total iron(II) concentrations, and the calculated curves, are shown in Figures 3—5 together with the concentration distributions of the complexes. The calculated kinetic and n.m.r. parameters are collected in Table 1.

Ethylenediamine system. The relaxation processes of the Fe^{2+}–ethylenediamine complexes are controlled by chemical exchange; no paramagnetic shift could be detected in the range studied [see equation (4); *i.e.* $\tau_M^{-2}/\Delta\omega_M$ is rather small if $\tau_M^{-1} \ll \Delta\omega_M$]. The measured paramagnetic relaxation rates could be interpreted by the dissociation of the parent complexes [equations (6)—(8)]. The kinetic calculations indicated an interaction between Fe^{2+} and Hen^+ [equation (9)].

$$[Fe(en)]^{2+} \overset{k_1^d}{\rightleftharpoons} Fe^{2+} + en \quad (6)$$

$$[Fe(en)_2]^{2+} \overset{k_2^d}{\rightleftharpoons} [Fe(en)]^{2+} + en \quad (7)$$

$$[Fe(en)_3]^{2+} \overset{k_3^d}{\rightleftharpoons} [Fe(en)_2]^{2+} + en \quad (8)$$

$$v = k_H^f[Fe^{2+}][Hen^+] \quad (9)$$

Malonate system. The fast dissociation processes of the Fe^{2+}–malonate complexes are in the range of paramagnetic relaxation-controlled kinetics [see equations (3) and (4) if $\tau_M^{-1} \gg \Delta\omega_M$] and there is a considerable shift contribution to the measured data. The paramagnetic relaxation rate and shift values could be interpreted as a dissociation effect of the mono and bis complexes [equations (10) and (11)] and the concentration product of Fe^{2+} and the protonated ligand [equation (12)].

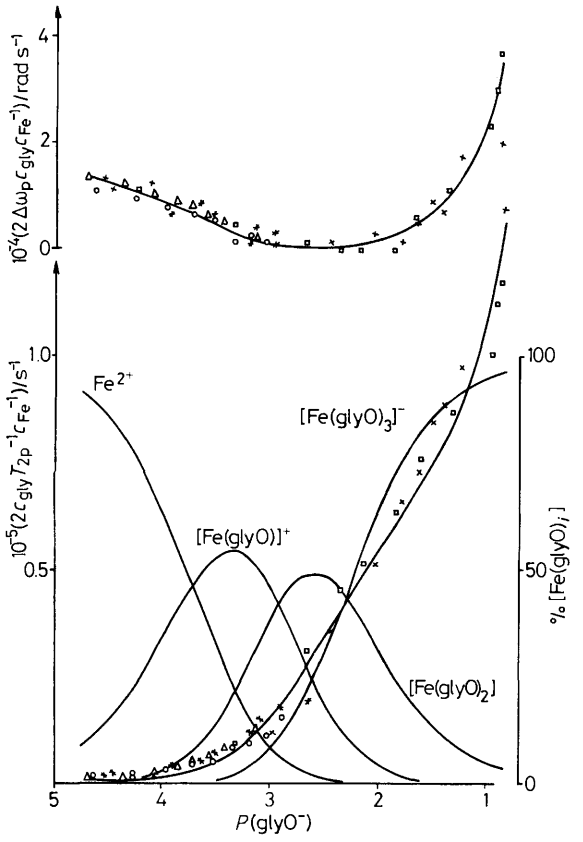

Figure 5. Normalized paramagnetic relaxation rate and shift data for the Fe^{2+}–glycinate system from the CH_2 protons of the ligand, together with the concentration distribution. $c_H^0 = 1.5000$, $c_{gly}^0 = 1.5000$, $c_{Fe}^0 = 4.511 \times 10^{-3}$ (×), 9.028×10^{-3} (□), or 6.244×10^{-2} (△); $c_H^0 = 1.3636$, $c_{gly}^0 = 1.3636$, $c_{Fe}^0 = 1.561 \times 10^{-2}$ (×) or 3.122×10^{-2} (○) mol dm^{-3}

$$[Fe(mal)] \overset{k_1^d}{\rightleftharpoons} Fe^{2+} + mal^{2-} \quad (10)$$

$$[Fe(mal)_2]^{2-} \overset{k_2^d}{\rightleftharpoons} [Fe(mal)] + mal^{2-} \quad (11)$$

$$v = k_H^f[Fe^{2+}][Hmal^-] \quad (12)$$

Glycinate system. The dissociation of the parent complexes had an effect only on the measured paramagnetic relaxation rates, equations (13)—(15). These processes are controlled by

$$[Fe(glyO)] \overset{k_1^d}{\rightleftharpoons} Fe^{2+} + glyO^- \quad (13)$$

$$[Fe(glyO)_2] \overset{k_2^d}{\rightleftharpoons} [Fe(glyO)]^+ + glyO^- \quad (14)$$

$$[Fe(glyO)_3]^- \overset{k_3^d}{\rightleftharpoons} [Fe(glyO)_2] + glyO^- \quad (15)$$

chemical exchange [see equation (4); *i.e.* $\tau_M^{-2}/\Delta\omega_M$ is rather small if $\tau_M^{-1} \ll \Delta\omega_M$].

The decreasing part of the measured paramagnetic shifts could be attributed to the interaction between the Fe^{2+} and the gly ligand. No paramagnetic relaxation rate contribution could be detected for this process because of the strong relaxation control [see equation (3); *i.e.* $\Delta\omega_M^2/\tau_M^{-1}$ is rather small if $\tau_M^{-1} \gg \Delta\omega_M$] and thus there were insufficient data for calculation of the kinetics parameters.

On increasing the free-ligand concentration after the formation of the tris complex a sharp change in the relaxation rate and shift values could be detected, in accord with an interaction between the tris complex and the free ligand [equation (16)].

$$v = k_4^f[Fe(glyO)_3^-][glyO^-] \quad (16)$$

Table 2. Published formation rate constants and those of the iron(II) complexes together with the K_{os} values of the mono complexes ($K_{os} = k^f/k^{Fe-H_2O}$)

Complex or kinetic process	k^f/ dm^3 mol^{-1} s^{-1}	K_{os}/ dm^3 mol^{-1}	Ref.
$[Fe(bipy)]^{2+}$	1.6×10^5	0.05	2
$[Fe(phen)]^{2+}$	5.6×10^4	0.02	2
$[Fe(terpy)]^{2+}$	8.0×10^4	0.03	3
$[Fe(tptz)]^{2+}$	1.3×10^5	0.04	4
$[Fe(glyO)(H_2O)_4]^+$	$(5.4 \pm 1.6) \times 10^6$	1.7	
$[Fe(glyO)_2(H_2O)_2]$	$(5.0 \pm 0.3) \times 10^6$		
$[Fe(glyO)_2] + glyO^-$	4.0×10^4		5
$[Fe(glyO)_3]^-$	$(1.9 \pm 0.1) \times 10^6$		
$[Fe(glyO)_3]^- + glyO^-$	$(4.7 \pm 0.5) \times 10^4$		
$Fe^{2+} + Hen^+$	$(1.5 \pm 0.6) \times 10^4$		
$[Fe(en)(H_2O)_4]^{2+}$	$(7.1 \pm 1.5) \times 10^7$	22.9	
$[Fe(en)_2(H_2O)_2]^{2+}$	$(1.8 \pm 0.1) \times 10^7$		
$[Fe(en)_3]^{2+}$	$(2.1 \pm 0.1) \times 10^6$		
$Fe^{2+} + Hmal^-$	$(4.2 \pm 0.6) \times 10^5$		
$[Fe(mal)(H_2O)_4]$	$(6.8 \pm 1.1) \times 10^7$	21.9	
$[Fe(mal)_2(H_2O)_2]^{2-}$	$(1.3 \pm 0.1) \times 10^7$		

It should be noted that the sensitivities of the applied equilibrium and kinetic examination methods are different. Using pH-metry only the stability constants of the parent complexes could be determined, while the n.m.r. relaxation method is sensitive to the undeterminable minor species. This gave the possibility of revealing the formation of $[Fe(gly)]^{2+}$, $[Fe(Hen)]^{3+}$, and $[Fe(Hmal)]^+$ complexes.

The earlier published ligand-exchange rate constant[5] for reaction (17) (see Table 2) was determined in the concentration

$$[Fe(glyO)_2] + glyO^{-*} \overset{k_{ex}}{\rightleftharpoons} [Fe(glyO)(glyO^*)] + glyO^- \quad (17)$$

range up to 1 mol dm^3 $glyO^-$ supposing log $K_3^{glyO} < 1$. These data are unacceptable, because log $K_3^{glyO} = 2.22$ and in this free-ligand concentration range the formation of the tris complex is dominant.

The interaction between $[Fe(glyO)_3]^-$ and $glyO^-$ could be interpreted by the 'carboxyl displacement'. The nitrogen donor group of the free ligand can displace the weaker bonded carboxyl group from the chelate ring, resulting in two chelated and two unidentate ligands in the co-ordination sphere. This strongly distorted structure has a very low stability and large lability. Unfortunately, no activation parameters could be given for this process. In the concentration range (pL < 1.2) where the above-mentioned interaction was detected the formation of $[Fe(glyO)_3]^-$ is dominant. The mathematical evaluation of the temperature-dependent measurements required the common consideration of these two processes but the authenticity of the separation was rather low.

The examination of the Fe^{2+}-malonate system illustrates the upper limit of the application of this type of n.m.r. relaxation method. The stability constant of the bis(malonato) complex is very small (determined pH-metrically) and has a relatively large experimental error which appears in the dissociation rate constant. The determination of the small relaxation contribu-

tions calculated from the paramagnetic relaxation rates required relatively small ligand–metal ratios which is a lower limit of the adoption. However, the kinetic results seem to be correct.

Published formation rate constants and those of the complexes studied together with the outer-sphere stability constants (K_{os}) calculated for the mono complexes are collected in Table 2. The mechanism of complex formation of Fe^{2+} with aromatic ligands containing nitrogen-donor groups was revealed in detail [2–4] and a comparison of the K_{os} values with our data reflects the differences. Relatively large K_{os} values were found in the cases of $[Fe(en)]^{2+}$ and [Fe(mal)], which could be interpreted by the internal conjugate base mechanism[9] for coordination of en and by the two negative charges of mal^{2-}. Further work is in progress in our laboratory to elucidate the mechanism of formation of this type of iron(II) complex.

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