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KINETICS AND MECHANISM OF COMPLEX FORMATION REACTION OF IRON(II) WITH 4-METHYL-8-DI(CARBOXYMETHYL)AMINOMETHYL UMBELLIFERRONE: ROLE OF THE FOURTH CHELATING GROUP IN TRIPODAL (NO_3)-TYPE TETRADENTATE LIGAND STRUCTURE ON THE STABILIZATION OF THE IRON(II) COMPLEX

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Abstract—Thermodynamic stability and kinetics and mechanism of the formation of the iron(II) complex of 4-methyl-8-di(carboxymethyl)aminomethyl umbelliferrone (**1**, H_3muia) have been studied spectrophotometrically in an aqueous sodium perchlorate solution (0.10 mol dm^{-3}) at 25°C. A 1 : 1 (metal : ligand) complex of iron(II) with **1** forms in an acidic medium with a stability constant, log β_{11} (mol dm^{-3}), of 14.42 ± 0.20, in contrast to no formation of the iron(II) complex with the related terdentate ligands having a mono(carboxymethyl) ligating group. This complex formation reaction proceeds through a single pathway of Fe^{2+} with Hmuia^{2-} ligand species with a rate constant, k_{21} (mol^{-1} dm^3 s^{-1}), of $(7.04 \pm 0.20) \times 10^4$. The coordination reaction mechanism is discussed in detail.

In a previous paper,[1] the coordination behaviour of iron(III) was investigated with a series of aromatic aminocarboxylate ligands containing a coumarin skeleton. A tripodal tetradentate ligand of 4-methyl-8-di(carboxymethyl)aminomethyl umbelliferrone (**1**, H_3muia) (*cf* Scheme 1), as well as related terdentate ligands of 4-methyl-8-(carboxymethyl)aminomethyl umbelliferrone and 4-methyl-8-(*N*-carboxymethyl-*N*-methyl)aminomethyl umbelliferrone, formed a 1 : 1 (metal : ligand) complex with iron(III). In a subsequent investigation, it was discovered that the ligand **1** coordinated to iron(II) with a relatively large stability constant, but that these terdentate ligands do not form any iron(II) complexes in perceptible concentration in aqueous solution.

Knowledge of coordination reaction mechanism of multidentate aminocarboxylate ligands to iron(II) is a very important aspect of bioinorganic chemistry.[2,3] However, nothing has been reported on the kinetics and mechanism of the coordination reaction of **1** to iron(II). The present paper aims at elucidating the thermodynamics and the kinetics and mechanism of the iron(II) complex of **1** in aqueous media.

EXPERIMENTAL

Materials

The synthesis of **1** has been reported in the previous paper.[1] An aqueous iron(II) solution was prepared in the same manner as has been described elsewhere.[2] All other chemicals used were of analytical or equivalent grade.

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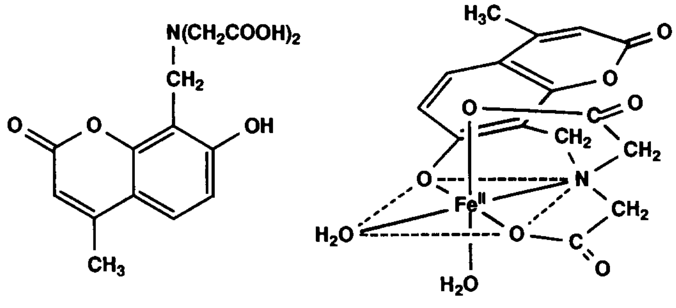


1 (H_3muia) **2** (Fe(muia)$^-$)

Scheme 1.

Measurements

The same apparatus as has been given in the previous paper[1] was used for the thermodynamic and kinetic investigation. The general procedure for the determination of observed rate constant has been stated elsewhere,[2] except that the ionic strength was kept constant at 0.10 mol dm^{-3} $NaClO_4$. Kinetic runs were made using a stopped-flow spectrophotometer[1] at 520 nm under pseudo-first-order reaction conditions with a constant and excess metal ion concentration at 25.0±0.2°C.

The other apparatus used has been described in the previous paper.[1]

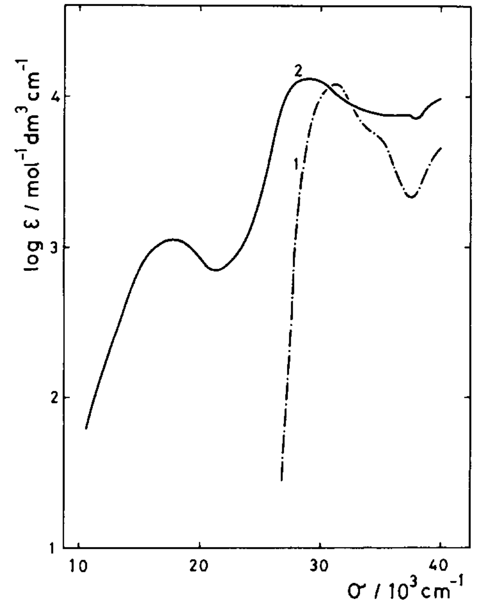


Fig. 1. Absorption spectra of the ligand **1** and its iron(II) complex. 1, H_2muia$^-$ (pH 3.60) ; 2, Fe(muia)$^-$ (pH 3.60).

RESULTS AND DISCUSSION

Electronic absorption spectra

The absorption spectrum of the iron(II) complex of **1** is depicted in Fig. 1. This spectrum is characteristic in that it has an absorption maximum at 17.8×10^3 cm^{-1} [molar absorption coefficient, log ε (mol^{-1} dm^3 cm^{-1}) = 3.1], being assignable to a charge-transfer transition from the central metal atom to the ligand by taking into consideration that the iron(II) complex of **1** with an [Fe(N)$(O)_5$]-type primary coordination unit is estimated to have a high-spin d^6 configuration. Another absorption maximum at 29.0×10^3 cm^{-1} [log ε (mol^{-1} dm^3 cm^{-1}) = 4.1], which corresponds to the absorbance maximum of the free ligand [λ_{max} (cm^{-1}) = 31.0×10^3; log ε (mol^{-1} dm^3 cm^{-1}) = 4.1], is due to the $\pi^* \leftarrow \pi$ intraligand electronic transition of the coumarin ring.

The phenolate-oxygen-protonated species of **1** gave an intense fluorescence with an excitation spectral maximum at 29.9×10^3 cm^{-1} and an emission spectral maximum at 22.3×10^3 cm^{-1}. On the contrary, the iron(II) complex of **1** exhibited a very weak fluorescence (quantum yield, *ca* 1.7×10^{-5}) with an excitation spectral maximum at 29.1×10^3 cm^{-1} and an emission spectral maximum at 21.6×10^3 cm^{-1}. These fluorescence spectral features indicate that, following the excitation process, a $\pi^* \rightarrow e_g(O_h)$ ligand-to-metal charge-transfer process predominantly proceeds immediately, in place of a radiative $\pi^* \rightarrow \pi$ intraligand transition process in the coordinated coumarin chromophore, although the latter process is noticed in small fraction with a decreased energy gap between the lowest excited and ground states (7.5×10^3 cm^{-1}) as compared with the free coumarin chromophore (7.6×10^3 cm^{-1}). This $\pi^* \rightarrow e_g(O_h)$ ligand-to-metal charge-transfer process is probably followed by a radiationless deactivation process in the metal-centred chromophore through its many intermediate d-electronic energy states.

It is concluded from these results that the absorption maximum at 17.8×10^3 cm^{-1} certainly has a $\pi^* \leftarrow t_{2g}(O_h)$ metal-to-ligand charge-transfer (MLCT) characteristic.[2] This absorption band is suitable for thermodynamic and kinetic investigation on the formation of the iron(II) complex with **1**.

Thermodynamic stability

A preliminary study by the method of continuous variations[4] revealed the formation of a unique 1 : 1 (metal : ligand) complex of iron(II) with **1**. The stability constant (β_{11}) was determined spectrophotometrically at 520 nm under the conditions of $C_M \gg C_L$, on the basis of a general principle and procedure given in previous papers,[1,2] where C_M and C_L are the total concentrations of the metal and the ligand, respectively.

$$\begin{aligned}\beta_{11} &= [\mathrm{Fe(muia)^-}]/[\mathrm{Fe^{2+}}][\mathrm{muia^{3-}}] \\ &\times \log{(A_{\max}-A)/(A-A_{\min})} \\ &= \log{\{K_{\mathrm{a(amNH)}}K_{\mathrm{a(PhOH)}}K_{\mathrm{a(COOH)}}[\mathrm{H^+}]^3} \\ &+K_{\mathrm{a(amNH)}}K_{\mathrm{a(PhOH)}}[\mathrm{H^+}]^2 \\ &+K_{\mathrm{a(amNH)}}[\mathrm{H^+}]+1\} \\ &-\log C_M-\log\beta_{11}. \qquad (1)\end{aligned}$$

Here $A_{\max}$, $A_{\min}$ and A represent the absorbance of the iron(II) complex, the free ligand, and the complex and the free ligand co-existing at the hydrogen ion concentration of $[H^+]$. The protonation constants of **1** are denoted by $K_{\mathrm{a(amNH)}}$, $K_{\mathrm{a(PhOH)}}$ and $K_{\mathrm{a(COOH)}}$ for the amino nitrogen, phenolate oxygen and carboxylate oxygen atoms,[1] respectively. No contribution of $\mathrm{Fe(OH)^+}$ [and other hydrolyzed iron(II) species] to the complex formation equilibrium was considered here because the iron(II) complex of **1** forms in a weakly acidic aqueous solution of around pH 3 and because the hydrolysis constant of $\mathrm{Fe^{2+}}$ to $\mathrm{Fe(OH)^+}$ is too small $\{\log K_{\mathrm{OH}}{}^{11}$ (mol dm^{-3}) $= -9.5$ (1.0 mol dm^{-3}, $\mathrm{NaClO_4}$, 25°C), $K_{\mathrm{OH}}{}^{11} = [\mathrm{Fe(OH)^+}][\mathrm{H^+}]/[\mathrm{Fe^{2+}}]^5\}$ for the $\mathrm{Fe(OH)^+}$ species to be present in appreciable fraction.

Figure 2 depicts the experimental data plots for the estimation of the stability constant. A linear relation was found between the absorbance term and the hydrogen ion concentration term of eq. (1) with a slope of unity, which confirms the result by the method of continuous variations. The value of β_{11} was calculated from the intercept of the experimental linear relation; it is given in Table 1 together with the stability constants of the iron(II) complexes of the ligands of related concern.

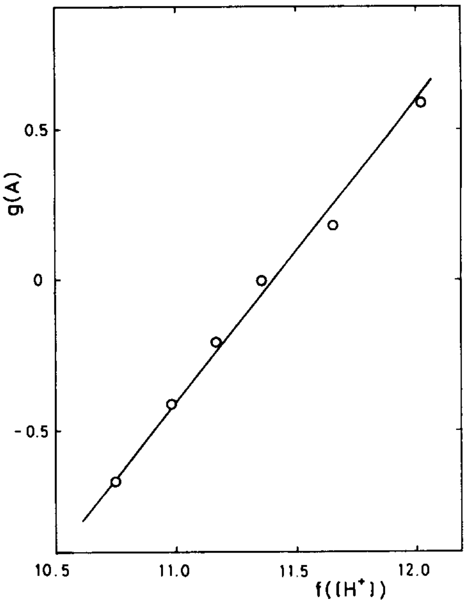


Fig. 2. Relation between the absorbance term, $g(A)$, and the hydrogen ion concentration term, $f([\mathrm{H^+}])$, of the iron(II)–**1** system. $g(A) \equiv \log\ (A_{\max}-A)/(A-A_{\min})$. $f([\mathrm{H^+}]) \equiv \log\ \{K_{\mathrm{a(amNH)}}K_{\mathrm{a(PhOH)}}K_{\mathrm{a(COOH)}}[\mathrm{H^+}]^3+K_{\mathrm{a(amNH)}}K_{\mathrm{a(PhOH)}}[\mathrm{H^+}]^2+K_{\mathrm{a(amNH)}}[\mathrm{H^+}]+1\}$. $C_M \gg C_L$; C_M: 1.00×10^{-3} mol dm^{-3}; C_L: 1.00×10^{-4} mol dm^{-3}. 0.10 mol dm^{-3} ($\mathrm{NaClO_4}$), 25°C. Wavelength: 520 nm. Bold line is a theoretical line drawn by using the values of $\log K_{\mathrm{a(amNH)}}$ (mol^{-1} dm^3) = 11.50, $\log K_{\mathrm{a(PhOH)}}$ (mol^{-1} dm^3) = 6.78, $\log K_{\mathrm{a(COOH)}}$ (mol^{-1} dm^3) = 1.90, $\log \beta_{11}$ (mol^{-1} dm^3) = 14.42 and $\log K_{\mathrm{OH}}{}^{11}$ (mol dm^{-3}) = −2.78.

The stability constant of $\mathrm{Fe^{II}(muia)^-}$ (**2**) is considerably larger than that of $\mathrm{Fe^{II}(nta)^-}$ (*cf* Table 1), in which the 7-hydroxycoumarin group of **1** is substituted by a carboxymethyl group. An increased basicity of the coordinating phenolato oxygen [$\log K_{\mathrm{a(PhOH)}}$ (mol^{-1} dm^3) = 6.78[1]] as compared with the carboxylato oxygen [$\log K_{\mathrm{a(COOH)}}$ (mol^{-1} dm^3) = 2.49[6]] is mainly responsible for this increased stability constant. On the contrary, the stability constant of $\mathrm{Fe^{II}(muia)^-}$ is smaller than that of $\mathrm{Fe^{III}(muia)^-}$ (*cf* Table 1). This result con-

Table 1. Stability constants

Complex	$\log \beta_{11}$ (mol^{-1} dm^3)	Reference
2 [$\mathrm{Fe^{II}(muia)^-}$]	14.42±0.20	This work[a]
$\mathrm{Fe^{II}(nta)^-}$	8.33±0.01	11[b]
$\mathrm{Fe^{III}(muia)}$	18.67±0.20	1[c]

[a] 0.10 mol dm^{-3} ($\mathrm{NaClO_4}$), 25°C.

[b] $\mathrm{H_3nta}$: nitrilotriacetic acid, 0.10 mol dm^{-3} (no citation), 20°C.

[c] 0.10 mol dm^{-3} ($\mathrm{NaNO_3}$), 25°C.

forms to a trend of the stability constants of iron(II) and iron(III) complexes of aminopolycarboxylate ligands [e.g. log β_{11} (mol^{-1} dm^3) of Fe^{II}(nta)$^-$ is 8.33 and that of Fe^{III}(nta) is 15.87 (0.1 mol dm^{-3}, KCl, 20°C)[7]].

Kinetics and mechanism

The formation reaction kinetics of the iron(II) complex of **1**, which was followed under the conditions of $C_M \gg C_L$ in the acidity region of pH 4.5–5.5, exhibited a single exponential absorbance vs time curve for more than 3.5 half-life periods, indicating that the reaction has monophasic characteristics.

The rate equation for the reaction was derived in an analogous way to that described previously[1,2] with the consideration that the protonation/deprotonation processes are always in equilibrium as compared with the coordination process (*cf* Scheme 2).

$$k_{obs}\{K_{a(amNH)}K_{a(PhOH)}K_{a(COOH)}[H^+]^3 + K_{a(amNH)}K_{a(PhNH)}[H^+]^2 + K_{a(amNH)}[H^+]+1\}/C_M = k_{22}K_{a(amNH)}K_{a(PhOH)}[H^+]^2 + k_{21}K_{a(amNH)}[H^+]+k_{20}. \qquad (2)$$

Here k_{2j} ($j = 0$–2) refers to the rate constant for the formation reaction pathway related to the species Fe^{2+} and $H_j$muia$^{(2-j)-}$. Figure 3 depicts the experimental data plots of the relation between the left-hand side of eq. (2) and [H$^+$]. A linear dependence was obtained on this relation with a zero intercept within experimental error, indicating that only the pathway of k_{21} exists in the coordination reaction process. The value of k_{21} calculated from the experimental data is given in Table 2, together with the rate constants for the complex formation reactions of interest to the present investigation.

The rate constant, k_{21}, for the iron(II) complex of **1** is of the same magnitude as that for the iron(II) complex of acetohydroxamic acid [*cf* Table 2: log $K_{a(OH)}$ (mol^{-1} dm^3) = 9.33±0.01 (0.10 mol dm^{-3}, NaClO$_4$, 10°C); $K_{a(OH)}$: protonation constant[8]], which is the only ligand reported so far on the formation rate constant with oxygen donor atoms. The k_{21} of the iron(II) complex of **1** is about two orders of magnitude smaller than the water-exchange rate constant of [Fe(H$_2$O)$_6$]$^{2+}$ [(1.0–3.2) × 10^6 s^{-1}, 25°C[9]]. Taking into consideration the intrinsic kinetic nature of iron(II) having a dissociative interchange (I_d) mechanism,[10] this smaller rate constant of k_{21} of the iron(II) complex of **1** implies a steric (molecular structural) influence of the Hmuia^{2-} ligand species on the rate-limiting access of its donor atom to the hexaaquairon(II) cation. Hydrogen-bonded phenolato oxygen or nitrogen donor atom may have a role in the mechanistic rate-determining step.

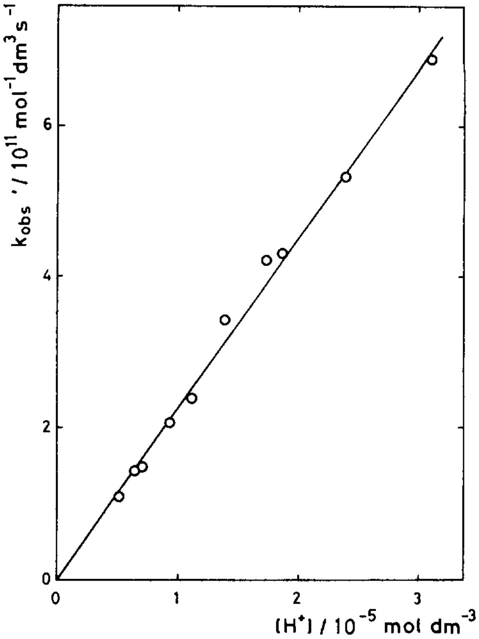
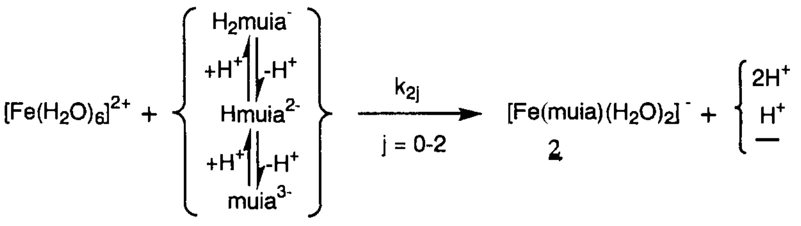


Fig. 3. Dependence of k'_{obs} on [H$^+$] of the iron(II)–**1** system. $k'_{obs} \equiv k_{obs}\{K_{a(amNH)}K_{a(PhOH)}K_{a(COOH)}[H^+]^3 + K_{a(amNH)}K_{a(PhOH)}[H^+]^2 + K_{a(amNH)}[H^+]+1\}/C_M$. $C_M \gg C_L$; C_M: 1.00 × 10^{-3} mol dm^{-3}; C_L: 1.00 × 10^{-4} mol dm^{-3}. 0.10 mol dm^{-3} (NaClO$_4$), 25°C. Wavelength: 520 nm. Bold line is a theoretical line drawn by using the values of $K_{a(amNH)}$, $K_{a(PhOH)}$ and $K_{a(COOH)}$ of **1** given in Fig. 2 and k_{21} (mol^{-1} dm^3 s^{-1}) = 7.04 × 10^4.

There are two possibilities for the coordination



Scheme 2.

Table 2. Reaction rate constants

Ligand	Pathway	k_{21} (mol^{-1} dm^3 s^{-1})	Reference
1 (H_3muia)	Fe^{2+} + $Hmuia^{2-}$ (k_{21})	$(7.04 \pm 0.20) \times 10^4$	This work[a]
H_2qhqs[b]	Fe^{2+} + $Hqhqs^{-}$ (k_{21})	$(3.16 \pm 0.20) \times 10^5$	2[b]
H_2thqs[c]	Fe^{2+} + $Hthqs^{-}$ (k_{21})	$(1.86 \pm 0.20) \times 10^3$	3[c]
Hahx[d]	Fe^{2+} + Hahx(k_{21})	$(6.69 \pm 0.20) \times 10^4$	12[d]

[a] 0.10 mol dm^{-3} ($NaClO_4$), 25°C.

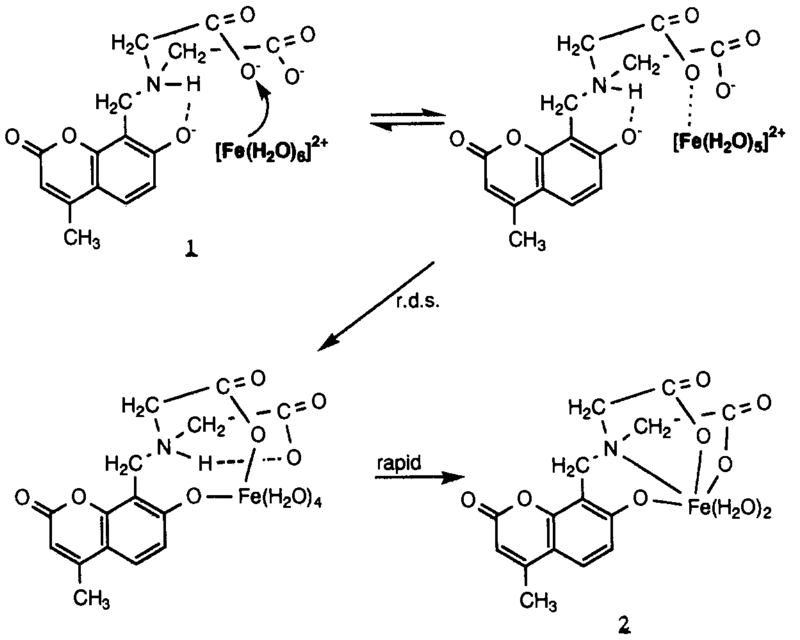
[b] 8-Hydroxy-7-(8-quinolyl)azo-5-quinolinesulphonic acid. 0.10 mol dm^{-3} (NaCl), 25°C.

[c] 8-Hydroxy-7-(2-thiazolyl)azo-5-quinolinesulphonic acid. 0.10 mol dm^{-3} (NaCl), 25°C.

[d] Acetohydroxamic acid ($CH_3CONHOH$). log $K_{a(OH)}$ (mol^{-1} dm^3) = 9.33 ± 0.01.[8]

mechanism of the donor atoms. Of these, first a rapid donation of either of the carboxylato oxygens rather than the first and rate-limiting donation of the phenolato oxygen and/or amino nitrogen to the iron(II) may be more plausible because the $Hmuia^{2-}$ ligand species is expected to have an intramolecular hydrogen bond between the phenolato oxygen and nitrogen donor atoms. The mechanistic rate-determining step may be the coordination of the phenolato oxygen to the iron(II), based on the magnitude of k_{21} and on the higher affinity to the proton of the amino nitrogen [$K_{a(amNH)}$] than phenolate oxygen [$K_{a(PhOH)}$] in these hydrogen-bonded donor atoms (*cf* Table 1), in just the same way as in the iron(II) complexes of 8-hydroxy-7-(8-quinolyl)azo-5-quinolinesulphonic acid[2] and 8-hydroxy-7-(2-thiazolyl)azo-5-quinolinesulphonic acid.[3] The coordination reaction mechanism is shown in Scheme 3.

Hence, it is concluded that the iron(II) ion reacts with the ligand **1** through the pathway of Fe^{2+} with $Hmuia^{2-}$ with the rapid ionic association with one of the carboxylato oxygens and then a mechanistic rate-determining coordination of the phenolato oxygen, which is followed by rapid donations of amino nitrogen and another carboxylato oxygen to complete one six-membered and two five-membered chelate rings. Further kinetic data relating to various multidentate ligands other than **1** and its analogues are needed before the deduction of the detailed intrinsic metal chelate complex formation reaction characteristics of iron(II) with nitrogen and oxygen donor atoms, and this will be our continuing interest.



Scheme 3.

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