Interaction of N,N'-ethylene bis(salicylamide) with iron (III):
A magneto-structural, electrochemical, and mechanistic investigation

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The reaction of N,N'-ethylene bis(salicylamide) (H₂SALM) with ion(III) results in the formation of a 1:1 complex in solution. The rate and activation parameters for the reactions, Fe(OH)₃⁺ + H₂SALM → Fe(OH)₂(SALMH)³⁺, and Fe(OH)₃⁺(OH)⁻ + H₂SALM → Fe(OH)₂(SALMH)³⁺ are: k(25°C)/dm³ mol⁻¹ s⁻¹ = 2.1 ± 0.6, (2.67 ± 0.1) x 10⁸; ΔH (kJ mol⁻¹) = 97 ± 8, 64 ± 1; ΔS(J K⁻¹ mol⁻¹) = 87 ± 28, 35 ± 4 (l = 1.0 NaClO₄, 8% v/v MeOH/H₂O) respectively; the mechanism is I. for hexa-aquairon(III) and I. for hydroxopentaaquairon(III). The substantially large values of the activation parameters as compared to those reported for the water exchange reactions of the iron(III) species are accountable in terms of the solvent shell reorganisation in the process. The species Fe(OH)₂(SALMH)³⁺ undergoes facile deprotonation of the phenolic and amide functions which strongly suggests that these remain coordinated to the iron(III) centre (N bonding for -C=ONH⁻) in the complex. While the complexion reaction displays a single relaxation mode in the stopped flow time scale, the amide deprotonation of the complex obeys biphasic kinetics (Fe(SALM)⁺→ Fe(SALM-H), k₁; Fe(SALM-H)→ Fe(SALM-2H), k₂) with general base catalysis (k_H₂O < k_OH < k_tris < k_H₂BO₃, tris = trishydroxymethylaminomethane, k = k₁ or k₂). The complex isolated in the solid state as [Fe(SALM)(NO₃)(OH)₂]H₂O displays I. R. bands characteristic of H₂O and NO₃⁻ coordinated to iron(III) centre. Its µ_g = 5.96 B M and 4 line (broad) X-band ESR spectrum are characteristics of high spin iron(III) with five unpaired electrons. The cyclic voltamogram (Ag/AgCl reference) of the insitu generated complex, Fe(SALM)⁺ (pH = 5.01, 10% v/v MeOH/H₂O, 1.0 KNO₃, 25°C) shows quasi-reversible redox process with E° and E° as -0.391V and -0.326V respectively.

This work stems from our interest in the complexion reaction of salicylate and phenolate ligands as well as the current research activities on the synthesis, structure and kinetic investigations of a wide variety of the complexes of iron(II/III) of both chemical and biological significance. In the biological domain, both iron(II) and iron(III) play dominant role in hydrolytic, redox and dioxygen transfer processes. The structure and functions of iron bearing heme, and nonheme enzymes continue to activate a good deal of research. Of several such enzymes the intradiol catechol dioxygenases are important ones which involve novel activation mechanism in which catechol binds iron(III) site. Iron(III) complexes dismuting superoxide are used as SOD (superoxide Dismutase) mimics. The search for suitable polydentate ligands to take care of the iron overload under biological conditions and further to provide safe iron loading under conditions of its deficiency also continues unabated. The complexes incorporating the phenolic and amide functions as chelating moieties in the same ligand can be considered as models for carrying out important biological reactions. Sigel et al. and Collins have reviewed the potential ligand properties of amide ligands and the physico-chemical behaviour of their complexes. The iron(III) complexes of the ligands of such functionality have not been investigated in detail. We present herein a kinetic and equilibrium study of the interaction of iron(III) with one such ligand, N,N'-ethylene bis(salicylamide) hereafter denoted by H₂SALM. This ligand has a unique feature encompassing the potentialities of phenol and amide functions and can exist in multiple stages of deprotonation with charges varying from 0 to -4 under suitable pH conditions in solution. The iron(III) complex of this ligand envisages the metal ion promoted deprotonation of the amide function and the deprotonated amide dependent structural transformation of the corresponding complex as the additional novel features which we feel is worth investigating. This ligand also closely resembles the Schiff base N,N'-ethylene bis (salicylidineimine) in terms of the...
ligational property except that the -C=N- function of the Schiff base is replaced by O=C-NH group in H₂SALM. Keeping in view the potentiality of H₂SALM as a quadridentate ligand, we investigated the kinetics and mechanism of its interaction with iron(III) and the structural and electrochemical aspects of the complex formed.

I : N,N' ethylene bis(salicylamide)

Materials and Methods

The ligand H₂SALM was prepared by refluxing ethylenediamine with methylsalicylate in the proportion 1:2 on a sand bath for four hrs. It was recrystallised from ethanol: mp, 183°C (lit. value: 185°C). Anal. Calcd. for C₁₆H₁₆N₂O₈: C, 64.0; H, 5.37; N, 9.33%. Found: C, 64.7; H, 5.55; N, 9.52%. \(^{1}H\) NMR (CDCl₃, TMS ref. d ppm): 11.9 (singlet, OH), 3.21 - 3.34 (triplet, -CH₂-CH₂-), 6.65 - 7.99 (complex multiplets, aromatic). The complex multiplets in the range 3.85 - 5.03 ppm presumably arise due to the hydrogen bonding of the amide N-H. IR (KBr, cm⁻¹): 3387, 2954, 1591, 1495, 1445, 1367, 1305, 1245, 1146, 1035, 870, 744, and 696. The strong and broad band at 3387 cm⁻¹ is indicative of the coordinated nitrate. Bands at 1600, and 1580 cm⁻¹ may be due the C=O stretch of the amide and the OH bending. A strong band at 1380 cm⁻¹ is indicative of the coordinated nitrate. Besides, bands of medium intensity at 1550, 1530, 1470, 1440, 1230, 1150 and 760 cm⁻¹ are also observed.

Analar grade chemicals were used. Stock solution of iron(III) perchlorate was prepared as described earlier. Iron(III) was estimated by complexometric titration with EDTA (disodium salt) using sulphosalicylic acid as indicator. The free acid content of the iron(III) perchlorate solution was estimated by a combined ion-exchange and acidimetric procedure taking account of the H⁺ liberated due to the exchange of iron(III). Dowex 50W-X8 resin in H⁺ form was used for ion-exchange experiments. Sodium perchlorate was prepared by neutralising Na₂CO₃ with HClO₄ and evaporating the solution to the point of crystallisation of NaClO₄. The pH of the stock NaClO₄ solution (2 mol dm⁻³) was adjusted to 6 with dilute NaOH. The concentration of NaClO₄ was further checked by a combined ion-exchange and acidimetric procedure.

Instrumentation

The UV-visible spectra were recorded on a Perkin Elmer Lamda 20 UV-visible spectrophotometer using 10mm matched quartz cells. The IR spectra were recorded in KBr pellet on a Perkin Elmer Paragon 500 FT IR spectrometer. The conductivity measurements were made on a Systronics (India) conductivity bridge which was calibrated using standard KCl solution. A Cypress (U.S.A.) OMNI 90 potentiostat coupled with the Electrochemical Data Acquisition system (ECDA) from CONSERV (India) and interfaced by an IBM 586 P C and Wipro LQ 1050 DX printer with appropriate software was used to record the cyclic voltammogram. A conventional three electrode system such as Ag/AgCl/CI⁻ reference electrode, bright platinum as auxiliary electrode and working electrode were used. The X-band ESR spectrum at room temperature for the iron(III)-SALM complex soluble in water but readily soluble in methanol. The methanolic solution (10⁻³ mol dm⁻³) of the complex had \(\Lambda_{\text{m}} = 68 \, \text{ohm}^{-1} \, \text{cm} \, \text{dm}^2 \, \text{mol}^{-1}\) indicating that it is a 1:1 electrolyte in methanol. The IR spectrum of the solid specimen (KBr phase) displays bands at 3530(sh), 3260 and 3080 cm⁻¹ which are indicative of the coordinated and lattice water and also the amide (O=C-N-H) function. The strong bands at 1600, and 1580 cm⁻¹ may be due the C=O stretch of the amide and the OH bending. A strong band at 1380 cm⁻¹ is indicative of the coordinated nitrate. Besides, bands of medium intensity at 1550, 1530, 1470, 1440, 1230, 1150 and 760 cm⁻¹ are also observed.
(solid specimen) was recorded on a Varian E-112 ESR spectrometer operating at 9.38 GHz; DPPH was used as calibrant. The magnetic measurement was made at room temperature on EG & G PARC VSM 155 vibrating sample magnetometer. Iron(III) in the complex was estimated by atomic absorption spectrometry using a Perkin Elmer Atomic Absorption Spectrometer model 3100 available at Regional Research Laboratory, Bhubaneswar. The elemental analysis was done at CDRI, Lucknow. The ESR and magnetic measurements were made at Regional Sophisticated Instrumentation Centre, I. I. T. Chennai (India). The 1H NMR measurement was done at the sophisticated Instrumentation centre, NEHU, Shillong using a Bruker 300 MHz FTNMR spectrometer.

**Kinetics**

Rate measurements were made on a HITECH SF 51 stopped flow spectrophotometer interfaced with an APPLE II GS P.C. The flow module and the drive syringes were thermostatted by circulating water from a thermostat C85D through a cooler FC 200 from HITECH (U. K.). Runs were made in the usual manner under pseudo-first order conditions. The monitoring wave length was 530 nm for the formation of the iron(III)-SALM complex and 450 nm for its NH-deprotonation process respectively. Always the output signal for the formation of the complex was a single exponential (absorbance increased with time) characteristic of the first order kinetics. The rate constants were calculated by a nonlinear least squares program available as stopped flow software from HITECH. Each rate constant ($k_{obs}$) quoted is average of at least seven replicate runs and its error denotes standard deviation. However, the amide deprotonation of the iron(III)-SALM complex displayed biphasic kinetics ($\lambda = 450$ nm) and the stopped flow trace of any run (absorbance decreases with time for both slow and fast phases) was fitted to a double exponential equation: $A_y - A_i = C_1 \exp(-k_f t) + C_2 \exp(-k_s t)$ where $k_f$ and $k_s$ denoted the observed rate constants for the fast and slow phases of the reactions respectively and all other terms had their usual meaning. In such cases at least five replicate measurements were made for each run and the average avalues of $k_f$ and $k_s$ with their standard deviations were reported.

All kinetic and equilibrium measurements were made at 1.0 mol dm$^{-3}$ ionic strength (adjusted with NaClO$_4$) and in 8% v/v MeOH + H$_2$O medium as the ligand was sparingly soluble in water. All other calculations were made on an IBM 486 P.C. Data were fitted to appropriate equations by weighted nonlinear and linear least squares programs and each data point was weighted as inverse of its variance.

**Results**

1. Acid dissociation of $H_2$SALM

Figure 1 depicts the remarkable spectral changes for $H_2$SALM as the $pH$ of the reaction medium in-
increased from 1.26 to 11.43 (25°C). It is highly stable to both acid and base catalysed hydrolysis. The observed spectral changes as also the isosbestic point at 306 nm (ε = 6500 dm⁻³ mol⁻¹ cm⁻¹) are attributed to the ionisation of the phenolic groups of the molecule (Eqs 1 and 2):

\[
\begin{align*}
\text{H₂SALM} & \rightleftharpoons K_1 \text{HSALM}^+ + \text{H}^+ \quad \ldots \quad (1) \\
\text{HSALM}^+ & \rightleftharpoons K_2 \text{SALM}^{2+} + \text{H}^+ \quad \ldots \quad (2)
\end{align*}
\]

The absorbance data (330 nm) in the range of pH 1.27 to 8.4 ([H₂SALM]ₜ = (1.0 - 2.0) x 10⁻⁴ mol dm⁻³) were fitted to Eq (3)

\[
\varepsilon_{\text{obs}} = \left(\varepsilon_{\text{H}_2\text{L}} + \varepsilon_{\text{HL}} K_1/[\text{H}^+]\right)/(1 + K_1/[\text{H}^+])
\]

where ε_{obs} = A_{obs}/[H₂SALM]ₜ, ε_{H₂L} and ε_{HL} are the molar extinction coefficients of H₂SALM and HSALM respectively. The calculated values of ε_{H₂L}, ε_{HL}, and K₁ are (5.4 ± 0.4) x 10², (3.93 ± 0.60) x 10³ dm⁻¹ mol⁻¹ cm⁻¹ and (5.3 ± 1.7) x 10⁴ mol⁻¹ dm³ respectively. Similarly the absorbance data (330 nm) in the range of pH 8.4 to 11.5 were fitted to Eq (4) using the known value of ε_{HL}:

\[
\varepsilon_{\text{obs}} = \left(\varepsilon_{\text{HL}} + \varepsilon_2 K_2/[\text{H}^+]\right)/(1 + K_2/[\text{H}^+])
\]

where ε_{obs} and ε₂ denote the observed extinction coefficient of H₂SALM and that of SALM²⁺ respectively. We obtained ε₂K₂ = (3.28 ± 0.14) x 10⁻⁵ cm⁻¹, K₂ = (2.61 ± 0.12) x 10⁻⁹ mol dm³ and ε₂ = (12.5 ± 0.5) x 10³ dm³ mol⁻¹ cm⁻¹. In these and all other subsequent calculations [H⁺] computed from the pH data was taken to be 10⁻⁷. The values of K₁ and K₂ may be contrasted with those reported by Bhattamisra et al.² from pH-titration (K₁ = 5.1 x 10⁻⁹, K₂ = 1.97 x 10⁻¹⁰ mol dm⁻³, 30°C, 0.1 mol dm⁻³ KNO₃, 45%v/v EtOH/H₂O).

2. Equilibrium between Iron(III) and H₂SALM

An intense purple colour develops when H₂SALM is added to iron(III) solution. This is characteristic of iron(III)-phenolate interaction. The UV-visible spectrum of the mixture of iron(III) and H₂SALM (see Fig 2) displays a broad maximum around 480 nm in support of the phenolate to iron(III) charge transfer interaction. However, the position of the maximum shifts to lower wave length as pH increases and this, we presume, is due to the acid-base equilibrium of the complex, FeSALMH₂⁺. The absorbance data (Aₜ) at 530 nm (at which the complex is the only absorbing species) for the mixtures of iron(III), and H₂SALM with [Fe³⁺]ₜ = (1.0 - 20.0)
x 10^{-3}, [H_{2}SALM]_{T} = 3.0 \times 10^{-4} ([H^{+}]_{T} = 0.05 - 0.3 \text{ mol dm}^{-3}, 25^\circ C) were analysed in accord with equilibrium shown in Eq. (5):

\[
\text{Fe}^{2+} + H_{2}\text{SALM} \rightleftharpoons \text{Fe(SALM)}^{2+} + H^{+} \tag{5}
\]

for which

\[
A_{\text{obs}} = \varepsilon_{\text{Fe(SALM)}^{2+}} K_{M}[\text{Fe}^{2+}][\text{L}]_{T}/([H^{+}] + K_{M}[\text{Fe}^{2+}]) \tag{6}
\]

where \(\varepsilon_{\text{Fe(SALM)}^{2+}}\) denotes the molar extinction coefficient of \(\text{Fe(SALM)}^{2+}\), \([\text{L}]_{T} = [H_{2}\text{SALM}]_{T}\) and all other terms have their usual significance. Data fitted to Eq. (6) yielded \(\varepsilon_{\text{Fe(SALM)}^{2+}} K_{M} = (4.9 \pm 0.2) \times 10^{4} \text{ dm}^{2} \text{ mol}^{-1} \text{ cm}^{-1}, K_{M} = 23.3 \pm 1.4\) and \(\varepsilon_{\text{Fe(SALM)}^{2+}} = (2.13 \pm 0.15) \times 10^{3} \text{ dm}^{2} \text{ mol}^{-1} \text{ cm}^{-1}\). The linear plot of \([\text{L}]_{T}/A_{\text{obs}}\) versus \([H^{+}]/[\text{Fe}^{2+}]\) (see Fig 3, corr. coeff. = 0.997) also shows the satisfactory fit of the data to Eq. (6). An alternative to equilibrium (5) is the simultaneous loss of two protons (phenolic) resulting in the formation of \(\text{Fe(SALM)}^{+}\). However, data fitted badly to the corresponding relationship involving \([H^{+}]^{2}\) term further supporting that the complex virtually exists as the monoprotonated species at \([H^{+}] = 0.05 - 0.3 \text{ mol dm}^{-3}\).

### 3. Deprotonation of the coordinated ligands

The acid-base equilibrium of iron(III)-SALM complex is rapidly established as indicated by the spectral changes. The value of \(K_{M}\) shows that the complex formation is substantial even under the condition \([\text{iron(III)}] = [H_{2}\text{SALM}]_{T}\) when pH is greater than 2. The complex is also stable to hydrolytic splitting of the amidic function(s). Figure 4 shows the variation of \(\varepsilon_{\text{obs}}(= A_{\text{obs}}/[\text{complex}]_{T})\) for the complex with pH (at 450 nm) which is indicative of the deprotonation of the coordinated phenol group and amidic function(s). In the pH range 2.0 - 5.2 the increase of absorbance of the complex (450 nm) and consequent shift of the absorption maxima to lower wave length (see Fig 4) is ascribed to the deprotonation of the coordinated phenol group in \(\text{Fe(SALM)}^{2+}\) as the absorbances due to the free \(\text{Fe}^{2+}\) and its hydrolysed species, \(\text{FeOH}^{2+}\) as well as the ligand were negligible.

### 4. Variation of absorbance with pH

Considering Eqs (5) and (7) and the hydrolysis of \(\text{Fe}^{3+}\) (\(\text{Fe}^{3+} = \text{FeOH}^{2+} + \text{H}^{+}, K_{H}^{\text{FeOH}}\)) the absorbance data of the \(\text{insitu}\) generated complex \([\text{Fe}^{3+}]_{T} = [\text{L}]_{T} = (2.0 - 3.0) \times 10^{-4} \text{ mol dm}^{-3}\) were fitted to Eq (8a) by an iterative nonlinear least squares program; the free ligand concentration, \([\text{L}]_{r}\) was calculated from Eq (8b):

\[
\varepsilon_{\text{obs}} = \frac{(\varepsilon_{\text{Fe(SALM)}^{2+}} K_{M}^{\text{Fe(SALM)}^{2+}} + \varepsilon_{\text{Fe(SALM)}^{2+}})}{1 + K_{H}^{\text{FeOH}} ([H^{+}] + K_{H}^{\text{FeOH}})/[\text{Fe}^{3+}][\text{L}]_{T})} \tag{8a}
\]

\[
(1 + K_{H}^{\text{FeOH}})[K_{H}^{\text{FeOH}}][\text{L}]_{T} + (1 + K_{H}^{\text{FeOH}})[\text{L}]_{T} = 0 \tag{8b}
\]

The hydrolysis constant of \(\text{Fe}^{3+}\) was taken to be 1.98 x 10^{-3} (see later). To start with, the data were fitted to Eq. (8a) neglecting the \([\text{L}]_{r}\) dependent term and an approximate value of \(K_{H}^{\text{FeOH}}\) was obtained for further re-
finement. In the final cycle, $\varepsilon_{\text{FeL}}$ was held fixed at $2.64 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (see later); we obtained $K_d = (5.3 \pm 0.7) \times 10^4 \text{ mol dm}^{-3}$ and $\varepsilon_{\text{FeL-H}} = (2.35 \pm 0.62) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (at 450 nm). We assume the following equilibrium in the pH range 5.5 - 11.3 considering the fact that the coordinated phenol group in FeSALMH$^{2+}$ is deprotonated fully at pH > 5,

$$K_{1}^{NH} \quad FeL^{+} \quad Fe(\text{L-H}) + (H^+),$$

$$K_{2}^{NH} \quad Fe(\text{L-2H})^{+} + (H^+)$$

where FeL$^+$ denotes the chelate species (II) and $K_{1}^{NH}$, $K_{2}^{NH}$ are the first and second dissociation constants of its amide protons respectively.

Accordingly the observed absorbance (at 450 nm) of the complex at different pH's ($5.0 \leq \text{pH} \leq 11.3$) is given by Eq. (9):

$$A_{\text{obs}} = \frac{\varepsilon_{\text{FeL}} + \varepsilon_{\text{FeL-H}} K_{1}^{NH}[H^+] + \varepsilon_{\text{FeL-H}} K_{1}^{NH} K_{2}^{NH}[H^+]^2}{1 + K_{1}^{NH}[H^+] + K_{1}^{NH} K_{2}^{NH}[H^+]^2} \quad \ldots\ldots(9)$$

Data were fitted to Eq. (9) by an iterative least squares program. The values of $\varepsilon_{\text{FeL}}$ and $\varepsilon_{\text{FeL-H}}$ were finally fixed at $2.63 \times 10^3$ and $2.8 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ as adjudged from the values of $\varepsilon_{\text{obs}} (A_{\text{obs}} /[\text{complex}]_T, [\text{complex}]_T = [\text{L}]_T = [\text{Fe}^{3+}]_T)$, see Fig 4 at pH 5 and 11 respectively. We obtained $\varepsilon_{\text{FeL-H}} K_{1}^{NH} = (2.57 \pm 0.24) \times 10^4 \text{ cm}^{-1}$, $K_{1}^{NH} K_{2}^{NH} = (1.25 \pm 0.04) \times 10^{-14} \text{ mol}^2 \text{ dm}^{-2}$ and $K_{1}^{NH} = (1.81 \pm 0.20) \times 10^{-2} \text{ mol dm}^{-3}$ which yielded $\varepsilon_{\text{FeL-H}} = (1.42 \pm 0.21) \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; $pK_{1}^{NH} = 6.74 \pm 0.05$; $pK_{2}^{NH} = 7.16 \pm 0.05$ (25°C, $I = 1.0 \text{ mol dm}^{-3}$, 8% v/v MeOH).

4. Fast Complexation Reaction

The complexation of H$_2$SALM with iron(III) was studied under varying concentrations of the metal ion and H$^+$ and at 20 - 40°C. The observed pseudo-first order rate constants ($k_{\text{obs}}$) are collected in Table 1. The dependence of $k_{\text{obs}}$ with [Fe$^{3+}$], at constant [H$^+$] is linear with positive intercept in support of the approach to equilibrium kinetics. The intercepts and gradients of such plots show inverse [H$^+$] dependence which is reconciled with the greater reactivity of Fe(OH)$_2$(OH)$_2$ as compared to that of Fe(OH)$_2$ since the ligand (H$_2$SALM) under the acidity conditions ([H$^+$] = 0.05 - 0.3 mol dm$^{-3}$) is likely to exist exclusively in the unionised form. Accordingly Scheme 1 is proposed:

$$K_h \quad Fe(OH)_2(SALM)H^+ + H^+ \quad \text{Fe(OH)}_2(SALM)H^+ + H^+$$

It is presumed that the final product is an iron(III) chelate in which SALM$^+$ (or its monoprotonated form) acts as a quadridentate ligand. Furthermore the H$^+$ scrambling in the Fe(OH)$_2$(OH)$_2$/H$_2$SALM reaction is too fast and complete to yield Fe(OH)$_2$(SALM)$^+$ rather than Fe(OH)$_2$(OH)(SALM)$^+$. It can be easily shown for Scheme 1 that $k_{\text{obs}}$ takes the form:

$$k_{\text{obs}} = k_1 [\text{Fe}^{3+}] + k_i \quad \ldots\ldots(10)$$

where

$$k_i = (k_1 + k_2 K_h /[H^+])/(1 + K_h /[H^+]) \quad \ldots\ldots(11)$$

and

$$k_r = (k_1 [H^+] + k_2 K_d)/(1 + K_d /[H^+]) \quad \ldots\ldots(12).$$

The values of $10^3 K_h$, calculated from the available data$^{22}$ are 1.64 (20°C), 1.98 (25°C), 2.4 (30°C), 2.9 (35°C), and 3.4 (40°C) (I = 0.3 mol dm$^{-3}$, 8% v/v MeOH/H$_2$O by extrapolation). It turns out that $K_h /[H^+]$ is much less than 1 and the equilibrium study indicated that the complex exists exclusively as Fe(SALMH)$^{2+}$ under the conditions of acidity used.
Table 1 - Rate constants ($k_{obs}$/s$^{-1}$) for the complexation of $H_2$SALM with iron(III).*

* 530nm; [L] = (0.5 - 2.0) x 10$^{-4}$, $I$ = 1.0 mol dm$^{-3}$; 8% v/v MeOH.

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<th>[H$^+$] (mol dm$^{-3}$)</th>
<th>10$^2$[Fe$^{3+}$] (mol dm$^{-3}$)</th>
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<th>25.0 ± 0.1$^a$</th>
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<td>2.09 ± 0.08</td>
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<td>1.02 ± 0.05</td>
<td>1.92 ± 0.10</td>
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<td>6.69 ± 0.24</td>
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</table>
Table 2 - Calculated rate and equilibrium parameters for the complexation of $H_2$SALM with iron(III).

<table>
<thead>
<tr>
<th>Temp. $^\circ$C</th>
<th>$k_1$ (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$k_2 K_m$ (s$^{-1}$)</th>
<th>$10^3 k_2^*$ (dm$^3$ mol$^{-1}$ s$^{-1}$)</th>
<th>$10^3 K_m^i$</th>
<th>P$^*$</th>
</tr>
</thead>
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<tr>
<td>20.0</td>
<td>1.1 ± 0.4</td>
<td>2.76 ± 0.11</td>
<td>1.67 ± 0.073</td>
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<td>2.67 ± 0.10</td>
<td>2.77 ± 0.14</td>
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<td>3.96 ± 0.08</td>
<td>2.40 ± 0.17</td>
<td>97</td>
</tr>
<tr>
<td>35.0</td>
<td>9.7 ± 2.4</td>
<td>17.9 ± 0.6</td>
<td>6.17 ± 0.21</td>
<td>2.34 ± 0.09</td>
<td>85</td>
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<td>13.0 ± 3.6</td>
<td>32.3 ± 0.7</td>
<td>9.50 ± 0.21</td>
<td>2.19 ± 0.10</td>
<td>59</td>
</tr>
</tbody>
</table>

$\Delta H^*$ (kJ mol$^{-1}$)

$\Delta S^*$

(i.e. $K/[H^+] <<<< 1$). Setting $k_1 = k_1/K_m$ and $k_2 = k_2 K_m/K_m$, Eq. (10) can be easily transformed to Eq. (13):

$$k_{obs} = (k_1 + k_2 K_m/[H^+]) \times ([Fe^{3+}] + K_m^{-1}[H^+])$$

...(13).

Data were fitted to Eq. (13) and the calculated values of $k_1$, $k_2$, $K_m^{-1}$ and also the associated activation parameters are collected in Table 2.

5. Deprotonation of the coordinated amide

The kinetics of deprotonation of amide in FeSALM$^+$ was studied at 25$^\circ$C in the pH range 8.16 - 9.3 (tris and borate buffers, $I = 1.0$ mol dm$^{-3}$, 8% v/v MeOH/H$_2$O). At the lowest pH used both the first and second stage of NH-deprotonation of FeSALM$^+$ can be taken to be essentially complete ($pK_{\text{NH}}^1 = 6.74$, $pK_{\text{NH}}^2 = 7.16$ for FeSALM$^+$). The rate constants for the observed biphasic kinetics collected in Table 3 are interpreted in terms of Scheme 2:

The observed rate constant for both fast and slow phases ($k_{obs} = k_1$ or $k_2$) is given by Eq. (14):

$$k_{obs} = k_{H_2O} + k_{OH} [OH^-] + k_x [X]$$

...(14)

where $[X] = [\text{Tris}]_{\text{free}}$ or $[H_2BO_3^-]$ and $k_x$ denotes the corresponding rate constant. Data were fitted to Eq. (14) using $[\text{OH}] = K_{\text{w}}/10^{\text{pH}}$ and $[X]$ as calculated from $[X]_T$, pH data and the measured dissociation constants of protonated tris ($pK = 8.1$) and boric acid ($pK = 8.85$) under the experimental conditions. The calculated values of the rate parameters are collected in Table 3.

Discussion

Magnetic and structural data for the iron(III)-$H_2$SALM complex

The coordination of H$_2$O and NO$_3^-$ in the complex [FeSALM(OH$_2$)(NO$_3$)$_2$]H$_2$O is indicated by the IR spectral data. The value of $\mu_{\text{eff}} = 5.96$ B M shows high spin state of iron(III) with five unpaired electrons. The X-band ESR spectrum (see Fig. 5) of the complex is broad and displays 4 line spectrum also supporting the high spin state of iron(III) (at best a five line spectrum is expected)$^{33}$. Its molar conductivity in methanol (see experimental section) further indicates that the complex behaves as a 1:1 electrolyte in solution. Hence the coordinated NO$_3^-$ is fully ionised in solution.
Table 3 - Rate constants for the amide deprotonation of Fe(SALM)+.

<table>
<thead>
<tr>
<th>pH</th>
<th>(k_1) (s(^{-1}))</th>
<th>(k_2) (s(^{-1}))</th>
<th>pH</th>
<th>(k_1) (s(^{-1}))</th>
<th>(k_2) (s(^{-1}))</th>
</tr>
</thead>
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<tr>
<td>8.12</td>
<td>0.126 ± 0.007</td>
<td>1.21 ± 0.22</td>
<td>8.17</td>
<td>0.161 ± 0.010</td>
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<tr>
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<td>8.33</td>
<td>0.160 ± 0.006</td>
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<tr>
<td>8.26</td>
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<td>8.39</td>
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<tr>
<td>8.29</td>
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<td>8.44</td>
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<tr>
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<td>2.74 ± 0.24</td>
<td>8.70</td>
<td>0.379 ± 0.012</td>
<td>2.91 ± 0.20</td>
</tr>
<tr>
<td>8.70</td>
<td>0.379 ± 0.012</td>
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<td>8.77</td>
<td>0.394 ± 0.030</td>
<td>2.97 ± 0.15</td>
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<tr>
<td>8.87</td>
<td>0.493 ± 0.020</td>
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<td>0.810 ± 0.050</td>
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</tr>
<tr>
<td>9.18</td>
<td>0.880 ± 0.080</td>
<td>6.42 ± 0.19</td>
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<tr>
<td>8.70</td>
<td>0.379 ± 0.012</td>
<td>2.91 ± 0.20</td>
<td>8.77</td>
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<td>8.87</td>
<td>0.493 ± 0.020</td>
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<td>7.38 ± 0.28</td>
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<tr>
<td>9.30</td>
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<td>8.24 ± 0.36</td>
<td>100</td>
<td>2.8 ± 1.6</td>
<td>55.2 ± 17.0</td>
</tr>
</tbody>
</table>

*25.0°C, 8% v/v MeOH/H\(_2\)O; \(l = 450\) nm; \([\text{Fe(SALM)}^+\]_T = 6.0 \times 10^{-4} ; l = 1.0 \text{ mol dm}^{-3} .

\* [H\(_2\)BO\(_4\)] + [H\(_2\)BO\(_3\)] = 0.0125; [Tris] = 0.060 mol dm\(^{-3}\); \(pK_{\text{eqp}} = 8.85, 7.90\) for H\(_2\)BO\(_3\) and trisH\(^+\) (\(l = 1.0 \text{ mol dm}^{-3}\) NaClO\(_4\), 8% v/v MeOH, 25°C) respectively; \(K_m = 2.5 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}\)

\(10^3k_{\text{HBO}^\circ} \cdot c\) = 2.8 ± 0.8; 55.2 ± 17.0

\(10^3k_{\text{OH}^\circ} \cdot c\) = 2.0 ± 0.3; 12.8 ± 1.4

\(10^3k_{\text{H}_{2}\text{BO}_3^\circ} \cdot c\) = 0.19 ± 0.10; 1.28 ± 0.74

where B denotes any base such as H\(_2\)O, OH\(^-\), and the basic component of the buffers (tris or H\(_2\)BO\(_3\)).
Electrochemistry

The cyclic voltametry of the insitu generated complex ([Fe$^{3+}$] = [H$_2$SALM] = 1.0 x 10$^{-3}$, 10% v/v MeOH/H$_2$O, pH = 5.01, 1.0 mol dm$^{-3}$ KNO$_3$) indicates a quasi-reversible redox process (see Fig. 6). The scan initiated at 0.2V (initial cathodic) displays $E_{\text{pc}} = -0.391$ V and $E_{\text{pa}} = -0.326$ V ($\Delta E = 0.065$ V) characteristic of one electron redox process. The i-V profile of the repetitive scans and $\Delta E > 0.059$ V may be indicative of H$^+$-coupling in the redox process and the requirements of the innersphere reorganisation energy. Note that the redox generated [Fe$^{II}$SALM]$^0$ will have stronger proton affinity than [Fe$^{III}$(SALM)]$^+$.

Solution stability of FeSALM$^+$

H$_2$SALM has strong affinity for iron(III) as indicated by the calculated values of the stability constants of FeSALMH$^+$ and FeSALM$^+$, 4.3 x 10$^8$ and 8.8 x 10$^8$ dm$^{-3}$ mol$^{-1}$ respectively ($K_{\text{adh}} = K_w/K_1$ and $K_2K_w/(K_1K_2)$ for FeSALMH$^+$ and FeSALM$^+$ respectively). These calculated values ensure the quadridentate nature of the ligand. Further stabilisation of the complex at pH > 7 also occurs due to the amide deprotonation and as the charge of the ligand increases to 4. The fact that the first and second dissociation constants of H$_2$SALM (phenolic groups) are remarkably enhanced on its coordination to iron(III) is a clear indication of the iron(III)-phenolate bonding. The amide proton is a very weak acid ($pK_{\text{NH}} \geq 15$). A greater than 8 $pK$ unit enhancement of $pK_{\text{NH}}$ of the amide protons in the present case with $pK_{\text{NH}}^{\text{Fe}} < pK_{\text{NH}}^{\text{SALM}}$ is a clear indication of the profound effect of N-coordination in FeSALM$^+$ in preference to the O- of the -C(=O)NH- moiety.

The two step base catalysed N-H deprotonation in the neutral/mild alkaline region of pH is a clear indication of the iron(III) mediation in the process, the effect being relatively more significant for FeSALM$^+$ as compared to Fe(SALM-H). This is in line with the expected electrostatic effect of the metal centre. The rate constants ($k_b$) for both slow and fast steps follow the sequence $k_{\text{H}_2\text{O}} < k_{\text{H}_2\text{BO}_3^-} < k_{\text{OH}^-}$ in agreement with the Bronsted theory of base catalysis.

It is pertinent here to consider the two step proton ionisation of the aqua ligands in Fe(OH$_2$)$_2$(SALM)$^+$ as an alternative to the amide deprotonation and at the charge of the ligand increases to 4. The fact that the first and second dissociation constants of H$_2$SALM (phenolic groups) are remarkably enhanced on its coordination to iron(III) is a clear indication of the iron(III)-phenolate bonding. The amide proton is a very weak acid ($pK_{\text{NH}} \geq 15$). A greater than 8 $pK$ unit enhancement of $pK_{\text{NH}}$ of the amide protons in the present case with $pK_{\text{NH}}^{\text{Fe}} < pK_{\text{NH}}^{\text{SALM}}$ is a clear indication of the profound effect of N-coordination in FeSALM$^+$ in preference to the O- of the -C(=O)NH- moiety.

The two step base catalysed N-H deprotonation in the neutral/mild alkaline region of pH is a clear indication of the iron(III) mediation in the process, the effect being relatively more significant for FeSALM$^+$ as compared to Fe(SALM-H). This is in line with the expected electrostatic effect of the metal centre. The rate constants ($k_b$) for both slow and fast steps follow the sequence $k_{\text{H}_2\text{O}} < k_{\text{H}_2\text{BO}_3^-} < k_{\text{OH}^-}$ in agreement with the Bronsted theory of base catalysis.

It is pertinent here to consider the two step proton ionisation of the aqua ligands in Fe(OH$_2$)$_2$(SALM)$^+$ as an alternative to the amide deprotonation. A recent work shows that the $pK_1$ and $pK_2$ of some Fe(N$_4$)(OH)$_2$ complexes (N$_4$ = tetraazamacrocycles) differ by $> 3$ $pK$ units ($pK_1 = 3.5 - 4.1$, $pK_2 = 7.3 - 7.7$). The observed difference in the values of $pK_1$ and $pK_2$ of Fe(OH$_2$)$_2$(SALM)$^+$ is only 0.4 $pK$ unit. Furthermore proton transfer from the coordinated H$_2$O to OH$^-$ or any base is not likely to be as slow as observed. From these considerations, we believe that the coordinated amide functions are involved in the ionisation process. The grossly cis planar arrangement of SALM$^2$-, and the low overall charge of the complex due to iron(III)-phenolate interaction are
responsible for weak acidity of the coordinated water protons. In any case the solution state structures of \([\text{Fe(H}_2\text{O})_2(\text{SALM})]^+\), \([\text{Fe(OH}_2\text{)}_2(\text{SALM-H})]^+\) and \([\text{Fe(OH}_2\text{)}_2(\text{SALM-2H})]^+\) are but tentative as we expect that one or both axial \(\text{H}_2\text{O}\) molecules may be weakly bound to the metal centre due to coulombic and distortion effects imposed by the multidentate ligand.

**Mechanism of complexation of \(\text{H}_2\text{SALM}\) with iron(III)**

The value of \(k_1\) may be compared with those of the rate constant for complexation of \(\text{Fe(OH}_2\text{)}_6^{3+}\) with several uninegative ions and uncharged ligands \(\{k_1/(L)/\text{dm}^3\text{mol}^{-1}\text{s}^{-1}\}\) at 25°C: 9.4\((\text{Cl}^-)\), 20\((\text{Br}^-)\), 51\((\text{H}_2\text{SO}_4)\), 95\((\text{NCS}^-)\), 4.8\((\text{CH}_3\text{CO}_2\text{H})\), 2.2\((\text{CH}_2\text{ClCO}_2\text{H})\), 11.4\((\text{HF})\), 25\((\text{C}_6\text{H}_5\text{OH})\), 24.6\((\text{C}_6\text{H}_4\text{o}(\text{o})\text{OH}(\text{CHO})\), 3.0\((\text{C}_6\text{H}_4\text{o}(\text{o})\text{OH})(\text{CO}_2\text{H})\), 5.2\((\text{acetylacetone-enol form})\), 0.28\((\text{acetyl acetone-keto form})\)^44,55. It is generally observed that the complexation of any ligand with \(\text{Fe(OH}_2\text{)}_6^{3+}\)\((\text{OH})^{2+}\) occurs at least 10^3 times faster than with \(\text{Fe(OH}_2\text{)}_6^{3+}\). This trend is observed for the water exchange reactions of \(\text{Fe(OH}_2\text{)}_5^{2+}\text{OH}(\text{Fe}^{3+})/k_{\text{ex}}^{10}\text{Fe(OH}_2\text{)}^{2+}\)\((\text{Fe}^{3+})/k_{\text{ex}}^{10}\text{Fe(OH}_2\text{)}^{2+}\) = 0.9 x 10^3 at 25°C. A similar trend \((k/k_{\text{ex}} = 1.3 \times 10^3\) at 25°C) is observed for the reactions of these iron(III) species with \(\text{H}_2\text{SALM}\). This reactivity trend reflects the relative labilising action of the coordinated aqua and hydroxo groups as also the mechanistic difference, the charge effect being relatively unimportant at least for the uncharged and bulky ligands. The volume of activation in conjunction with the activation enthalpy and entropy data for complexation stand in favour of the \(\text{SALM}^+\) and \(\text{Fe(OH}_2\text{)}_6^{3+}\) respectively^44,55 point to the substantial energy demand for the aqua ligand substitution process. Since the rate determining step is preceded by the diffusion controlled association of the reactants, it is likely that both \(\Delta H^\circ\) and \(\Delta S^\circ\) for this equilibrium preassociation process will contribute to the overall activation parameters. Since \(\text{H}_2\text{SALM}\) is a bulky ligand with both hydrophobic and hydrophilic sites, its association with \(\text{Fe(OH}_2\text{)}_6^{3+}\) and \(\text{Fe(OH}_2\text{)}_5^{2+}\)\((\text{OH})^{2+}\) (outer-sphere) is bound to disrupt the hydrogen bonded water structure prevalent around the iron(III) species, and relatively more so in the case of the tripositive hexaaaquiron(III). In consequence the solvation components of the activation parameters may be substantial and cannot be overlooked.

It is further important to note that despite the quadridentate nature of \(\text{H}_2\text{SALM}\), the overall complexation reaction does not show more than one relaxation. Neither there is any evidence of kinetically detectable structural isomerisation of the iron(III) complex over the wide range of pH used (except the stepwise dissociation of the coordinated amide protons). It is, however, very unlikely that all the donor functions of \(\text{H}_2\text{SALM}\) in the preassociated aggregates, \{\text{Fe(OH}_2\text{)}_6^{3+}\text{H}_2\text{SALM}\} and \{\text{Fe(OH}_2\text{)}_5^{2+}\text{H}_2\text{SALM}\}, will replace the aqua ligands from the metal centre in a single step. Rather the rate controlling step is associated with the formation of the bidentate chelate; the subsequent chelation of iron(III) by the pendant moiety of the ligand in the corresponding intermediate being unimolecular is a relatively fast process.

**Acknowledgement**

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**References**