

## Mixed ligand complex formation of Fe<sup>III</sup> with boric acid and typical N-donor multidentate ligands

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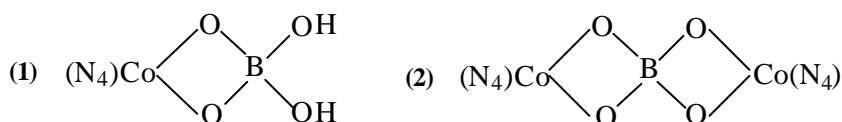
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**Abstract.** Equilibrium study of the mixed ligand complex formation of Fe<sup>III</sup> with boric acid in the absence and in the presence of 2,2'-bipyridine, 1,10-phenanthroline, diethylenetriamine and triethylenetetramine (L) in different molar ratios provides evidence of formation of Fe(OH)<sup>2+</sup>, Fe(OH)<sub>2</sub><sup>+</sup>, Fe(L)<sup>3+</sup>, Fe(H<sub>2</sub>BO<sub>4</sub>), Fe(OH)(H<sub>2</sub>BO<sub>4</sub>)<sup>-</sup>, Fe(OH)<sub>2</sub>(H<sub>2</sub>BO<sub>4</sub>)<sup>2-</sup>, Fe(L)(H<sub>2</sub>BO<sub>4</sub>) and Fe<sub>2</sub>(L)<sub>2</sub>(BO<sub>4</sub>)<sup>+</sup> complexes. Fe(L)<sub>2</sub><sup>3+</sup>, Fe(L)<sub>2</sub>(H<sub>2</sub>BO<sub>4</sub>) and Fe<sub>2</sub>(L)<sub>4</sub>(BO<sub>4</sub>)<sup>+</sup> complexes are also indicated with 2,2'-bipyridine and 1,10-phenanthroline. Complex formation equilibria and stability constants of the complexes at 25 ± 0.1°C in aqueous solution at a fixed ionic strength, I = 0.1 mol dm<sup>-3</sup> (NaNO<sub>3</sub>) have been determined by potentiometric method.

**Keywords.** Mixed ligand-Fe<sup>III</sup>-borate complexes; complex equilibria; N-donor multidentate ligands.

### 1. Introduction

Enhancement of acidity of boric acid (H<sub>3</sub>BO<sub>3</sub>) in presence of *cis*-1,2-diols, *cis*-2-hydroxy acids and *cis*-1,2-dicarboxylic acids due to the formation of chelated structures with tetravalent electron deficient B<sup>III</sup> is well-known<sup>1</sup>. Acidity of aqueous solution of H<sub>3</sub>BO<sub>3</sub> is found to be enhanced in the presence of *cis*-diaqua Co<sup>III</sup> complexes: *cis*-[Co<sup>III</sup>(N<sub>4</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup>, where, (N<sub>4</sub>) = (2,2'-bipyridine)<sub>2</sub> or (1,3-diaminopropane)<sub>2</sub> or triethylenetetramine, due to the formation of mononuclear (1) and binuclear (2) mixed ligand borate complexes through *pseudo substitution* reactions, in which Co–O bonds remain intact and substitution of Co–OH moiety takes place on the electron-deficient B<sup>III</sup> centre with release of the proton<sup>2</sup>.



Acidity of aqueous solution of H<sub>3</sub>BO<sub>3</sub> is also enhanced in the presence of coordinately unsaturated labile complexes, [M<sup>II</sup>(L)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, M = Co, Ni, Cu and Zn, L = (N<sub>2</sub>), (N<sub>4</sub>) amine formed *in situ* in ternary M<sup>II</sup>-L-H<sub>3</sub>BO<sub>3</sub> mixtures<sup>3</sup>. With the view to studying the

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effect of coordinately unsaturated  $[\text{Fe}^{\text{III}}(\text{amine})(\text{H}_2\text{O})_2]^{3+}$  complexes on the acidity of  $\text{H}_3\text{BO}_3$ , complex formation equilibria of  $\text{Fe}^{\text{III}}$  with  $\text{H}_3\text{BO}_3$  in the absence and in the presence of 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) (hereafter,  $\text{L}^1$ ) and diethylenetriamine (den), triethylenetetramine (trien) (hereafter,  $\text{L}^2$ ) have been investigated by potentiometric methods using different molar ratios of the reactants  $\text{Fe}^{\text{III}}$ , ( $\text{L}^1$  or  $\text{L}^2$ ) and  $\text{H}_3\text{BO}_3$  in aqueous solution at a fixed ionic strength  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ) at  $25 \pm 0.1^\circ\text{C}$ . Stoichiometry and the formation constants of the complexes and complex formation equilibria have been evaluated by a computerised method<sup>4</sup>.

## 2. Experimental

Boric acid, bipy, phen, sodium nitrate, nitric acid were of AR grade. Den and trien (AR) were converted into their corresponding nitrate salts, den.3 $\text{HNO}_3$  and trien.4 $\text{HNO}_3$  respectively, air-dried and analysed<sup>5</sup>. Ferric nitrate solution was prepared by dissolving freshly precipitated, alkali-free  $\text{Fe}(\text{OH})_3$  in standard  $\text{HNO}_3$  and standardised by combined acid-base, ion exchange and complexometric titrations<sup>5</sup>.

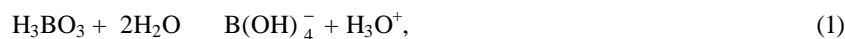
The equilibrium study involved *pH*-metric titrations<sup>3</sup> in aqueous medium of a series of solutions ( $0.025 \text{ dm}^3$ ) containing known amounts ( $0.0005$ – $0.005 \text{ mol dm}^{-3}$ ) of  $\text{H}_3\text{BO}_3$  and/or L ( $\text{L} = \text{bipy, phen, den and trien in their protonated forms}$ ) and known amount ( $0.01 \text{ mol dm}^{-3}$ ) of free  $\text{HNO}_3$ , in the absence and in the presence of known amounts ( $0.0005$ – $0.001 \text{ mol dm}^{-3}$ ) of  $\text{Fe}^{\text{III}}$ -nitrate, keeping the  $\text{Fe}^{\text{III}} : \text{L} : \text{H}_3\text{BO}_3$  ratios 1:1:1, 1:2:1, 2:2:1 and 2:4:1 as required, with carbonate-free<sup>6</sup> standard  $0.1 \text{ mol dm}^{-3}$   $\text{NaOH}$  solution, maintaining a fixed ionic strength,  $I = 0.1 \text{ mol dm}^{-3}$  ( $\text{NaNO}_3$ ).

Ionic product of water at the experimental temperature and activity coefficient of  $\text{H}^+$  ion at the experimental ionic strength were obtained from literature<sup>7,8</sup>. Analytical concentrations of  $\text{H}^+$  ion corresponding to the *pH*-meter readings were obtained by the usual procedure<sup>9</sup>. Formation constants (table 1) were calculated with the aid of the SCOGS computer program<sup>4</sup>. Complex formation equilibria were elucidated with the help of speciation curves.

## 3. Results and discussion

### 3.1 Proton-ligand equilibria

In the *pH*-range of investigation bipy and phen up to two protons, den bind up to three and trien binds up to four protons (table 1).  $\text{H}_3\text{BO}_3$  titrates as a weak monobasic acid ( $pK_{\text{H}_3\text{BO}_3}^{\text{H}} = 9.00$ ) in aqueous solution due to its ionisation, not as a proton donor, but as a Lewis acid, accepting an  $\text{OH}^-$  according to equilibrium (1)<sup>10</sup>:



$$K_{\text{H}_3\text{BO}_3}^{\text{H}} = \frac{[\text{H}_3\text{O}^+][\text{B}(\text{OH})_4^-]}{[\text{H}_3\text{BO}_3]}. \quad (1a)$$

Charges are not shown in the expressions for clarity.

### 3.2 Hydrolytic equilibria of $\text{Fe}^{\text{III}}$

$\text{Fe}^{\text{III}}$  is so extensively hydrolysed in aqueous solution that  $\text{Fe}(\text{aq})^{3+}$  hardly exceeds 25% even at  $p\text{H} < 2$ , in as low as  $5 \times 10^{-4} \text{ mol dm}^{-3}$  concentration.

**Table 1.** Formation constants\* of mixed ligand Fe<sup>III</sup> - L - borate complexes with L = bipy, phen, den and trien in aqueous solution. I = 0.1 M (NaNO<sub>3</sub>); Temperature = 25°C

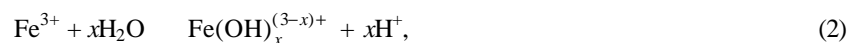
(a) <i>Hydrolysis constants of Fe(aq)<sup>3+</sup> ions</i>					
$\log K_{\text{Fe}}^{\text{H}}$	-1.62	$\log K_{\text{Fe}}^{2\text{H}}$	-4.28	$\log K_{\text{Fe}}^{3\text{H}}$	-7.91
(b) <i>Formation constants of Fe<sup>III</sup> - H<sub>3</sub>BO<sub>3</sub> complexes</i>					
(i) Overall formation constants					
$\log b_{\text{Fe}(\text{H}_2\text{BO}_4)}^{\text{Fe}}$	3.67	$\log b_{\text{Fe}(\text{OH})(\text{H}_2\text{BO}_4)}^{\text{Fe}}$	1.16	$\log b_{\text{Fe}(\text{OH})_2(\text{H}_2\text{BO}_4)}^{\text{Fe}}$	-1.72
(ii) Effect of coordination with Fe(aq) <sup>3+</sup> , Fe(OH) <sup>2+</sup> and Fe(OH) <sub>2</sub> <sup>+</sup> on ionisation of H <sub>3</sub> BO <sub>3</sub>					
$\log K_{[\text{Fe}+\text{H}_3\text{BO}_3+\text{H}_2\text{O}]}^{3\text{H}}$	-5.33	$\log K_{[\text{Fe}(\text{OH})+\text{H}_3\text{BO}_3+\text{H}_2\text{O}]}^{3\text{H}}$	-6.22	$\log K_{[\text{Fe}(\text{OH})_2+\text{H}_3\text{BO}_3+\text{H}_2\text{O}]}^{3\text{H}}$	-6.44
	-	( $\Delta \log K_{\text{Fe}}$ ) <sub>1</sub>	-0.89	( $\Delta \log K_{\text{Fe}}$ ) <sub>2</sub>	-1.11
	-				
Ligands (L)					
Constants	bipy	phen	den	trien	
(c) <i>Proton-ligand constants</i>					
$\log K_{\text{HL}}^{\text{H}}$	4.23	4.86	9.76	9.44	
$\log K_{\text{H}_2\text{L}}^{\text{H}}$	1.32	1.90	8.90	8.92	
$\log K_{\text{H}_3\text{L}}^{\text{H}}$	-	-	4.05	6.74	
$\log K_{\text{H}_4\text{L}}^{\text{H}}$	-	-	-	3.56	
(d) <i>Fe<sup>III</sup> - L binary constants</i>					
(i) Overall formation constants					
$\log K_{\text{FeL}}^{\text{Fe}}$	9.13	10.41	18.76	21.77	
$\log b_{\text{Fe}(\text{L})(\text{OH})}^{\text{Fe}}$	6.96	8.54	15.18	15.47	
( $\Delta \log K_{\text{Fe}}$ ) <sub>1</sub>	-0.55	-0.25	-1.96	-4.68	
$\log b_{\text{Fe}(\text{L})(\text{OH})_2}^{\text{Fe}}$	5.11	6.43	10.91	10.85	
( $\Delta \log K_{\text{Fe}}$ ) <sub>2</sub>	0.26	0.30	-3.57	-6.64	
$\log K_{\text{FeL}_2}^{\text{Fe}}$	18.11	19.92	-	-	
$\log b_{\text{Fe}(\text{L})_2(\text{OH})}^{\text{Fe}}$	14.74	16.43	-	-	
( $\Delta \log K_{\text{Fe}}$ ) <sub>1</sub>	-1.75	-1.87	-	-	
$\log b_{\text{Fe}(\text{L})_2(\text{OH})_2}^{\text{Fe}}$	10.76	12.52	-	-	
( $\Delta \log K_{\text{Fe}}$ ) <sub>2</sub>	-3.07	-3.12	-	-	

(Continued...)

**Table 1.** (Continued)

Constants	Ligands (L)			
	bipy	phen	den	trien
(ii) Hydrolysis constants of Fe(L)				
$\log K_{\text{Fe(L)}}^{\text{H}}$	-2.17	-1.87	-3.58	-6.30
$\log K_{\text{Fe(L)}}^{2\text{H}}$	-4.02	-3.98	-7.85	-10.92
$\log K_{\text{Fe(L)}_2}^{\text{H}}$	-3.37	-3.39	-	-
$\log K_{\text{Fe(L)}_2}^{2\text{H}}$	-7.35	-7.40	-	-
(e) $\text{Fe}^{\text{III}} - \text{L} - \text{H}_3\text{BO}_3$ ternary constants				
(i) Overall formation constants				
$\log b_{1121}$	14.39	14.78	21.89	24.52
$\log b_{2201}$	24.06	25.02	37.68	43.97
$\log b_{1221}$	21.28	22.82	-	-
$\log b_{2401}$	36.78	39.91	-	-
(ii) Effect of coordination with Fe(L) and Fe(L) <sub>2</sub> on ionisation of H <sub>3</sub> BO <sub>3</sub>				
$\log K_{[\text{Fe(L)(OH)}_2 + \text{H}_3\text{BO}_3]}^{\text{H}}$	0.28	-0.65	-	-
$\log K_{[2\text{Fe(L)(OH)}_2 + \text{H}_3\text{BO}_3]}^{\text{H}}$	4.84	3.16	-	-
$\log K_{[\text{Fe(L)}_2 + \text{H}_3\text{BO}_3 + \text{H}_2\text{O}]}^{3\text{H}}$	-5.83	-6.10	-	-
$\log K_{[\text{Fe(L)} + \text{H}_3\text{BO}_3 + \text{H}_2\text{O}]}^{3\text{H}}$	-	-	-5.87	-6.25
$\log K_{[\text{Fe(L)}_2(\text{OH}) + \text{H}_3\text{BO}_3]}^{2\text{H}}$	-2.46	-2.61	-	-
$\log K_{[2\text{Fe(L)}_2 + \text{H}_3\text{BO}_3 + \text{H}_2\text{O}]}^{5\text{H}}$	-8.44	-8.93	-	-
$\log K_{[2\text{Fe(L)} + \text{H}_3\text{BO}_3 + \text{H}_2\text{O}]}^{5\text{H}}$	-	-	-8.84	-8.57
$\log K_{[\text{Fe(L)}_2(\text{OH}) + \text{H}_3\text{BO}_3]}^{2\text{H}}$	-1.70	-1.95	-	-

\*Limits of error in the constants:  $\pm (0.02 \sim 0.05)$  in log scale

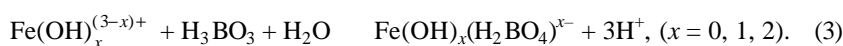


$$K_{\text{Fe}}^{x\text{H}} = ([\text{Fe}(\text{OH})_x][\text{H}]^x)/[\text{Fe}], \quad (x = 1, 2, 3). \quad (2a)$$

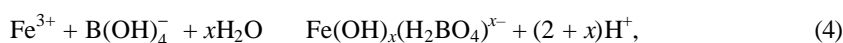
The predominant  $\text{Fe}^{\text{III}}$  species in the range  $p\text{H} \sim 2-4$ , are  $\text{Fe}(\text{OH})^{2+}$  and  $\text{Fe}(\text{OH})_2^+$ . The concentration of  $\text{Fe}(\text{OH})_3$ , is negligibly small. Although  $\text{Fe}^{\text{III}}$  has a profound tendency to form polynuclear *μ*-dioxo species, concentrations of such species in the experimental concentration range are negligible<sup>11</sup>.

### 3.3 *Fe<sup>III</sup>-H<sub>3</sub>BO<sub>3</sub> binary equilibria*

In the presence of Fe<sup>III</sup>, the buffer region corresponding to the ionisation (1) of H<sub>3</sub>BO<sub>3</sub> is shifted to lower pH regions due to the formation of Fe(H<sub>2</sub>BO<sub>4</sub>), Fe(H<sub>2</sub>BO<sub>4</sub>)(OH)<sup>-</sup> and Fe(H<sub>2</sub>BO<sub>4</sub>)(OH)<sub>2</sub><sup>2-</sup> complexes according to



pH measurements, however, could not be extended above pH ≥ 4 due to commencement of precipitation, probably of electroneutral Fe(OH)<sub>3</sub> and/or Fe(H<sub>2</sub>BO<sub>4</sub>), which respectively constitute ~20% and 5% of total Fe<sup>III</sup>. Formation constants of [Fe(OH)<sub>x</sub>(H<sub>2</sub>BO<sub>4</sub>)]<sup>x-</sup> complexes may be defined according to

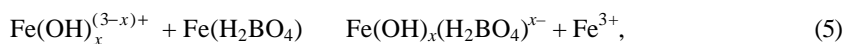


$$\mathbf{b}_{\text{Fe(OH)}_x(\text{H}_2\text{BO}_4)}^{\text{Fe}} = ([\text{Fe(OH)}_x(\text{H}_2\text{BO}_4)]/[\text{Fe}][\text{B(OH)}_4^-])^{(2+x)}. \quad (4a)$$

$\mathbf{b}_{\text{Fe(OH)}_x(\text{H}_2\text{BO}_4)}^{\text{Fe}}$  values may be obtained as computer output<sup>4</sup>, from which the equilibrium constants of the reactions (3) may be calculated using

$$\log K_{[\text{Fe(OH)}_x(\text{H}_2\text{BO}_4)]}^{x\text{H}} = \log \mathbf{b}_{\text{Fe(OH)}_x(\text{H}_2\text{BO}_4)}^{\text{Fe}} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} + \log K_{\text{Fe}}^{x\text{H}}. \quad (3a)$$

Speciation curves of Fe<sup>III</sup>-H<sub>3</sub>BO<sub>3</sub> system also indicate the formation of the [Fe(OH)<sub>x</sub>(H<sub>2</sub>BO<sub>4</sub>)]<sup>x-</sup> complexes according to the reproportionation equilibria,



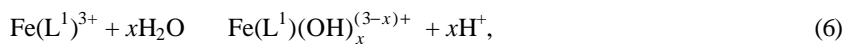
for which the (ΔlogK<sub>Fe</sub>)<sub>x</sub> values<sup>12</sup> may be calculated using

$$(\Delta \log K_{\text{Fe}})_x = \log \mathbf{b}_{\text{Fe(OH)}_x(\text{H}_2\text{BO}_4)}^{\text{Fe}} - \log \mathbf{b}_{\text{Fe(H}_2\text{BO}_4)}^{\text{Fe}} - \log K_{\text{Fe}}^{x\text{H}}. \quad (5a)$$

Predominant Fe<sup>III</sup> species in this system are Fe(OH)<sub>2</sub><sup>2+</sup>, Fe(OH)<sub>2</sub><sup>+</sup> and Fe(OH)<sub>2</sub>(H<sub>2</sub>BO<sub>4</sub>)<sup>2-</sup>. Percentages of Fe(H<sub>2</sub>BO<sub>4</sub>) and Fe(OH)(H<sub>2</sub>BO<sub>4</sub>)<sup>-</sup> are very small in the entire pH range studied. Negative values of (ΔlogK<sub>Fe</sub>)<sub>x</sub> (table 1) indicate much less relevance of the re-proportionation equilibria (5) as compared to that of equilibria (4).

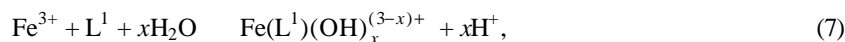
### 3.4 *Fe<sup>III</sup>-(L<sup>1</sup>/L<sup>2</sup>) binary equilibria (L<sup>1</sup> = bipy, phen; L<sup>2</sup> = den, trien)*

Predominant Fe<sup>III</sup> species at lower pH (~2) values in Fe<sup>III</sup>-L<sup>1</sup>-H<sub>3</sub>BO<sub>3</sub> systems are Fe(L<sup>1</sup>)(aq)<sup>3+</sup>, which with rise of pH undergo hydrolysis to produce Fe(L<sup>1</sup>)(OH)<sub>x</sub><sup>(3-x)+</sup> according to



$$K_{\text{Fe(L}^1\text{)}}^{x\text{H}} = ([\text{Fe(L}^1\text{)(OH)}_x]/[\text{Fe(L}^1\text{)}][\text{H}]^x)/[\text{Fe(L}^1\text{)}], \quad (x = 1, 2, 3). \quad (6a)$$

The overall formation constants ( $\mathbf{b}_{\text{Fe(L}^1\text{)(OH)}_x}^{\text{Fe}}$ ) of these ternary hydroxo complexes,  $\text{Fe(L}^1\text{)(OH)}_x^{(3-x)+}$ , defined according to



$$\mathbf{b}_{\text{Fe(L}^1\text{)(OH)}_x}^{\text{Fe}} = \frac{[\text{Fe(L}^1\text{)(OH)}_x][\text{H}]^x}{([\text{Fe}][\text{L}^1])}, \quad (7a)$$

may be obtained as computer output<sup>4</sup>, from which the hydrolysis constants,  $K_{\text{Fe(L}^1)}^{x\text{H}}$ , may be calculated using the relations

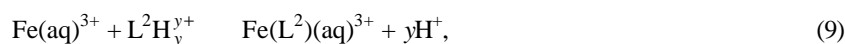
$$\log K_{\text{Fe(L}^1)}^{x\text{H}} = \log \mathbf{b}_{\text{Fe(L}^1\text{)(OH)}_x}^{\text{Fe}} - \log K_{\text{Fe(L}^1)}^{\text{Fe}}, \quad (7b)$$

where  $K_{\text{Fe(L}^1)}^{\text{Fe}}$  is the stability constant of the binary  $\text{Fe(L}^1)$  complex, defined according to



$$K_{\text{Fe(L}^1)}^{\text{Fe}} = \frac{[\text{FeL}^1]}{([\text{Fe}][\text{L}^1])}. \quad (8a)$$

In the range pH 2–4, the ligands  $\text{L}^2$  (den and trien) exist in their protonated ( $\text{L}^2\text{H}_y^+$ ) forms ( $y = 1, 2, 3, 4$ ). 1:1 binary  $\text{Fe(L}^2\text{)(aq)}^{3+}$  complexes are formed according to



$$K_{\text{Fe(L}^2)}^{\text{Fe}} = \frac{[\text{FeL}^2]}{([\text{Fe}][\text{L}^2])}. \quad (9a)$$

Speciation curves of these systems also indicate reproportionation equilibria of the type (5), for which the  $(\Delta \log K_{\text{Fe}})_x$ , ( $x = 1, 2$ ) values corresponding to  $\text{Fe(OH)}_x(\text{L})^{(3-x)+}$  complexes may be calculated using relations of the type (5a) substituting  $K_{\text{Fe(L)}}^{\text{Fe}}$  ( $\text{L} = \text{L}^1, \text{L}^2$ ) for  $\mathbf{b}_{\text{Fe(H}_2\text{BO}_4)}^{\text{Fe}}$ . While the  $(\Delta \log K_{\text{Fe}})_x$  values for  $\text{Fe(OH)}_x(\text{H}_2\text{BO}_4)^{x-}$  are more negative than the statistical values<sup>12</sup>, those of  $\text{Fe(OH)}_x(\text{L}^1)^{(3-x)+}$  are found to be less negative than the statistical values or even positive (table 1). Since both  $\text{OH}^-$  and  $\text{H}_2\text{BO}_4^{3-}$  are ‘**s**basic only’ ligands, whereas,  $\text{L}^1$  are ‘**s**basic and **p**acidic’ ligands, formation of ternary  $\text{Fe(OH)}_x(\text{H}_2\text{BO}_4)^{x-}$  complexes are disfavoured due to electronic repulsion arising from  $(\text{H}_2\text{BO}_4) \rightarrow \text{Fe} \leftarrow \text{OH}$  **s**bonding, whereas, the formation of  $\text{Fe(OH)}_x(\text{L}^1)^{(3-x)+}$  complexes are favoured due to  $(\text{L}^1) \leftarrow \text{Fe}$  **p**back bonding, which lowers electron–electron repulsion arising from  $\text{L}^1 \rightarrow \text{Fe} \leftarrow \text{OH}$  **s**bonding and strengthens the  $\text{L}^1$ -Fe bonds by synergistic effect.  $(\Delta \log K_{\text{Fe}})_x$  values (table 1) indicate slightly higher **p**acidity of phen over bipy in these complexes.

The difference between the hydrolysis constants of the uncomplexed  $\text{Fe(aq)}^{3+}$  ion and that of the complexed  $\text{Fe(L)(aq)}^{3+}$  ions ( $K_{\text{Fe}}^{x\text{H}}$  and  $K_{\text{Fe(L)}}^{x\text{H}}$  respectively) on the log scale (table 1) gives a measure of the difference in the acidity of coordinated  $\text{H}_2\text{O}$  in free and complexed  $\text{Fe}^{\text{III}}$  ions and also the relative strengths of the  $\text{L} \rightarrow \text{Fe}^{\text{III}}$  (**s**- and  $\text{L} \leftarrow \text{Fe}^{\text{III}}$  (**p**-bonds in these  $\text{Fe(L)(OH)}_x^{(3-x)+}$  complexes. It is observed that coordination of ‘**s**basic only’ ligands ( $\text{L}^2$ ), viz., den ( $\text{N}_3$ -**s**) and trien ( $\text{N}_4$ -**s**) to  $\text{Fe}^{\text{III}}$  lowers the acidity of the coordinated  $\text{H}_2\text{O}$ . On the other hand, in the coordination of ‘**s**basic and **p**acidic’ ligands

( $L^1$ ), viz., bipy, phen ( $N_2-S\mathbf{p}$ ) and (bipy)<sub>2</sub> and (phen)<sub>2</sub> ( $N_4-S\mathbf{p}$ ), although the acidity of the coordinated H<sub>2</sub>O tend to increase, their 'pacidic effects' cannot outweigh their 'S basic effects'. As a result, acidity of the H<sub>2</sub>O ligands coordinated to Fe<sup>III</sup>-L complexes are in the order: Fe(aq)<sup>3+</sup> > Fe ( $N_4-S\mathbf{p}$ )(aq)<sup>3+</sup> > Fe( $N_2-S\mathbf{p}$ )(aq)<sup>3+</sup> Fe( $N_3-S$ )(aq)<sup>3+</sup> > Fe( $N_4-S$ )(aq)<sup>3+</sup>.

### 3.5 $Fe^{III}-L-H_3BO_3$ general equilibria

Complex formation equilibria of Fe<sup>III</sup> with H<sub>3</sub>BO<sub>3</sub> in the presence of another ligand, L, in aqueous solution may be described according to the general equilibria (10):

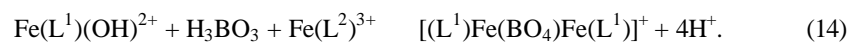
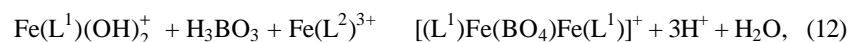


$$\mathbf{b}_{pqsr} = ([Fe_p(L)_q(H_sBO_4)_r]^{(3p+rs-5r)+} [H^+]^{r(4-s)}) / ([Fe^{3+}]^p [L]^q [B(OH)_4^-]^r), \quad (10a)$$

where  $p$ ,  $q$  and  $r$  are stoichiometric numbers of Fe<sup>3+</sup>, ligand L and BO<sub>4</sub><sup>5-</sup> group and  $s$  is the number of H<sup>+</sup> ions bound to the BO<sub>4</sub><sup>5-</sup> groups in the formula of the complex. The borate ion, B(OH)<sub>4</sub><sup>-</sup> is derived from the ionisation (1) of H<sub>3</sub>BO<sub>3</sub>, in aqueous solution.  $\mathbf{b}_{pqsr}$  may be obtained as computer output<sup>4</sup> along with the species distribution data for elucidation of the complex formation equilibria.

### 3.6 $Fe^{III}-L^1-H_3BO_3$ ternary equilibria ( $L^1 = \text{bipy, phen}$ )

In both 1:1:1 and 2:2:1 Fe<sup>III</sup>: L<sup>1</sup>: H<sub>3</sub>BO<sub>3</sub> systems, the concentrations of the Fe(L<sup>1</sup>)<sup>3+</sup> species are small from the very beginning of the reactions (pH ~ 2), in which Fe(L<sup>1</sup>)(OH)<sub>2</sub><sup>+</sup> and Fe(L<sup>1</sup>)(OH)<sub>2</sub><sup>+</sup> are the predominant Fe<sup>III</sup> species. The mixed ligand Fe<sup>III</sup>-borate complexes, Fe(L<sup>1</sup>)(H<sub>2</sub>BO<sub>4</sub>) and (L<sup>1</sup>)Fe(BO<sub>4</sub>)Fe(L<sup>1</sup>)<sup>+</sup> are formed according to the following equilibria at pH values above 2.5.

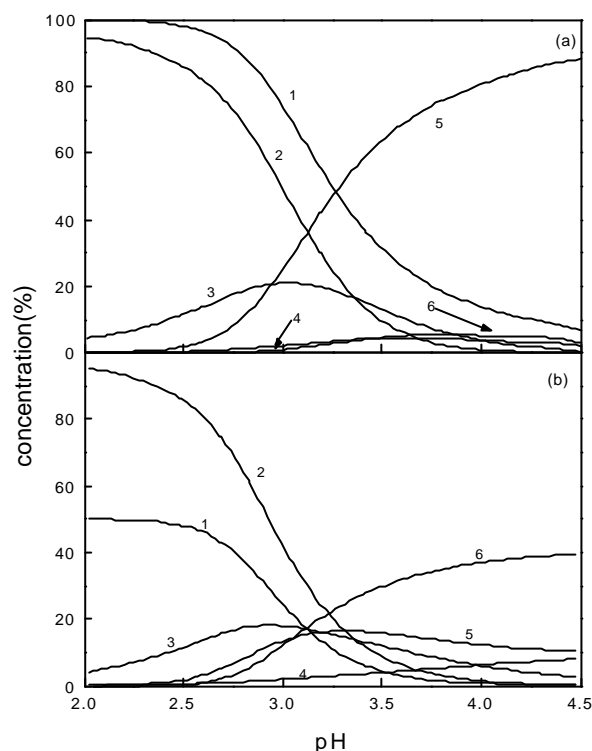


Binuclear [(L<sup>1</sup>)Fe(BO<sub>4</sub>)Fe(L<sup>1</sup>)]<sup>+</sup> complexes are formed from the very beginning of the reactions and represent the most predominant Fe<sup>III</sup> species in the 2:2:1 Fe<sup>III</sup>: L<sup>1</sup>: H<sub>3</sub>BO<sub>3</sub> systems. The overall formation constants,  $\mathbf{b}_{1121}$  and  $\mathbf{b}_{2201}$ , of [(L<sup>1</sup>)Fe(H<sub>2</sub>BO<sub>4</sub>)] and [(L<sup>1</sup>)Fe(BO<sub>4</sub>)Fe(L<sup>1</sup>)]<sup>+</sup> complexes, defined as below,

$$\mathbf{b}_{1121} = ([Fe(L^1)(H_2BO_4)][H]^2) / ([Fe][L^1][B(OH)_4]), \quad (15)$$

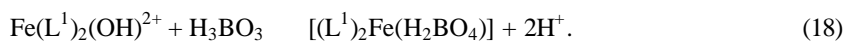
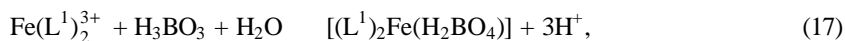
$$\mathbf{b}_{2201} = ([Fe_2(L^1)_2(BO_4)][H]^4) / ([Fe]^2[L^1]^2[B(OH)_4]), \quad (16)$$

may be obtained as computer output<sup>4</sup> along with the speciation data of these complexes.

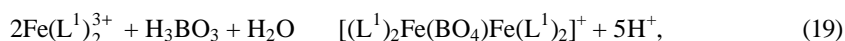


**Figure 1.** Speciation curves for  $\text{Fe}^{\text{III}}$ –bipy– $\text{H}_3\text{BO}_3$  systems.  $\text{Fe}^{\text{III}}$ : bipy:  $\text{H}_3\text{BO}_3$  = (a) 1: 2:1 and (b) 2:4:1; (1)  $\text{H}_3\text{BO}_3$ , (2)  $\text{Fe}(\text{bipy})_2^{3+}$ , (3)  $\text{Fe}(\text{bipy})_2(\text{OH})_2^+$ , (4)  $\text{Fe}(\text{bipy})_2(\text{OH})_2^+$ , (5)  $\text{Fe}(\text{bipy})_2(\text{H}_2\text{BO}_4)^+$ , (6)  $\text{Fe}_2(\text{bipy})_4(\text{BO}_4)^+$ .

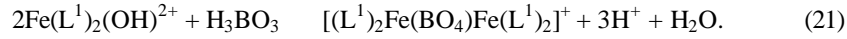
In the 1:2:1 and 2:4:1  $\text{Fe}^{\text{III}}$ :  $\text{L}^1$ :  $\text{H}_3\text{BO}_3$  systems (figure 1) the predominant  $\text{Fe}^{\text{III}}$  species at the beginning ( $\text{pH} \sim 2$ ) are  $\text{Fe}(\text{L}^1)_2^{3+}$ , ( $\sim 95\%$ ) and  $\text{Fe}(\text{L}^1)_2(\text{OH})_2^+$ , ( $\approx 5\%$ ). The dihydroxo complexes,  $\text{Fe}(\text{L}^1)_2(\text{OH})_2^+$ , appear at  $\text{pH} \sim 3$  and their concentrations hardly exceed  $\approx 10\%$  at the end of the reactions ( $\text{pH} \sim 4.5$ ). The major mixed ligand  $\text{Fe}^{\text{III}}$ -borate complexes that constitute about 90% of  $\text{Fe}^{\text{III}}$  and  $\text{pH} \geq 4$  in the 1:2:1  $\text{Fe}^{\text{III}}$ :  $\text{L}^1$ :  $\text{H}_3\text{BO}_3$  systems are  $\text{Fe}(\text{L}^1)_2(\text{H}_2\text{BO}_4)^+$ , formed mostly according to (17) and at least to some extent according to (18):



Concentrations of the binuclear  $[(\text{L}^1)_2\text{Fe}(\text{BO}_4)\text{Fe}(\text{L}^1)_2]^+$  complexes, however, hardly exceed  $\sim 5\%$  in the 1:2:1  $\text{Fe}^{\text{III}}$ :  $\text{L}^1$ :  $\text{H}_3\text{BO}_3$  systems. However, in the 2:4:1  $\text{Fe}^{\text{III}}$ :  $\text{L}^1$ :  $\text{H}_3\text{BO}_3$  systems, the mononuclear  $[(\text{L}^1)_2\text{Fe}(\text{H}_2\text{BO}_4)]$  complexes appear to be minor species where the binuclear  $[(\text{L}^1)_2\text{Fe}(\text{BO}_4)\text{Fe}(\text{L}^1)_2]^+$  complexes are formed mainly according to (19) and only slightly according to (20) and (21) at  $\text{pH} \geq 4$ :







Overall formation constants of  $[(\text{L}^1)_2\text{Fe}(\text{H}_2\text{BO}_4)]$  and  $[(\text{L}^1)_2\text{Fe}(\text{BO}_4)\text{Fe}(\text{L}^1)_2]^+$  complexes, defined according to (22) and (23) respectively,

$$\mathbf{b}_{1221} = ([\text{Fe}(\text{L}^1)_2(\text{H}_2\text{BO}_4)][\text{H}]^2)/([\text{Fe}][\text{L}^1]^2[\text{B}(\text{OH})_4]), \quad (22)$$

$$\mathbf{b}_{2401} = ([\text{Fe}_2(\text{L}^1)_4(\text{BO}_4)][\text{H}]^4)/([\text{Fe}]^2[\text{L}^1]^4[\text{B}(\text{OH})_4]), \quad (23)$$

are obtained as computer output<sup>4</sup> along with the speciation data of the complexes. Using computer-refined values of  $\mathbf{b}_{p,qsr}$ , the equilibrium constants of the complex formation reactions (11)–(14) and (17)–(21) may be calculated with the aid of the relations (11a)–(14a) and (17a)–(21a):

$$\log K_{[\text{Fe}(\text{L}^1)(\text{OH})_2+\text{H}_3\text{BO}_3]}^{\text{H}} = \log \mathbf{b}_{1121} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - \log \mathbf{b}_{\text{Fe}(\text{L}^1)(\text{OH})_2}^{\text{Fe}}, \quad (11a)$$

$$\log K_{[\text{Fe}(\text{L}^1)+\text{Fe}(\text{L}^1)(\text{OH})_2+\text{H}_3\text{BO}_3]}^{3\text{H}} = \log \mathbf{b}_{2201} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - \log K_{\text{Fe}(\text{L}^1)}^{\text{Fe}} - \log \mathbf{b}_{\text{Fe}(\text{L}^1)(\text{OH})_2}^{\text{Fe}}, \quad (12a)$$

$$\log K_{[2\text{Fe}(\text{L}^1)(\text{OH})_2+\text{H}_3\text{BO}_3]}^{\text{H}} = \log \mathbf{b}_{2201} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - 2\log \mathbf{b}_{\text{Fe}(\text{L}^1)(\text{OH})_2}^{\text{Fe}}, \quad (13a)$$

$$\log K_{[\text{Fe}(\text{L}^1)+\text{Fe}(\text{L}^1)(\text{OH})+\text{H}_3\text{BO}_3]}^{4\text{H}} = \log \mathbf{b}_{2201} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - \log K_{\text{Fe}(\text{L}^1)}^{\text{Fe}} - \log \mathbf{b}_{\text{Fe}(\text{L}^1)(\text{OH})}^{\text{Fe}}, \quad (14a)$$

$$\log K_{[\text{Fe}(\text{L}^1)_2+\text{H}_3\text{BO}_3+\text{H}_2\text{O}]}^{3\text{H}} = \log \mathbf{b}_{1221} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - \log \mathbf{b}_{\text{Fe}(\text{L}^1)_2}^{\text{Fe}}, \quad (17a)$$

$$\log K_{[\text{Fe}(\text{L}^1)_2(\text{OH})+\text{H}_3\text{BO}_3]}^{2\text{H}} = \log \mathbf{b}_{1221} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - \log \mathbf{b}_{\text{Fe}(\text{L}^1)_2(\text{OH})}^{\text{Fe}}, \quad (18a)$$

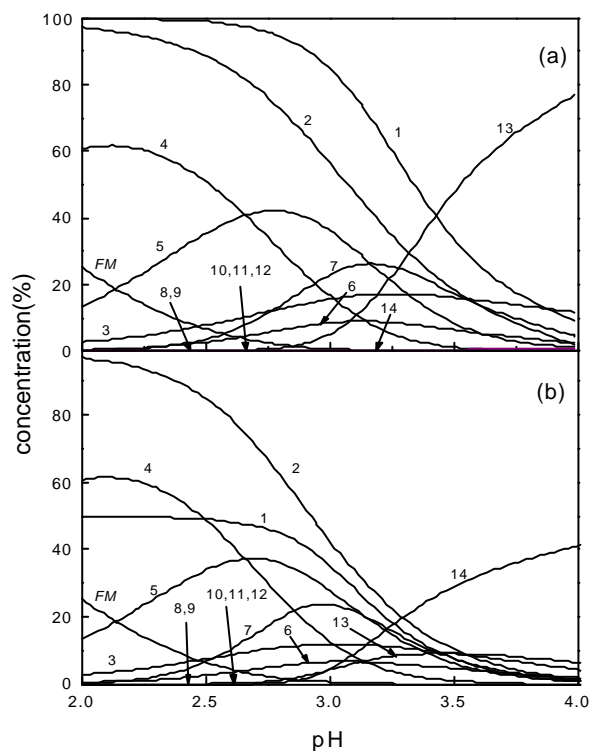
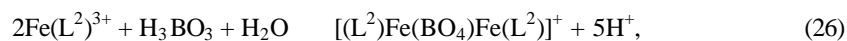
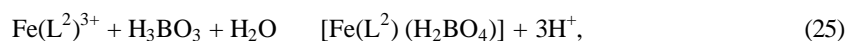
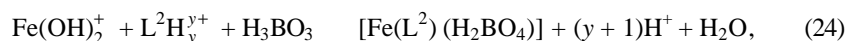
$$\log K_{[2\text{Fe}(\text{L}^1)_2+\text{H}_3\text{BO}_3+\text{H}_2\text{O}]}^{5\text{H}} = \log \mathbf{b}_{2401} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - 2\log \mathbf{b}_{\text{Fe}(\text{L}^1)_2}^{\text{Fe}}, \quad (19a)$$

$$\log K_{[\text{Fe}(\text{L}^1)_2+\text{Fe}(\text{L}^1)_2(\text{OH})+\text{H}_3\text{BO}_3]}^{4\text{H}} = \log \mathbf{b}_{2401} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - \log \mathbf{b}_{\text{Fe}(\text{L}^1)_2}^{\text{Fe}} - \log \mathbf{b}_{\text{Fe}(\text{L}^1)_2(\text{OH})}^{\text{Fe}}, \quad (20a)$$

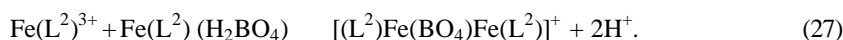
$$\log K_{[2\text{Fe}(\text{L}^1)_2(\text{OH})+\text{H}_3\text{BO}_3]}^{3\text{H}} = \log \mathbf{b}_{2401} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - 2\log \mathbf{b}_{\text{Fe}(\text{L}^1)_2(\text{OH})}^{\text{Fe}}. \quad (21a)$$

3.7  $Fe^{III}-L^2-H_3BO_3$  ternary equilibria ( $L^2 = \text{den, trien}$ )

Binary (1:1)  $Fe^{III}: L^2$  complexes are formed in both in the 1:1:1 and 2:2:1  $Fe^{III}: L^2: H_3BO_3$  systems from the very start of the reactions ( $pH \leq 2$ ) according to (9). Concentrations of  $Fe(H_2BO_4)$ ,  $Fe(OH)(H_2BO_4)^-$  and  $Fe(OH)_2(H_2BO_4)^{2-}$ ,  $Fe(OH)(L^2)^{2+}$  and  $Fe(OH)_2(L^2)^+$  are found to be negligible. The dominant  $Fe^{III}$  species at the early stages of the reactions in these systems are  $Fe(L^2)(aq)^{3+}$ ,  $Fe(OH)(aq)^{2+}$  and  $Fe(OH)_2(aq)^+$ . Therefore, ionisation of  $H_3BO_3$  at lower  $pH$  (2–3.5) values in the presence of  $Fe^{III}$  and  $L^2$  ligands is obviously due to the formation of mixed ligand  $Fe^{III}-L^2-H_3BO_3$  complexes according to the following equilibria as the speciation curves (figure 2) imply.



**Figure 2.** Speciation curves for  $Fe^{III} - \text{trien} - H_3BO_3$  system:  $Fe^{III}:\text{trien}:H_3BO_3 =$  (a) 1:1:1 and (b) 2:2:1; (1)  $H_3BO_3$ , (2)  $\text{trienH}_4^+$ , (3)  $\text{trienH}_3^{3+}$ , (4)  $Fe(OH)_2^+$ , (5)  $Fe(OH)_2^+$ , (6)  $Fe(OH)_3$ , (7)  $Fe(\text{trien})^{3+}$ , (8)  $Fe(\text{trien})(OH)^{2+}$ , (9)  $Fe(\text{trien})(OH)^+$ , (10)  $Fe(H_2BO_4)$ , (11)  $Fe(H_2BO_4)(OH)^-$ , (12)  $Fe(H_2BO_4)(OH)^{2-}$ , (13)  $Fe(\text{trien})(H_2BO_4)$ , (14)  $Fe_2(\text{trien})_2(BO_4)^+$ .



Equilibria (24)–(26) are common to both 1:1:1 and 2:2:1 Fe<sup>III</sup>: L<sup>2</sup>: H<sub>3</sub>BO<sub>3</sub> systems, whereas the equilibrium (27) is identifiable only in the 2:2:1 systems. The overall formation constants, **b**<sub>1121</sub> and **b**<sub>2201</sub> of the complexes [(L<sup>2</sup>)Fe(H<sub>2</sub>BO<sub>4</sub>)] and [(L<sup>2</sup>)Fe(BO<sub>4</sub>)Fe(L<sup>2</sup>)]<sup>+</sup> respectively, may be obtained as computer output<sup>4</sup>, from which the equilibrium constants of (24)–(27) may be calculated using the relations (24a)–(27a) below respectively.

$$\log K_{[\text{Fe}(\text{OH})_2 + \text{L}^2\text{H}_y + \text{H}_3\text{BO}_3]}^{(y+1)\text{H}} = \log \mathbf{b}_{1121} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} + \log K_{\text{L}^2\text{H}_y}^{\text{H}} - \log K_{\text{Fe}}^{2\text{H}}, \quad (24a)$$

$$\log K_{[\text{Fe}(\text{L}^2) + \text{H}_3\text{BO}_3 + \text{H}_2\text{O}]}^{3\text{H}} = \log \mathbf{b}_{1121} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - \log K_{\text{Fe}(\text{L}^2)}^{\text{Fe}}, \quad (25a)$$

$$\log K_{[2\text{Fe}(\text{L}^2) + \text{H}_3\text{BO}_3 + \text{H}_2\text{O}]}^{5\text{H}} = \log \mathbf{b}_{2201} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - 2\log K_{\text{Fe}(\text{L}^2)}^{\text{Fe}}, \quad (26a)$$

$$\log K_{[\text{Fe}(\text{L}^2) + \text{Fe}(\text{L}^2)(\text{H}_2\text{BO}_4)]}^{2\text{H}} = \log \mathbf{b}_{2201} + \log \mathbf{b}_{1121} - \log K_{\text{Fe}(\text{L}^2)}^{\text{Fe}}. \quad (27a)$$

Equilibrium (27) is a unique one of its kind as the equilibrium constant  $K_{[\text{Fe}(\text{L}^2) + \text{Fe}(\text{L}^2)(\text{H}_2\text{BO}_4)]}^{2\text{H}}$  gives a measure of the coordination tendency of the coordinated (H<sub>2</sub>BO<sub>4</sub>)<sup>3-</sup> ligand species to Fe(L<sup>2</sup>)(aq)<sup>3+</sup> ion having two H<sub>2</sub>O ligands in *cis*-positions.

The effect of coordination of borate species with Fe(aq)<sup>3+</sup>, Fe(L-**S**)<sup>3+</sup> and Fe(L-**S****P**)<sup>3+</sup> on the enhancement of acidity of H<sub>3</sub>BO<sub>3</sub> may be compared on the basis of the formation constants (table 1) of Fe<sup>III</sup>-borate and Fe<sup>III</sup>-L-borate complexes from the reactions of H<sub>3</sub>BO<sub>3</sub> with the corresponding Fe<sup>III</sup>-species. As a matter of fact, the enhancement of acidity of H<sub>3</sub>BO<sub>3</sub> due to the formation of mixed ligand borate complexes: (L<sup>1</sup>)<sub>z</sub>Fe(H<sub>2</sub>BO<sub>4</sub>) and (L<sup>1</sup>)<sub>z</sub>Fe(BO<sub>4</sub>)Fe(L<sup>1</sup>)<sub>z</sub><sup>+</sup>, where z = 1, 2, is much higher than that due to the formation of simple binary Fe(H<sub>2</sub>BO<sub>4</sub>) complex, because of (L<sup>1</sup>) ← Fe **p** bonding. However, this effect is not observed due to the formation of ternary (L<sup>2</sup>)Fe(H<sub>2</sub>BO<sub>4</sub>) and (L<sup>2</sup>)Fe(BO<sub>4</sub>)Fe(L<sup>2</sup>)<sup>+</sup> complexes because of the absence of such **p** bonding with these ligands.

The difference between the two constants  $\log K_{[(\text{L}^1)_2\text{Fe}(\text{OH}) + \text{H}_3\text{BO}_3]}^{3\text{H}}$ , (21a) and  $\log K_{[\text{Fe}(\text{OH}) + \text{H}_3\text{BO}_3]}^{3\text{H}}$ , (3a) shows a tremendous enhancement of acidity of H<sub>3</sub>BO<sub>3</sub> (by a factor of ~10<sup>4</sup>) due to its reaction with (L<sup>1</sup>)<sub>2</sub>Fe(OH)<sup>2+</sup> relative to Fe(OH)<sup>2+</sup>. In this regard the present Fe<sup>III</sup>-amine complexes may be arranged in the order: Fe<sup>III</sup>(bipy)<sub>z</sub> > Fe<sup>III</sup>(phen)<sub>z</sub> > Fe<sup>III</sup>(den) > Fe<sup>III</sup>(trien); z = 1, 2 and complexes with (z = 2) > those with (z = 1).

Although the binary Fe<sup>III</sup>(phen)<sub>z</sub>, z = 1, 2 complexes are relatively more stable than their bipy analogues, (bipy)<sub>z</sub>Fe(H<sub>2</sub>BO<sub>4</sub>) and (bipy)<sub>z</sub>Fe(BO<sub>4</sub>)Fe(bipy)<sub>z</sub><sup>+</sup> are more stable than their phen analogues. Bipy because of free rotation about the C<sub>1</sub>–C<sub>1</sub>' bond, can adjust much better than phen to the tetrahedral bond angles imposed on Fe<sup>III</sup> by the borate ligands H<sub>2</sub>BO<sub>4</sub><sup>3-</sup> and BO<sub>4</sub><sup>3-</sup>. Due to the structural rigidity of phen, the chelate rings of (phen)<sub>z</sub>Fe(H<sub>2</sub>BO<sub>4</sub>) and (phen)<sub>z</sub>Fe(BO<sub>4</sub>)Fe(phen)<sub>z</sub><sup>+</sup> are strained at the bond angles around Fe<sup>III</sup>, consequently, the phen complexes are less stable than their bipy analogues. The extent of metal to ligand **p** bonding and hence the stability is obviously higher for the Fe(L<sup>1</sup>)<sub>2</sub><sup>3+</sup> and Fe(L<sup>1</sup>)<sub>2</sub>(OH)<sup>2+</sup> complexes than those with Fe(L<sup>1</sup>)<sup>3+</sup> and Fe(L<sup>1</sup>)(OH)<sup>2+</sup>

complexes (table 1). Moreover, Fe<sup>III</sup> in Fe(L<sup>1</sup>)<sub>2</sub><sup>3+</sup> and Fe(L<sup>1</sup>)<sub>2</sub>(OH)<sup>2+</sup> may exist in low spin (*t*<sub>2g</sub><sup>5</sup>) states, and consequently act as a better  $\pi$ -electron donor than the high spin (*t*<sub>2g</sub><sup>3</sup>*e*<sub>g</sub><sup>2</sup>) in Fe(L<sup>1</sup>)<sub>3</sub><sup>3+</sup> and Fe(L<sup>1</sup>)(OH)<sup>2+</sup> complexes. This is also consistent with the order: Fe<sup>III</sup>(N<sub>4</sub>-**sp**) > Fe<sup>III</sup>(N<sub>2</sub>-**sp**) > Fe<sup>III</sup>(N<sub>3</sub>-**S**) > Fe<sup>III</sup>(N<sub>4</sub>-**S**) with regard to the effectiveness of the present Fe<sup>III</sup>-amine complexes in enhancing the ionisation of H<sub>3</sub>BO<sub>3</sub> through mixed ligand borate complex formation.

#### 4. Conclusions

Labile Fe(L)(aq)<sup>3+</sup> complexes, L = bipy, phen (N<sub>2</sub>), den (N<sub>3</sub>); (bipy)<sub>2</sub>, (phen)<sub>2</sub>, trien (N<sub>4</sub>), formed *in situ*, are structurally compatible with 1,2-*cis*-diols, like the substitution inert *cis*-[(N<sub>4</sub>)M<sup>III</sup>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> complexes (M = Co, Cr), with regard to the enhancement of acidity of boric acid in aqueous solution due to the formation of mononuclear and binuclear mixed ligand Fe<sup>III</sup>-borate complexes of the types [(L)Fe(H<sub>2</sub>BO<sub>4</sub>)] and [(L)Fe(BO<sub>4</sub>)Fe(L)]<sup>+</sup> respectively, in which the electron deficient B<sup>III</sup> attains tetra-covalency through chelation. The binuclear [(L)Fe(BO<sub>4</sub>)Fe(L)]<sup>+</sup> complexes are found to be more stable as compared to the mononuclear [(L)Fe(H<sub>2</sub>BO<sub>4</sub>)] complexes. The  $\pi$ -acidic nature of the ligands (L) increases the acidity of the coordinated H<sub>2</sub>O molecules in Fe<sup>III</sup>(L)(aq)<sup>3+</sup> complexes, which in turn, enhances the acidity of H<sub>3</sub>BO<sub>3</sub> to a greater extent than those without having metal to  $\pi$ -bonding.

#### Acknowledgement

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