

Mixed ligand complex formation of Fe^{III} with boric acid and typical N-donor multidentate ligands

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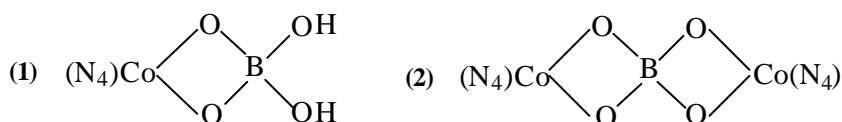
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Abstract. Equilibrium study of the mixed ligand complex formation of Fe^{III} with boric acid in the absence and in the presence of 2,2'-bipyridine, 1,10-phenanthroline, diethylenetriamine and triethylenetetramine (L) in different molar ratios provides evidence of formation of Fe(OH)²⁺, Fe(OH)₂⁺, Fe(L)³⁺, Fe(H₂BO₄), Fe(OH)(H₂BO₄)⁻, Fe(OH)₂(H₂BO₄)²⁻, Fe(L)(H₂BO₄) and Fe₂(L)₂(BO₄)⁺ complexes. Fe(L)₂³⁺, Fe(L)₂(H₂BO₄) and Fe₂(L)₄(BO₄)⁺ 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⁻³ (NaNO₃) have been determined by potentiometric method.

Keywords. Mixed ligand-Fe^{III}-borate complexes; complex equilibria; N-donor multidentate ligands.

1. Introduction

Enhancement of acidity of boric acid (H₃BO₃) 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^{III} is well-known¹. Acidity of aqueous solution of H₃BO₃ is found to be enhanced in the presence of *cis*-diaqua Co^{III} complexes: *cis*-[Co^{III}(N₄)(H₂O)₂]³⁺, where, (N₄) = (2,2'-bipyridine)₂ or (1,3-diaminopropane)₂ 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^{III} centre with release of the proton².



Acidity of aqueous solution of H₃BO₃ is also enhanced in the presence of coordinately unsaturated labile complexes, [M^{II}(L)(H₂O)₂]²⁺, M = Co, Ni, Cu and Zn, L = (N₂), (N₄) amine formed *in situ* in ternary M^{II}-L-H₃BO₃ mixtures³. 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 H_3BO_3 , complex formation equilibria of Fe^{III} with H_3BO_3 in the absence and in the presence of 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) (hereafter, L^1) and diethylenetriamine (den), triethylenetetramine (trien) (hereafter, L^2) have been investigated by potentiometric methods using different molar ratios of the reactants Fe^{III} , (L^1 or L^2) and H_3BO_3 in aqueous solution at a fixed ionic strength $I = 0.1 \text{ mol dm}^{-3}$ (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 method⁴.

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 HNO_3 and trien.4 HNO_3 respectively, air-dried and analysed⁵. Ferric nitrate solution was prepared by dissolving freshly precipitated, alkali-free $\text{Fe}(\text{OH})_3$ in standard HNO_3 and standardised by combined acid–base, ion exchange and complexometric titrations⁵.

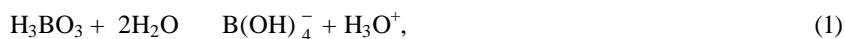
The equilibrium study involved *pH*-metric titrations³ in aqueous medium of a series of solutions (0.025 dm^3) containing known amounts (0.0005 – $0.005 \text{ mol dm}^{-3}$) of H_3BO_3 and/or L ($\text{L} = \text{bipy, phen, den and trien in their protonated forms}$) and known amount (0.01 mol dm^{-3}) of free HNO_3 , in the absence and in the presence of known amounts (0.0005 – $0.001 \text{ mol dm}^{-3}$) of Fe^{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-free⁶ standard 0.1 mol dm^{-3} NaOH solution, maintaining a fixed ionic strength, $I = 0.1 \text{ mol dm}^{-3}$ (NaNO_3).

Ionic product of water at the experimental temperature and activity coefficient of H^+ ion at the experimental ionic strength were obtained from literature^{7,8}. Analytical concentrations of H^+ ion corresponding to the *pH*-meter readings were obtained by the usual procedure⁹. Formation constants (table 1) were calculated with the aid of the SCOGS computer program⁴. 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). H_3BO_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 OH^- according to equilibrium (1)¹⁰:



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

Charges are not shown in the expressions for clarity.

3.2 Hydrolytic equilibria of Fe^{III}

Fe^{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^{III} - L - borate complexes with L = bipy, phen, den and trien in aqueous solution. $I = 0.1$ M ($NaNO_3$); Temperature = 25°C

(a) Hydrolysis constants of $Fe(aq)^{3+}$ ions					
$\log K_{Fe}^H$	-1.62	$\log K_{Fe}^{2H}$	-4.28	$\log K_{Fe}^{3H}$	-7.91
(b) Formation constants of Fe^{III} - H_3BO_3 complexes					
(i) Overall formation constants					
$\log b_{Fe(H_2BO_4)}^{Fe}$	3.67	$\log b_{Fe(OH)(H_2BO_4)}^{Fe}$	1.16	$\log b_{Fe(OH)_2(H_2BO_4)}^{Fe}$	-1.72
(ii) Effect of coordination with $Fe(aq)^{3+}$, $Fe(OH)^{2+}$ and $Fe(OH)_2^+$ on ionisation of H_3BO_3					
$\log K_{[Fe+H_3BO_3+H_2O]}^{3H}$	-5.33	$\log K_{[Fe(OH)+H_3BO_3+H_2O]}^{3H}$	-6.22	$\log K_{[Fe(OH)_2+H_3BO_3+H_2O]}^{3H}$	-6.44
	-	$(\Delta \log K_{Fe})_1$	-0.89	$(\Delta \log K_{Fe})_2$	-1.11
	-				
Ligands (L)					
Constants	bipy	phen	den	trien	
(c) Proton-ligand constants					
$\log K_{HL}^H$	4.23	4.86	9.76	9.44	
$\log K_{H_2L}^H$	1.32	1.90	8.90	8.92	
$\log K_{H_3L}^H$	-	-	4.05	6.74	
$\log K_{H_4L}^H$	-	-	-	3.56	
(d) Fe^{III} - L binary constants					
(i) Overall formation constants					
$\log K_{FeL}^{Fe}$	9.13	10.41	18.76	21.77	
$\log b_{Fe(L)(OH)}^{Fe}$	6.96	8.54	15.18	15.47	
$(\Delta \log K_{Fe})_1$	-0.55	-0.25	-1.96	-4.68	
$\log b_{Fe(L)(OH)_2}^{Fe}$	5.11	6.43	10.91	10.85	
$(\Delta \log K_{Fe})_2$	0.26	0.30	-3.57	-6.64	
$\log K_{FeL_2}^{Fe}$	18.11	19.92	-	-	
$\log b_{Fe(L)_2(OH)}^{Fe}$	14.74	16.43	-	-	
$(\Delta \log K_{Fe})_1$	-1.75	-1.87	-	-	
$\log b_{Fe(L)_2(OH)_2}^{Fe}$	10.76	12.52	-	-	
$(\Delta \log K_{Fe})_2$	-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) ₂ on ionisation of H ₃ BO ₃				
$\log K_{[\text{Fe(L)(OH)}_2 + \text{H}_3\text{BO}_3]}^{\text{H}}$	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



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

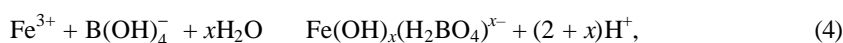
The predominant Fe^{III} species in the range $p\text{H} \sim 2-4$, are $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^+$. The concentration of $\text{Fe}(\text{OH})_3$, is negligibly small. Although Fe^{III} has a profound tendency to form polynuclear **μ**-dioxo species, concentrations of such species in the experimental concentration range are negligible¹¹.

3.3 Fe^{III} - H_3BO_3 binary equilibria

In the presence of Fe^{III} , the buffer region corresponding to the ionisation (1) of H_3BO_3 is shifted to lower pH regions due to the formation of $Fe(H_2BO_4)$, $Fe(H_2BO_4)(OH)^-$ and $Fe(H_2BO_4)(OH)_2^{2-}$ complexes according to



pH measurements, however, could not be extended above $pH \geq 4$ due to commencement of precipitation, probably of electroneutral $Fe(OH)_3$ and/or $Fe(H_2BO_4)$, which respectively constitute $\sim 20\%$ and 5% of total Fe^{III} . Formation constants of $[Fe(OH)_x(H_2BO_4)]^{x-}$ complexes may be defined according to

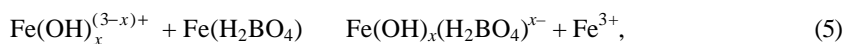


$$\mathbf{b}_{Fe(OH)_x(H_2BO_4)}^{Fe} = ([Fe(OH)_x(H_2BO_4)]/[H]^{(2+x)})/([Fe][B(OH)_4^-]). \quad (4a)$$

$\mathbf{b}_{Fe(OH)_x(H_2BO_4)}^{Fe}$ values may be obtained as computer output⁴, from which the equilibrium constants of the reactions (3) may be calculated using

$$\log K_{[Fe(OH)_x(H_2BO_4)]}^{xH} = \log \mathbf{b}_{Fe(OH)_x(H_2BO_4)}^{Fe} + \log K_{H_3BO_3}^H + \log K_{Fe}^{xH}. \quad (3a)$$

Speciation curves of Fe^{III} - H_3BO_3 system also indicate the formation of the $[Fe(OH)_x(H_2BO_4)]^{x-}$ complexes according to the reproportionation equilibria,



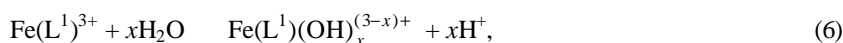
for which the $(\Delta \log K_{Fe})_x$ values¹² may be calculated using

$$(\Delta \log K_{Fe})_x = \log \mathbf{b}_{Fe(OH)_x(H_2BO_4)}^{Fe} - \log \mathbf{b}_{Fe(H_2BO_4)}^{Fe} - \log K_{Fe}^{xH}. \quad (5a)$$

Predominant Fe^{III} species in this system are $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe(OH)_2(H_2BO_4)^{2-}$. Percentages of $Fe(H_2BO_4)$ and $Fe(OH)(H_2BO_4)^-$ are very small in the entire pH range studied. Negative values of $(\Delta \log K_{Fe})_x$ (table 1) indicate much less relevance of the re-proportionation equilibria (5) as compared to that of equilibria (4).

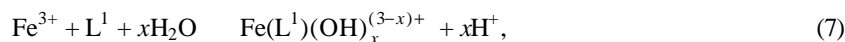
3.4 Fe^{III} - (L^1/L^2) binary equilibria ($L^1 = bipy, phen; L^2 = den, trien$)

Predominant Fe^{III} species at lower pH (~ 2) values in Fe^{III} - L^1 - H_3BO_3 systems are $Fe(L^1)(aq)^{3+}$, which with rise of pH undergo hydrolysis to produce $Fe(L^1)(OH)_x^{(3-x)+}$ according to



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

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



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

may be obtained as computer output⁴, from which the hydrolysis constants, $K_{\text{Fe(L}^1\text{)}}^{\text{xH}}$, may be calculated using the relations

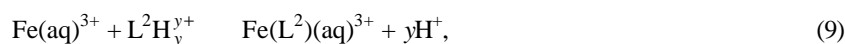
$$\log K_{\text{Fe(L}^1\text{)}}^{\text{xH}} = \log \mathbf{b}_{\text{Fe(L}^1\text{)(OH)}_x}^{\text{Fe}} - \log K_{\text{Fe(L}^1\text{)}}^{\text{Fe}}, \quad (7b)$$

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



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

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



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

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 $\mathbf{b}_{\text{Fe(H}_2\text{BO}_4\text{)}}^{\text{Fe}}$. 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 values¹², 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 OH^- and $\text{H}_2\text{BO}_4^{3-}$ are ‘**s**basic only’ ligands, whereas, 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 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 Fe(aq)^{3+} ion and that of the complexed Fe(L)(aq)^{3+} ions ($K_{\text{Fe}}^{\text{xH}}$ and $K_{\text{Fe(L)}}^{\text{xH}}$ respectively) on the log scale (table 1) gives a measure of the difference in the acidity of coordinated H_2O in free and complexed Fe^{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 (L^2), viz., den (N_3 -**s**) and trien (N_4 -**s**) to Fe^{III} lowers the acidity of the coordinated H_2O . On the other hand, in the coordination of ‘**s**basic and **p**acidic’ ligands

(L^1), viz., bipy, phen (N_2-Sp) and (bipy) $_2$ and (phen) $_2$ (N_4-Sp), although the acidity of the coordinated H_2O tend to increase, their 'pacidic effects' cannot outweigh their 'S basic effects'. As a result, acidity of the H_2O ligands coordinated to $Fe^{III}-L$ complexes are in the order: $Fe(aq)^{3+} > Fe(N_4-Sp(aq))^{3+} > Fe(N_2-Sp(aq))^{3+} > Fe(N_3-S(aq))^{3+} > Fe(N_4-S(aq))^{3+}$.

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

Complex formation equilibria of Fe^{III} with H_3BO_3 in the presence of another ligand, L, in aqueous solution may be described according to the general equilibria (10):

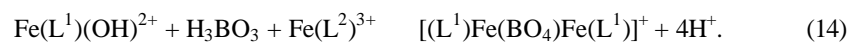
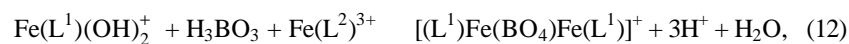


$$b_{pqsr} = ([Fe_p(L)_q(H_sBO_4)_r]^{(3p+rs-5r)+} [H^+]^{r(4-s)}) / ([Fe^{3+}]^p [L]^q [B(OH)_4^-]^r), \quad (10a)$$

where p , q and r are stoichiometric numbers of Fe^{3+} , ligand L and BO_4^{5-} group and s is the number of H^+ ions bound to the BO_4^{5-} groups in the formula of the complex. The borate ion, $B(OH)_4^-$ is derived from the ionisation (1) of H_3BO_3 , in aqueous solution. b_{pqsr} may be obtained as computer output⁴ along with the species distribution data for elucidation of the complex formation equilibria.

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

In both 1:1:1 and 2:2:1 $Fe^{III}: L^1: H_3BO_3$ systems, the concentrations of the $Fe(L^1)^{3+}$ species are small from the very beginning of the reactions ($pH \sim 2$), in which $Fe(L^1)(OH)^{2+}$ and $Fe(L^1)(OH)_2^+$ are the predominant Fe^{III} species. The mixed ligand Fe^{III} -borate complexes, $Fe(L^1)(H_2BO_4)$ and $(L^1)Fe(BO_4)Fe(L^1)^+$ are formed according to the following equilibria at pH values above 2.5.



Binuclear $[(L^1)Fe(BO_4)Fe(L^1)]^+$ complexes are formed from the very beginning of the reactions and represent the most predominant Fe^{III} species in the 2:2:1 $Fe^{III}: L^1: H_3BO_3$ systems. The overall formation constants, b_{1121} and b_{2201} , of $[(L^1)Fe(H_2BO_4)]$ and $[(L^1)Fe(BO_4)Fe(L^1)]^+$ complexes, defined as below,

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

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

may be obtained as computer output⁴ along with the speciation data of these complexes.

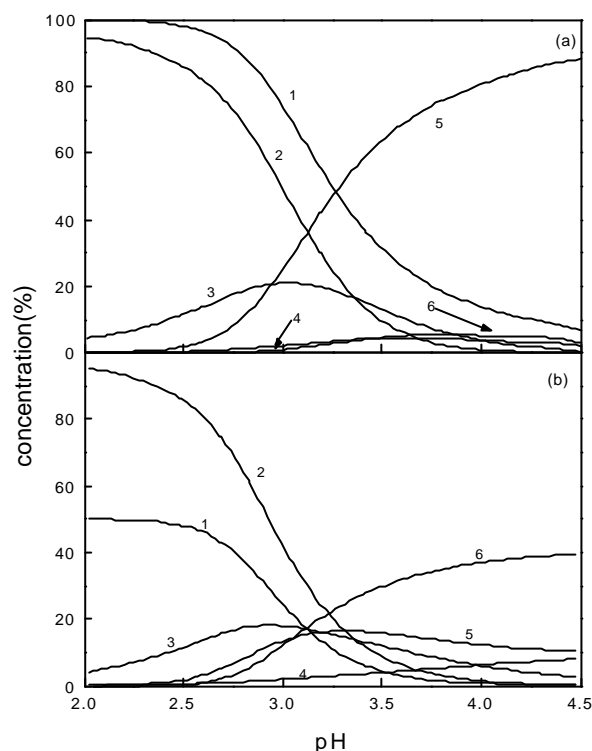
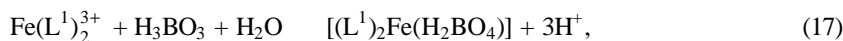
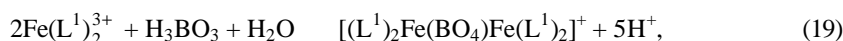


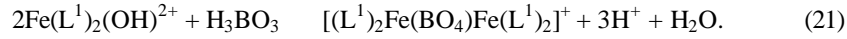
Figure 1. Speciation curves for Fe^{III} –bipy– H_3BO_3 systems. Fe^{III} : bipy: H_3BO_3 = (a) 1: 2:1 and (b) 2:4:1; (1) H_3BO_3 , (2) $\text{Fe}(\text{bipy})_2^{3+}$, (3) $\text{Fe}(\text{bipy})_2(\text{OH})_2^+$, (4) $\text{Fe}(\text{bipy})_2(\text{OH})_2^+$, (5) $\text{Fe}(\text{bipy})_2(\text{H}_2\text{BO}_4)^+$, (6) $\text{Fe}_2(\text{bipy})_4(\text{BO}_4)^+$.

In the 1:2:1 and 2:4:1 Fe^{III} : L^1 : H_3BO_3 systems (figure 1) the predominant Fe^{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 Fe^{III} -borate complexes that constitute about 90% of Fe^{III} and $\text{pH} \geq 4$ in the 1:2:1 Fe^{III} : L^1 : H_3BO_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 Fe^{III} : L^1 : H_3BO_3 systems. However, in the 2:4:1 Fe^{III} : L^1 : H_3BO_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 output⁴ 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):

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

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

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

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

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

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

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

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

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

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.

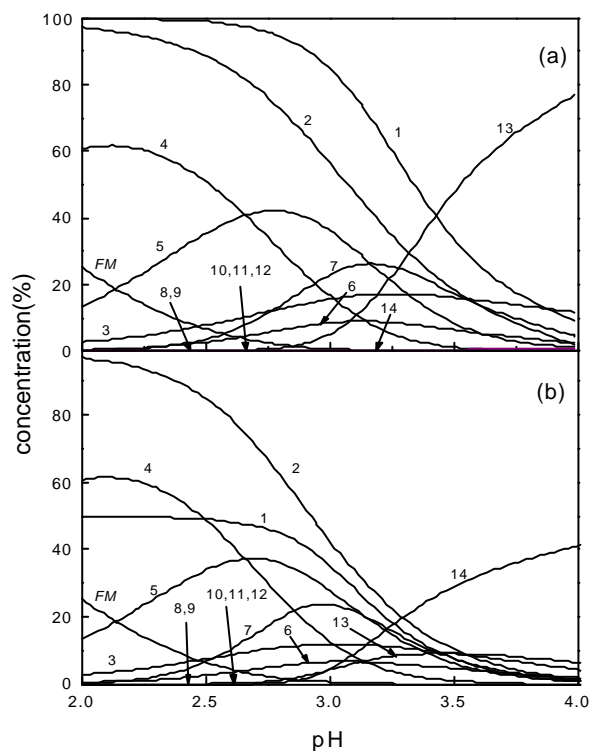
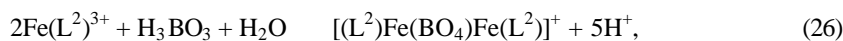
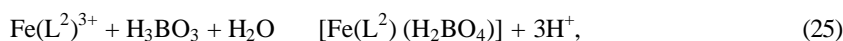
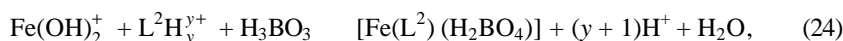
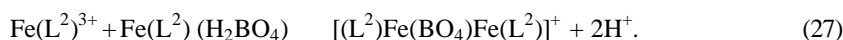


Figure 2. Speciation curves for $Fe^{III}-\text{trien}-H_3BO_3$ system: $Fe^{III}:\text{trien}:H_3BO_3=(a)$ 1:1:1 and **(b)** 2:2:1; (1) H_3BO_3 , (2) trienH_4^+ , (3) trienH_3^{3+} , (4) $Fe(OH)_2^+$, (5) $Fe(OH)_2^+$, (6) $Fe(OH)_3$, (7) $Fe(\text{trien})^{3+}$, (8) $Fe(\text{trien})(OH)^{2+}$, (9) $Fe(\text{trien})(OH)^+$, (10) $Fe(H_2BO_4)$, (11) $Fe(H_2BO_4)(OH)^-$, (12) $Fe(H_2BO_4)(OH)_2^{2-}$, (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^{III}: L²: H₃BO₃ systems, whereas the equilibrium (27) is identifiable only in the 2:2:1 systems. The overall formation constants, **b**₁₁₂₁ and **b**₂₂₀₁ of the complexes [(L²)Fe(H₂BO₄)] and [(L²)Fe(BO₄)Fe(L²)]⁺ respectively, may be obtained as computer output⁴, 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 (H₂BO₄)³⁻ ligand species to Fe(L²)(aq)³⁺ ion having two H₂O ligands in *cis*-positions.

The effect of coordination of borate species with Fe(aq)³⁺, Fe(L-**S**)³⁺ and Fe(L-**S****P**)³⁺ on the enhancement of acidity of H₃BO₃ may be compared on the basis of the formation constants (table 1) of Fe^{III}-borate and Fe^{III}-L-borate complexes from the reactions of H₃BO₃ with the corresponding Fe^{III}-species. As a matter of fact, the enhancement of acidity of H₃BO₃ due to the formation of mixed ligand borate complexes: (L¹)_zFe(H₂BO₄) and (L¹)_zFe(BO₄)Fe(L¹)_z⁺, where z = 1, 2, is much higher than that due to the formation of simple binary Fe(H₂BO₄) complex, because of (L¹) ← Fe **p** bonding. However, this effect is not observed due to the formation of ternary (L²)Fe(H₂BO₄) and (L²)Fe(BO₄)Fe(L²)⁺ 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 H₃BO₃ (by a factor of ~10⁴) due to its reaction with (L¹)₂Fe(OH)²⁺ relative to Fe(OH)²⁺. In this regard the present Fe^{III}-amine complexes may be arranged in the order: Fe^{III}(bipy)_z > Fe^{III}(phen)_z > Fe^{III}(den) > Fe^{III}(trien); z = 1, 2 and complexes with (z = 2) > those with (z = 1).

Although the binary Fe^{III}(phen)_z, z = 1, 2 complexes are relatively more stable than their bipy analogues, (bipy)_zFe(H₂BO₄) and (bipy)_zFe(BO₄)Fe(bipy)_z⁺ are more stable than their phen analogues. Bipy because of free rotation about the C₁-C₁' bond, can adjust much better than phen to the tetrahedral bond angles imposed on Fe^{III} by the borate ligands H₂BO₄³⁻ and BO₄³⁻. Due to the structural rigidity of phen, the chelate rings of (phen)_zFe(H₂BO₄) and (phen)_zFe(BO₄)Fe(phen)_z⁺ are strained at the bond angles around Fe^{III}, 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(L¹)₂³⁺ and Fe(L¹)₂(OH)²⁺ complexes than those with Fe(L¹)³⁺ and Fe(L¹)(OH)²⁺

complexes (table 1). Moreover, Fe^{III} in Fe(L¹)₂³⁺ and Fe(L¹)₂(OH)²⁺ may exist in low spin (*t*_{2g}⁵) states, and consequently act as a better *p*-electron donor than the high spin (*t*_{2g}³*e*_g²) in Fe(L¹)₃³⁺ and Fe(L¹)(OH)²⁺ complexes. This is also consistent with the order: Fe^{III}(N₄-**sp**) > Fe^{III}(N₂-**sp**) > Fe^{III}(N₃-**s**) > Fe^{III}(N₄-**s**) with regard to the effectiveness of the present Fe^{III}-amine complexes in enhancing the ionisation of H₃BO₃ through mixed ligand borate complex formation.

4. Conclusions

Labile Fe(L)(aq)³⁺ complexes, L = bipy, phen (N₂), den (N₃); (bipy)₂, (phen)₂, trien (N₄), formed *in situ*, are structurally compatible with 1,2-*cis*-diols, like the substitution inert *cis*-[(N₄)M^{III}(H₂O)₂]³⁺ 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^{III}-borate complexes of the types [(L)Fe(H₂BO₄)] and [(L)Fe(BO₄)Fe(L)]⁺ respectively, in which the electron deficient B^{III} attains tetra-covalency through chelation. The binuclear [(L)Fe(BO₄)Fe(L)]⁺ complexes are found to be more stable as compared to the mononuclear [(L)Fe(H₂BO₄)] complexes. The *p*-acidic nature of the ligands (L) increases the acidity of the coordinated H₂O molecules in Fe^{III}(L)(aq)³⁺ complexes, which in turn, enhances the acidity of H₃BO₃ to a greater extent than those without having metal to *p*-bonding.

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