

## Equilibrium study on the reactions of boric acid with some *cis*-diaqua Cr<sup>III</sup>-complexes

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**Abstract.** Substitution inert *cis*-diaqua Cr<sup>III</sup> complexes: *cis*-[(L<sup>x-</sup>)Cr<sup>III</sup>(H<sub>2</sub>O)<sub>2</sub>]<sup>(3-x)+</sup> derived from N-donor ligands (L<sup>x-</sup>) viz., bipyridine and 1,10-phenanthroline ( $x = 0$ ) and N,O-donor ligands viz., nitrilotriacetate and anthranilate N,N-diacetate ( $x = 3$ ) titrate as diprotic acids in aqueous solution and enhance the acidity of otherwise weakly acidic boric acid (H<sub>3</sub>BO<sub>3</sub>) producing mononuclear and binuclear mixed ligand Cr<sup>III</sup>-borate complexes: [(L)Cr(H<sub>2</sub>BO<sub>4</sub>)]<sup>x-</sup> and [(L)Cr(BO<sub>4</sub>)Cr(L)]<sup>(1-2x)+</sup> respectively through coordination of the H<sub>2</sub>O and/or OH<sup>-</sup> ligands, *cis*-coordinated in the Cr<sup>III</sup>-complexes on the electron deficient B<sup>III</sup>-atom in H<sub>3</sub>BO<sub>3</sub> with release of protons. Deprotonation of the parent Cr<sup>III</sup>-complexes and their reactions with H<sub>3</sub>BO<sub>3</sub> have been investigated by potentiometric method in aqueous solution,  $I = 0.1 \text{ mol dm}^{-3}$  (NaNO<sub>3</sub>) at  $25 \pm 0.1^\circ\text{C}$ . The equilibrium constants have been evaluated by computerized methods and the tentative stoichiometry of the reactions have been worked out on the basis of the speciation curves.

**Keywords.** *cis*-Diaqua Cr<sup>III</sup> complex–boric acid equilibria; mixed ligand Cr<sup>III</sup>-borate complexes; Cr<sup>III</sup>-borate complexes in solution.

### 1. Introduction

Aminopolycarboxylic acids often serve as model ligands for mimicking metal–protein interactions *in vitro*.<sup>1</sup> With chromium (III), such ligands form low molecular weight complexes, some of which are implicated in glucose tolerance in animals.<sup>2</sup> A Cr(III) complex species containing nicotinic acid, glycine, glutamic acid and cysteine has been isolated from Brewer's yeast.<sup>3</sup> Thus, the reactions of this group of ligands and particularly of their metal complexes have considerable biological relevance. Although these ligands are easily obtainable and their metal complexes are easy to prepare, relatively less attention has been devoted to the investigation of complexes of this group of ligands with trivalent metal ions.<sup>1,4</sup> The present paper describes the results of a systematic equilibrium study on the reactions of boric acid (H<sub>3</sub>BO<sub>3</sub>) with some *cis*-diaqua Cr<sup>III</sup>-complexes, *cis*-[(L<sup>x-</sup>)Cr<sup>III</sup>(H<sub>2</sub>O)<sub>2</sub>]<sup>(3-x)+</sup>, where, L = 2,2'-bipyridine, 1,10-phenanthroline ( $x = 0$ ) and some aminopolycarboxylates viz., nitrilotriacetate, anthranilate N,N-diacetate ( $x = 3$ ) in aqueous solution by potentiometric method at  $25 \pm 0.1^\circ\text{C}$  at a fixed ionic strength,  $I = 0.1 \text{ mol dm}^{-3}$  (NaNO<sub>3</sub>).

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## 2. Experimental

Boric acid, 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), nitrilotracetic acid (H<sub>3</sub>nta), chromium (III) chloride hexahydrate, sodium nitrate, and nitric acid used were of AR grade. Anthranilic acid N,N-diacetic acid (H<sub>3</sub>ada) was synthesised by condensing anthranilic acid (0.01 mol) with monochloroacetic acid (0.022 mol) in Na<sub>2</sub>CO<sub>3</sub> medium according to the literature procedure.<sup>5</sup> The *cis*-diaqua/aquahydroxo chromium (III) complexes: *cis*-[Cr(bipy)<sub>2</sub>(OH)(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub>,<sup>6</sup> *cis*-[Cr(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>·2H<sub>2</sub>O,<sup>6</sup> [Cr(ada)(H<sub>2</sub>O)<sub>2</sub>].3H<sub>2</sub>O<sup>7</sup> and [Cr(nta)(H<sub>2</sub>O)<sub>2</sub>]<sup>4c</sup> were prepared according to reported procedures. Purity of the complexes formed was checked by elemental analysis and spectral measurements (table 1). The absorption spectra of the complexes remained unchanged on keeping their aqueous solutions for several days at room temperature. This indicated that the complexes were kinetically quite stable towards substitution.

The following solutions (i)–(vi), each of initial volume 25 ml and ionic strength,  $I = 0.1 \text{ mol dm}^{-3}$  (NaNO<sub>3</sub>) were prepared in doubly distilled CO<sub>2</sub>-free water for pH metric measurements: (1), 0.01 M HNO<sub>3</sub>; (2), 0.01 M HNO<sub>3</sub> + 0.001 M H<sub>3</sub>BO<sub>3</sub>; (3), (1) + 0.001 M [(L)Cr(H<sub>2</sub>O)<sub>2</sub>]; (4), (3) + 0.001 M H<sub>3</sub>BO<sub>3</sub>; (5), (1) + 0.002 M [(L)Cr(H<sub>2</sub>O)<sub>2</sub>]; (6), (5) + 0.001 M H<sub>3</sub>BO<sub>3</sub>, where, L = (bipy)<sub>2</sub>, (phen)<sub>2</sub>, (nta<sup>3-</sup>), (ada<sup>3-</sup>). The solutions were thermostated at 25 ± 0.1°C and then pH-metrically titrated with carbonate free<sup>8</sup> standard 0.1 mol dm<sup>-3</sup> NaOH solution prepared from GR grade NaOH pellets.

pH measurements were made with a Systronics 335 pH-meter (accuracy: ± 0.01 pH) employing a special glass electrode (pH 1–14) in conjunction with an SCE. UV-Vis spectra were recorded on a Hitachi U-3501 spectrophotometer.  $pK_w$  of water at the experimental temperature and activity coefficient of hydrogen ion at the experimental ionic strength were obtained from the literature.<sup>9,10</sup> Analytical concentrations of H<sup>+</sup> ion at different pH-meter readings were obtained according to the usual procedure.<sup>11</sup> Equilibrium constants were evaluated by the computer program, SCOGS,<sup>12</sup> for which the stoichiometries of the complexes are described in table 2. Initial values of the ionisation constant of H<sub>3</sub>BO<sub>3</sub> and deprotonation constants of the *cis*-diaqua Cr<sup>III</sup>-complexes supplied to the computer as input data, were evaluated according to the method of Irving and Rossotti.<sup>13</sup> Computer-refined values of the equilibrium constants and other related constants corresponding the minimum standard deviation are presented in table 3.

**Table 1.** Elemental analysis and electronic spectral data for *cis*-diaqua chromium (III) complexes.

Complex	(% ) Found (calcd)				Spectral measurements $I^{\text{H}_2\text{O}}$ (nm) ( $\epsilon$ ) found [literature]
	C	H	N	Cr	
[Cr(bipy) <sub>2</sub> (OH)(H <sub>2</sub> O)](ClO <sub>4</sub> ) <sub>2</sub>	39.72 (40.11)	3.39 (3.17)	9.53 (9.36)	7.54 (7.36)	493 (44.7) [494 (44.8)]
[Cr(phen) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub> ·2H <sub>2</sub> O	43.57 (42.96)	3.88 (3.58)	14.82 (14.61)	8.91 (8.69)	497 (43.3) [496 (44.8)]
[Cr(nta)(H <sub>2</sub> O) <sub>2</sub> ]	26.24 (26.09)	3.74 (3.62)	4.96 (5.07)	18.52 (18.84)	558 (92.1) 407 (99.8) [556 (93)] <sup>a</sup> [405 (99.5)] <sup>a</sup>
[Cr(ada)(H <sub>2</sub> O) <sub>2</sub> ].3H <sub>2</sub> O	33.50 (33.67)	4.65 (4.59)	3.52 (3.57)	13.40 (13.26)	547 (83.6) 396 (86.0) [546 (85.1)] <sup>b</sup> [396 (87.1)] <sup>b</sup>

<sup>a</sup>Ref. [4c]; <sup>b</sup>Ref. [7]

**Table 2.** Stoichiometry of the complex species appearing in 1 : 1 and 2 : 1 *cis*-[(L<sup>x-</sup>)Cr<sup>III</sup>(H<sub>2</sub>O)<sub>2</sub>]<sup>(3-x)+</sup>-H<sub>3</sub>BO<sub>3</sub> systems, L = (bipy)<sub>2</sub>, (phen)<sub>2</sub> (x = 0) and nta<sup>3-</sup>, ada<sup>3-</sup> (x = 3).

Compd. No.*	Complex species	p	q	r
	H <sub>3</sub> BO <sub>3</sub>	0	1	-1
	B(OH) <sub>4</sub> <sup>-</sup>	0	1	0
<b>I</b>	[(L <sup>x-</sup> )Cr(H <sub>2</sub> O) <sub>2</sub> ] <sup>(3-x)+</sup>	1	0	0
<b>II</b>	[(L <sup>x-</sup> )Cr(OH)(H <sub>2</sub> O)] <sup>(2-x)+</sup>	1	0	1
<b>III</b>	[(L <sup>x-</sup> )Cr(OH) <sub>2</sub> ] <sup>(1-x)+</sup>	1	0	2
<b>IV</b>	[(L <sup>x-</sup> )Cr(H <sub>2</sub> BO <sub>4</sub> )] <sup>x-</sup>	1	1	2
<b>V</b>	[(L <sup>x-</sup> )Cr(BO <sub>4</sub> )M(L <sup>x-</sup> )] <sup>(1-2x)</sup>	2	1	4

\*These numbers (**I-V**) are also used for the speciation curves of the complexes (figures 1-2)

**Table 3.** Equilibrium constants\* of the reactions of *cis*-[(L<sup>x-</sup>)Cr<sup>III</sup>(H<sub>2</sub>O)<sub>2</sub>]<sup>(3-x)+</sup> complexes with H<sub>3</sub>BO<sub>3</sub> in aqueous solution. L = (bipy)<sub>2</sub>, (phen)<sub>2</sub> (x = 0) and nta<sup>3-</sup>, ada<sup>3-</sup> (x = 3). Temp. = 25°C; I = 0.1 mol dm<sup>-3</sup> (NaNO<sub>3</sub>), pK<sub>H<sub>3</sub>BO<sub>3</sub></sub><sup>H</sup> = 9.00

Constants	L			
	(bipy) <sub>2</sub>	(phen) <sub>2</sub>	nta <sup>3-</sup>	ada <sup>3-</sup>
log K <sub>I</sub> <sup>H</sup>	-3.14	-3.18	-5.79	-6.30
log K <sub>II</sub> <sup>H</sup>	-5.80	-5.78	-8.55	-8.54
Log b <sub>112</sub>	1.75	1.98	-1.17	-1.56
log b <sub>214</sub>	1.70	1.72	-3.45	-4.48
log K <sub>(H<sub>3</sub>BO<sub>3</sub>+II)</sub> <sup>2H</sup>	-4.11	-3.84	-4.38	-4.26
log K <sub>(H<sub>3</sub>BO<sub>3</sub>+2II)</sub> <sup>3H</sup>	-1.02	-0.92	-0.87	-0.88

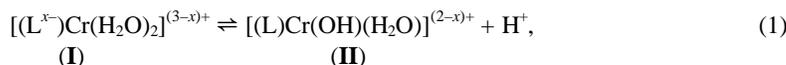
\*Limits of error: ± (0.02 ~ 0.05) in log unit

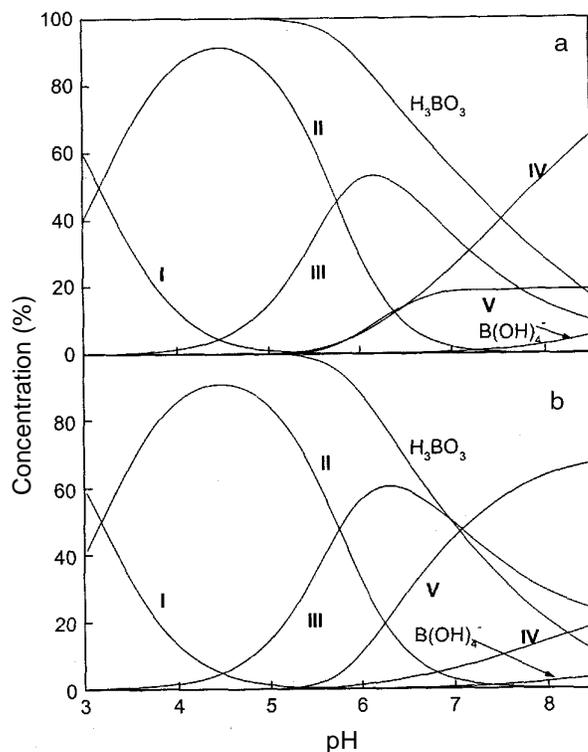
Tentative stoichiometries of the reactions were elucidated with the help of the speciation curves (figures 1-2).

### 3. Results and discussion

#### 3.1 Deprotonation equilibria of *cis*-[(L)Cr<sup>III</sup>(H<sub>2</sub>O)<sub>2</sub>] complexes

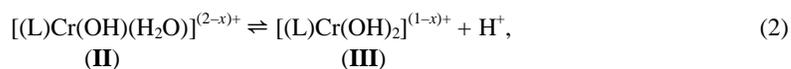
*cis*-Diaqua chromium (III) complexes, [(L<sup>x-</sup>)Cr<sup>III</sup>(H<sub>2</sub>O)<sub>2</sub>]<sup>(3-x)+</sup>, L = (bipy)<sub>2</sub>, (phen)<sub>2</sub> (x = 0) show two well-defined buffer regions, one in the pH range 3.0-4.5 and the other in the pH range 5.0-7.0. For the complexes with L = ada<sup>3-</sup> and nta<sup>3-</sup> (x = 3) the above two buffer regions are observed in the pH ranges 5.0-7.0 and 7.5-9.5 respectively. One mole of base per mole of the complexes is consumed in each of the two buffer regions, which is obviously due to successive deprotonation of the two coordinated H<sub>2</sub>O ligands in these *cis*-diaqua Cr<sup>III</sup>-complexes (**I**)<sup>4c,6-7</sup> to produce the corresponding mono-aqua-monohydroxo and dihydroxo complexes (**II** and **III** respectively) according to the equilibria (1) and (2) below as the speciation curves (figures 1-2) imply.





**Figure 1.** Species distribution curves of  $\text{cis-}[\text{Cr}(\text{bipy})_2(\text{H}_2\text{O})_2]^{3+} : \text{H}_3\text{BO}_3$ . (a) 1 : 1 and (b) 2 : 1 systems: (I)  $[\text{Cr}(\text{bipy})_2(\text{H}_2\text{O})_2]^{3+}$ , (II)  $[\text{Cr}(\text{bipy})_2(\text{OH})(\text{H}_2\text{O})]^{2+}$ , (III)  $[\text{Cr}(\text{bipy})_2(\text{OH})_2]^+$ , (IV)  $[\text{Cr}(\text{bipy})_2(\text{H}_2\text{BO}_4)]$ , (V)  $[\text{Cr}_2(\text{bipy})_4(\text{BO}_4)]^+$ .

$$K_{\text{I}}^{\text{H}} = \frac{(\text{II})[\text{H}]}{(\text{I})}, \quad (1a)$$

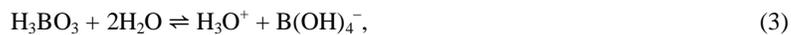


$$K_{\text{II}}^{\text{H}} = \frac{(\text{III})[\text{H}]}{(\text{II})}. \quad (2a)$$

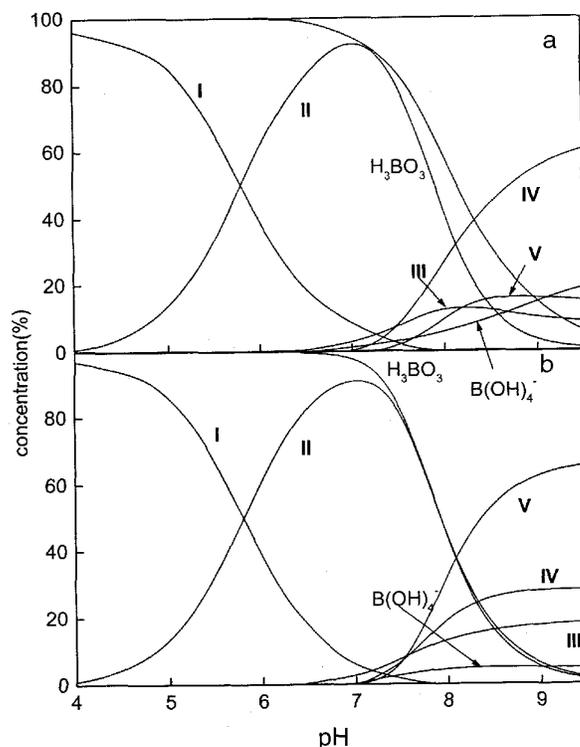
Charges are omitted from the mathematical expressions for clarity.

### 3.2 Reaction of $\text{H}_3\text{BO}_3$ with $\text{cis-}[(\text{L})\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2]$ complexes

Boric acid ( $\text{H}_3\text{BO}_3$ ) in aqueous solution ionises as a weak monobasic Lewis acid according to the following equilibria,<sup>14</sup>



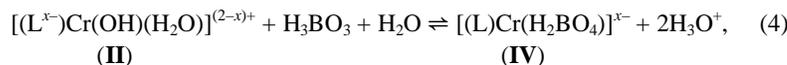
$$K_{\text{H}_3\text{BO}_3}^{\text{H}} = \frac{[\text{H}][\text{B}(\text{OH})_4^-]}{[\text{H}_3\text{BO}_3]}. \quad (3a)$$



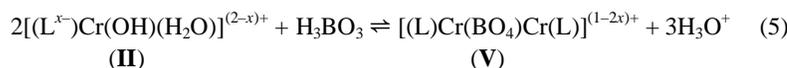
**Figure 2.** Species distribution curves of *cis*-[Cr(нта)(H<sub>2</sub>O)<sub>2</sub>]: H<sub>3</sub>BO<sub>3</sub>. (a) 1:1 and (b) 2:1 systems: (I) [Cr(нта)(H<sub>2</sub>O)<sub>2</sub>], (II) [Cr(нта)(OH)(H<sub>2</sub>O)]<sup>-</sup>, (III) [Cr(нта)(OH)<sub>2</sub>]<sup>2-</sup>, (IV) [Cr(нта)(H<sub>2</sub>BO<sub>4</sub>)<sub>3</sub>]<sup>3-</sup>, (V) [Cr<sub>2</sub>(нта)<sub>2</sub>(BO<sub>4</sub>)<sub>5</sub>]<sup>5-</sup>.

Two well-defined buffer regions are observed when 1:1 and 2:1 mixtures of the *cis*-[(L<sup>x-</sup>)Cr(H<sub>2</sub>O)<sub>2</sub>]<sup>(3-x)+</sup> complexes (L = (bipy)<sub>2</sub>, (phen)<sub>2</sub>, nta<sup>3-</sup> and ada<sup>3-</sup>) and H<sub>3</sub>BO<sub>3</sub> are pH-metrically titrated with NaOH. The first buffer regions are found to be superimposable with that of the first step deprotonation equilibria (1) of the parent complexes in the absence of H<sub>3</sub>BO<sub>3</sub> and the amounts of base consumed in these buffer regions are just equal to the molar concentrations of these complexes. The second buffer regions occur at pH values lower than the buffer regions corresponding to the second step deprotonation equilibria (2) of the parent complexes and the ionisation equilibria (3) of H<sub>3</sub>BO<sub>3</sub>. The amounts of base consumed in these second buffer regions are exactly equal to the sum of the molar concentrations of the Cr<sup>III</sup>-complexes and H<sub>3</sub>BO<sub>3</sub>. It is, therefore, evident from these observations that the monoaqua-monohydroxo complexes (II), resulting from deprotonation of the parent *cis*-diaqua complexes (I), having one OH group and one H<sub>2</sub>O ligand in *cis*-positions, are the actual species that react with H<sub>3</sub>BO<sub>3</sub> to release protons at lower pH values in the second buffer region. As there is no chance of any ligand exchange reaction under the present experimental conditions, the monoaqua-monohydroxo complexes (II) may react with H<sub>3</sub>BO<sub>3</sub> according to the equilibria (4) and (5) to produce the 1:1 and the 2:1 [(L)Cr(H<sub>2</sub>O)<sub>2</sub>]: borate complexes (IV and V

respectively) in the same manner as the *cis*-1,2-diols react with  $\text{H}_3\text{BO}_3$ .<sup>15</sup> These are also implied by the speciation curves (figures 1–2) of these systems in the experimental pH regions:



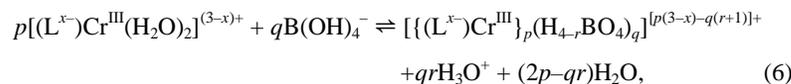
$$K_{(\text{H}_3\text{BO}_3+\text{II})}^{2\text{H}} = ([\text{IV}][\text{H}]^2)/([\text{II}][\text{H}_3\text{BO}_3]). \quad (4a)$$



$$K_{(\text{H}_3\text{BO}_3+2\text{II})}^{3\text{H}} = ([\text{V}][\text{H}]^3)/([\text{II}]^2[\text{H}_3\text{BO}_3]). \quad (5a)$$

### 3.1 Calculation of the equilibrium constants of the reactions of *cis*- $[(\text{L}^{x-})\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2]^{(3-x)+}$ with $\text{H}_3\text{BO}_3$

Reactions of *cis*- $[(\text{L}^{x-})\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2]^{(3-x)+}$  complexes with  $\text{H}_3\text{BO}_3$  may be represented according to the general equilibria (6):



and the equilibrium constants ( $\mathbf{b}_{pqr}$ ) of these reactions may be defined according to,

$$\mathbf{b}_{pqr} = \frac{[(\text{L})\text{Cr}^{\text{III}}]_p(\text{H}_{4-r}\text{BO}_4)_q [\text{H}]^{qr}}{[(\text{L})\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2]^p [\text{B}(\text{OH})_4]^{-q}}, \quad (6a)$$

where,  $p$  and  $q$  represent the stoichiometric numbers of  $[(\text{L})\text{Cr}^{\text{III}}(\text{H}_2\text{O})_2]$  and  $\text{B}(\text{OH})_4^-$  ions respectively and  $r$  is the number of protons released from the  $\text{B}(\text{OH})_4^-$  ion in forming the  $[(\text{L}^{x-})\text{Cr}^{\text{III}}]_p(\text{H}_{4-r}\text{BO}_4)_q]^{[p(3-x)-q(r+1)]+}$ .  $p$  and  $q$  may be zero or positive integers,  $r$  is a positive integer for a deprotonated or a hydroxo species, negative integer for a protonated species and zero for a neutral normal species. The equilibrium constants ( $\mathbf{b}_{112}$  and  $\mathbf{b}_{214}$ ) corresponding to the formation of mononuclear and binuclear mixed ligand complexes,  $[(\text{L})\text{Cr}(\text{H}_2\text{BO}_4)]^{x-}$  (IV) and  $[(\text{L})\text{Cr}(\text{BO}_4)\text{Cr}(\text{L})]^{(1-2x)+}$  (V) respectively may, therefore, be defined according to the relations:

$$\mathbf{b}_{112} = ([\text{IV}][\text{H}]^2)/([\text{I}][\text{B}(\text{OH})_4]), \quad (7)$$

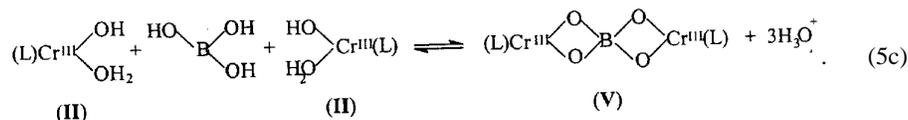
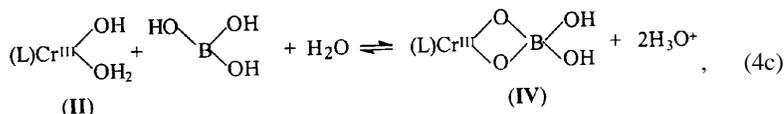
$$\mathbf{b}_{214} = ([\text{V}][\text{H}]^4)/([\text{I}]^2[\text{B}(\text{OH})_4]). \quad (8)$$

These constants ( $\mathbf{b}_{112}$  and  $\mathbf{b}_{214}$ ) along with the deprotonation constants,  $\mathbf{b}_{01-1}$  ( $K_{\text{H}_3\text{BO}_3}^{\text{H}}$ ),  $\mathbf{b}_{101}$  ( $K_1^{\text{H}}$ ),  $\mathbf{b}_{102}$  ( $K_1^{\text{H}} K_2^{\text{H}} = K_1^{2\text{H}}$ ) (table 2) may be directly obtained as computer output, from which the equilibrium constants of the reactions (4) and (5) as defined according to (4a) and (5a), may be calculated using the relations (4b) and (5b) respectively.

$$\log K_{(\text{II}+\text{H}_3\text{BO}_3)}^{2\text{H}} = \log b_{112} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - \log K_{\text{I}}^{\text{H}}, \quad (4\text{b})$$

$$\log K_{(2\text{II}+\text{H}_3\text{BO}_3)}^{3\text{H}} = \log b_{214} + \log K_{\text{H}_3\text{BO}_3}^{\text{H}} - 2\log K_{\text{I}}^{\text{H}}. \quad (5\text{b})$$

Since the *cis*-[(L<sup>x-</sup>)Cr<sup>III</sup>(H<sub>2</sub>O)<sub>2</sub>]<sup>(3-x)+</sup> complexes are substitution inert, in these reactions (4) and (5), the Cr<sup>III</sup>-OH or Cr<sup>III</sup>-OH<sub>2</sub> bonds remain intact, while coordination of the Cr<sup>III</sup> bound OH or OH<sub>2</sub> ligands to the electron-deficient B<sup>III</sup>-centre of H<sub>3</sub>BO<sub>3</sub> takes place with release of H<sub>3</sub>O<sup>+</sup>, as may be visualised according to the (4c) and (5c) respectively, omitting charges on the complexes (II, IV and V):



Formation and rupture of O-H bond being very fast, these equilibria, (4c) and (5c), are established quite rapidly.

#### 4. Conclusions

Like the *cis*-[(N<sub>4</sub>)Co<sup>III</sup>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> complexes (N<sub>4</sub> = (bipy)<sub>2</sub>, (tn)<sub>2</sub>, (trien)<sup>16</sup> the *cis*-[(L<sup>x-</sup>)Cr<sup>III</sup>(H<sub>2</sub>O)<sub>2</sub>]<sup>(3-x)+</sup> complexes (L = (bipy)<sub>2</sub>, (phen)<sub>2</sub>, nta<sup>3-</sup>, ada<sup>3-</sup>) are structurally similar to *cis*-1,2-diols and react with H<sub>3</sub>BO<sub>3</sub> in aqueous solution to form mixed ligand borate complexes, [(L)Cr(H<sub>2</sub>BO<sub>4</sub>)]<sup>x-</sup> and [(L)Cr(BO<sub>4</sub>)Cr(L)]<sup>(1-2x)+</sup> enhancing the acidity of the aqueous solution of otherwise weak H<sub>3</sub>BO<sub>3</sub>. Cr<sup>III</sup> being substitution inert, formation of such complexes occur through coordination of the Cr<sup>III</sup> bound OH or OH<sub>2</sub> ligands on the electron deficient B<sup>III</sup> centre of H<sub>3</sub>BO<sub>3</sub>, keeping the Cr<sup>III</sup>-OH or Cr<sup>III</sup>-OH<sub>2</sub> bonds intact, with concomitant release of protons in aqueous solution.

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