

# Potentiometric and Spectroscopic Studies with Chromium(III) Complexes of Hydroxysalicylic Acid Derivatives in Aqueous Solution

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The stoichiometries and stability constants of the chromium(III) complexes of hydroxysalicylic acid ligands (2,x-dihydroxy benzoic acids; 2,x-DHBA, x = 4-6)(H<sub>3</sub>L) were determined in aqueous solution by potentiometry and spectroscopy at 25 °C and at an ionic strength of 0.1 mol L<sup>-1</sup> (KNO<sub>3</sub>). The existence of Cr(HL)<sup>+</sup> type complex was verified. The stability constants of coordination species that exist in Cr(III):2,x-DHBA systems were defined. In the acidic medium the major coordination species involve salicylate type coordination. The formation of monohydroxo complexes was observed at higher pH values.

**Key Words:** Potentiometry, equilibria, chromium, stability constants, hydroxo complex.

## Introduction

Chromium is a first row transition element in the periodic table. It may resemble the group 16 elements of the oxygen group but only in the acidity of the trioxide and in its covalent nature. Cr(III) with its d<sup>3</sup> configuration forms thousands of inert complexes; an important characteristic of these complexes, in aqueous solutions, is their relative kinetic inertness. The radius of Cr(III) is 0.76 Å for coordination number 6 and it acts as a hard acid in aqueous solution. Its complex-formation equilibria are rather complicated, due to the strong affinity of Cr(III) ions to bind hydroxo groups. The hexaaqua ion [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> in aqueous solution is acidic (pK<sub>a</sub> = 4) and gives predominantly hydroxo ions Cr(OH)<sup>2+</sup>, Cr(OH)<sub>2</sub><sup>+</sup> and dimeric hydroxo bridged species by hydrolytic reactions; further polymerization proceeds stepwise via OH-bridges to give trimers [Cr<sub>3</sub>(μ-OH)<sub>4</sub>(OH)<sub>(n+1)</sub>]<sup>(4-n)+</sup> (n = 0, 1, 2), tetramers, hexamers, etc.<sup>1-2</sup>.

Phenolate oxygens have been shown to be very effective donors, especially for metal ions with a strong tendency to form hydroxo species in aqueous solutions<sup>3-4</sup>. Salicylic acid (SA) is the simplest representative of the phenolic ligands and it contains 2 potential binding sites; it also provides an anchoring carboxylate group. Thus it can act as a mono- or bidentate ligand; the prevalence of 1 of the 2 possibilities depends on

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the pH values of the solution and the charge/radius ratio of the metal ion<sup>5-7</sup>. The hydroxy derivatives of salicylic acid (2,x-DHBA) are important as ligands, due to the positions of hydroxide groups; they contain 3 potential binding sites, and for that reason they can exhibit mixed bonding modes  $\text{COO}^-$ ,  $\text{O}^-$ ;  $\text{O}^-$ ,  $\text{O}^-$  or tridentate  $\text{CO}_2^-$ ,  $\text{O}^-$ ,  $\text{O}^-$ . Depending on the arrangement of donor groups within the molecule, the simultaneous coordination of both binding sites is also possible. As a result, (2,x-DHBA) can form monomeric and dimeric species in aqueous solution<sup>8</sup>. It was noted that in their complexes the metal ion coordinates 1 or 2 ligands through the carboxylate and adjacent phenolate groups<sup>9</sup>.

The tendencies of salicylic acid derivatives towards some metal ions like Al(III), Sc(III), VO(IV), Y(III), Fe(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), La(III) and Th(IV), which form hydroxo species in aqueous solution, were determined by various groups<sup>5-13</sup>. The formation of  $\text{ML}$ ,  $\text{ML}_2$  and  $\text{ML}_3$  type complexes of Al(III) with SA ( $\text{H}_2\text{L}$ ) as a hydroxy aromatic ligand were investigated in detail<sup>12-13</sup>. Kiss et al. noted that in the interaction of oxovanadium (IV) with SA in aqueous solution salicylate type ( $\text{COO}^-$ ,  $\text{O}^-$ ) coordination occurs over a low pH range<sup>13</sup>. Özer et al.<sup>5</sup> determined the protonation constants of 2,x-DHBA ( $x = 4-5$ ). Sc(III) and Y(III) are typical first and second transition series metal ions and form  $\text{YHL}^{+2}$  and  $\text{Y(HL)}_2^+$  and  $\text{ScL}^+$  and  $\text{ScL}_2^{-3}$   $\text{Sc(HL)L}$  type complexes with 2,x-DHBA ( $x = 4-6$ )<sup>6-7</sup>.

The complex forming tendencies of Cr(III) with phenolic ligands, such as 5-sulfosalicylic acid, pyrocatechol violet and 1-(2-hydroxy-5-sulfophenolazo)-2-naphthol, have been analyzed previously<sup>3,10-14</sup>, but those of 2,x-DHBA ( $x = 4-6$ ) with Cr(III) have not been studied. While Cr(III) is a rather hard metal ion, its ionic potential is 0.25 V. It can coordinate hard carboxylate and phenolate ions. The binding ability of Cr(III) should decrease in the order of decreasing hardness of the ligands, since Martell et al.<sup>12</sup> have shown that the product of the protonation constants indicates the hardness of the bidentate hydroxoaliphatic and hydroxoaromatic ligands.

The first aim of this work was to investigate the Cr(III) complexes of 2,x-DHBA ( $x = 4-6$ ) in various mol ratios by comparing the protonation constants of ligands. The second aim was to evaluate the stoichiometries of the complexes formed and to determine their stability constants. The stability constants of the complexes were determined by previously explained potentiometric and spectrophotometric methods. and spectrophotometric methods.

## Experimental

### Materials

All the chemicals used in this research were of analytical reagent grade, since Gran's plot of the ligand requires high purity in potentiometric studies<sup>16</sup>. For the same reason, the ligands, 2,4-DHBA (Fluka, 99% purity), 2,5-DHBA (Aldrich, 99% purity) and 2,6-DHBA (Aldrich, 99% purity), were used as received. The stock solution of Cr(III) was prepared by dissolving appropriate amounts of  $\text{Cr(NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Merck) in a small excess of  $\text{HNO}_3$  (Merck, 100% purity,  $d = 1.52$ ) to avoid hydrolysis. The concentration of Cr(III) stock solution was checked by EDTA titration<sup>17</sup>. The concentration of free acid in the Cr(III) solution was systematically checked by potentiometric titrations before each series of experiments.

## Potentiometric measurements

The stability constants of complexes and the protonation constants of the ligands were determined by a previously described potentiometric method<sup>16,18</sup>. At least 3 different potentiometric titrations were carried out for each Cr(III):H<sub>3</sub>L system in a  $1.97 \times 10^{-3}$  -  $7.88 \times 10^{-3}$  mol L<sup>-1</sup> concentration range of Cr(III). In order to maintain the ionic strength at constant level, 0.1 mol L<sup>-1</sup> KNO<sub>3</sub> was added. The pH values were measured by a Schott - pH meter, equipped with a combination electrode. In all cases the temperature was kept constant at  $25.0 \pm 0.10$  °C by means of a B. Braun Thermomix UB Thermostat. When drifts in pH readings were observed, due to the hydrolytic reactions in lower than 2.0 ratios of ligands to Cr(III) ion, the titration curves could be treated quantitatively only to pH ~5.0; then at these pH values a foam was first formed, which was followed by the development of a fine precipitate.

## Spectroscopic measurements (UV-VIS)

The aqueous solutions of Cr(III), in the concentration range  $1 \times 10^{-2}$  -  $1 \times 10^{-3}$  mol L<sup>-1</sup>, were prepared from CrCl<sub>3</sub>.6H<sub>2</sub>O for spectrophotometric studies. The optical absorbance spectra of the samples were recorded on a Shimadzu UV-2100 spectrophotometer, with a 1 cm quartz cell, at appropriate pH values. The stoichiometries of these complexes were determined by taking the spectra of systems including Cr(III) ions and 2,x-DHBA ligands in definite mol ratios in the 300-400 nm range<sup>9</sup>. Thus, the results of the potentiometric studies were also validated by Job's method<sup>15</sup>.

## Calculations

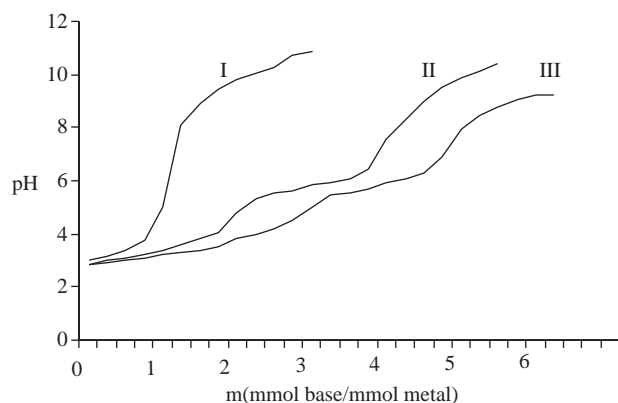
It is not possible to determine the concentration of the most basic form of (H<sub>3</sub>L) type ligands that were shown to be very hard donor groups in aqueous solution<sup>12</sup>. Due to large changes in liquid junction potentials, potentiometric pH measurements cannot be carried out accurately above pH 12. The protonation constant of the OH group ortho to the carboxylate group and of 2,6-DHBA could not be determined<sup>19</sup>. The first and second protonation constants of 2,x-DHBA type ligands were determined by several authors<sup>12-13</sup>. The protonation constants measured by Kiss et al.<sup>13</sup> were inserted into the necessary equations using the OSBEP computer program parts I and II. Then the stability constants of Cr(III):2,x-DHBA complexes that are in 1:1 and 1:2 stoichiometries of Cr(III) to ligands were calculated by OSBEP (Table). For each system, the best complex that accounts for the experimental data was accepted. Non-linear least-squares analysis of the data in terms of assumed reactions gave a satisfactory fit in the buffer regions of the complex systems, in different mol ratios.

The values of  $\bar{n}$  (the average number of ligand(s) bound per mol of Cr(III) ion and logL (L= free concentration of anionic form of the ligand) were computed by the third part of OSBEP for the 6 different systems of Cr(III) analyzed. They are tabulated in the Table as log $\beta$  values that are the mean  $\pm$  standard deviations for 6 data sets.

## Results and Discussion

### Cr(III):2,4-DHBA system

In the potentiometric titrations of 1:1 Cr(III):2,x-DHBA ( $x = 4-6$ ) systems, the inflection points were observed at  $m = 2.0$  and  $m = 3.0$  ( $m = \text{mmol base}/\text{mmol metal}$ ). The drifts were seen after  $m = 2.0$  in pH readings due to hydrolytic reactions. Only one of the titration curves of 2,4-DHBA systems is given for one concentration in Figure 1, since they are superimposable for each mol ratio. The formation of  $\text{Cr(HL)}^+$  type coordination ion in the  $m = 0.0-2.0$  range by equilibrium (4) and its hydrolytic reaction by equilibrium (5) in the  $m = 2.0-3.0$  range were assumed. When the potentiometric titration data of Cr(III):2,x-DHBA system were evaluated, the assumption of salicylate type monomeric complex  $\text{Cr(HL)}^+$  was valid in the acidic region; its stability constant was determined in the pH 2.9-4.1 range ( $m = 0.0-2.0$ ) (Table). Thus, the OH group in position  $x = 4$  is protonated and the less acidic phenolic OH of the salicylic function is deprotonated and coordinated to Cr(III) in  $\text{Cr(HL)}^+$  type coordination ions. Therefore, the coordination of 2,x-DHBA ligand thorough  $\text{COO}^-$  and  $\text{O}^-$  of salicylic acid to Cr(III) can be concluded. The deprotonation of the uncoordinated hydroxyl at position  $x = 4$  would take place only at higher pH, since the protonation constant of the OH group in position  $x = 4$  is 4.4 log unit smaller than that of the  $\text{Cr(HL)}^+$  complex formed (c f. rows 2 and 6 in the Table). The  $\text{Cr(HL)}^+$  complex loses a proton from the coordinated water molecule at pH  $\sim 5.00$  when the mol ratios smaller than 2.0; as a result  $\text{Cr(HL)(OH)}$  complex precipitates. When the mol ratio of Cr(III) to 2,4-DHBA is 1:2, the inflections of the potentiometric titration curves are at  $m = 3.0$  and  $m \cong 4.0$ ; the drops were also observed after  $m = 3.0$  due to the precipitation of hydrolytic products. Earlier solid state studies have shown that at low pH levels, the carboxylic group could be the main donor in 2,x-DHBA complexes<sup>9</sup>. The occurrences of equilibria (6) and (7) were assumed in which the coordination of the first ligand is from salicylate sites but the coordination of the second ligand is only from one salicylate site. The hydroxide ions can displace the coordinated salicylate sites again in  $\text{Cr(HL)(H}_2\text{L)}$  type complex and through the mixed hydroxo complex formation occurred. The existence of this type of hydroxo complexes was also observed for the Al(III):2,x-DHBA system<sup>13</sup>. Then the stability constants of  $\text{Cr(HL)(H}_2\text{L)}$  and  $\text{Cr(HL)(H}_2\text{L)(OH)}^-$  complexes were found (Table) for a 1:2 mol ratio.



**Figure 1.** Potentiometric titrations of Cr(III):2,4-DHBA system in  $0.1 \text{ mol L}^{-1} \text{ KNO}_3$  at  $25^\circ \text{C}$  with different molar ratios of 2,4-DHBA to Cr(III) ion.

I: Ligand alone; II: Cr(III):2,4-DHBA system in 1:1 mol ratio; III: Cr(III):2,4-DHBA system in 1:2 mol ratio

**Cr(III):2,5-DHBA system**

In the potentiometric titrations of the Cr(III):2,5-DHBA system for a 1:1 mol ratio, inflections were found at  $m = 2.0$  and around  $m = 3.9$ . The drifts in pH readings were around  $m = 2.0$ . The occurrence of reactions similar to the Cr(III):2,4-DHBA system were considered for the Cr(III):2,5-DHBA system. The stability constants of  $\text{Cr(HL)}^+$  and  $\text{Cr(HL)(OH)}$  complexes were determined (Table). The formation of  $\text{Cr(HL)(H}_2\text{L)}$  type complex was also concluded from the results of the Cr(III):2,5-DHBA system in a 1:2 mol ratio; its potentiometric titration curve has inflections at  $m = 3.0$  and  $m = 4.0$ . The formation of hydroxo complex was considered in a 1:2 mol ratio, and its existence was verified (Table).

**Cr(III):2,6-DHBA system**

The inflection points were at  $m = 2.0$  and  $m = 3.6$  for the 1:1 Cr(III):2,6-DHBA system; the drifts in lower pH readings were at around  $m = 2.0$ . The  $\text{Cr(HL)}^+$  type complex was assumed to be formed followed by its hydrolysis. Then the stability constants of  $\text{Cr(HL)}^+$  and  $\text{Cr(HL)(OH)}$  complexes were calculated. In the case of a 1:2 mol ratio of the Cr(III):2,6-DHBA system, the inflections were at  $m = 3.0$  and  $m = 4.4$ . The existence of  $\text{Cr(HL)(H}_2\text{L)}$  and  $\text{Cr(HL)(H}_2\text{L)(OH)}^-$  type complexes was verified by calculation (Table).

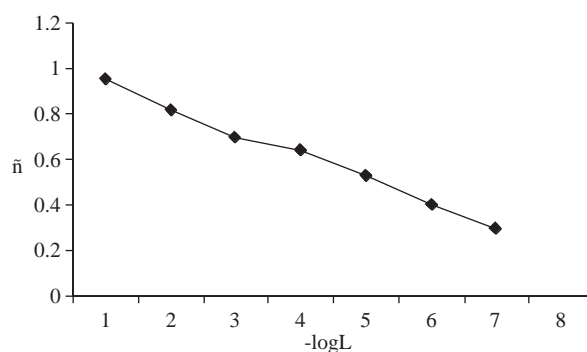
**Table.** Protonation constants ( $\log K$ ), Cr(III) complex formation constants ( $\log \beta$ ) for 2,x-DHBA ( $x = 4-6$ ) at  $25 \pm 0.0$  °C and  $I = 0.1$  M  $\text{KNO}_3$

Row	Equilibrium	2,4-DHBA ( $x = 4$ )	2,5-DHBA ( $x = 5$ )	2,6-DHBA ( $x = 6$ )
1	Proton complexes ( $\log K$ )			
2	$2\text{-OH (L}^{-3} + \text{H}^+ \rightleftharpoons \text{HL}^{-2})$	$> 14^{13}$	$> 14^{13}$	$> 14^{13}$
3	$x\text{-OH (HL}^{-2} + \text{H}^+ \rightleftharpoons \text{H}_2\text{L}^-)$	$8.64^{13}, (8.49 \pm 0.01)^a$	$10.06^{13}, (9.94 \pm 0.02)^a$	$13.1^{13}$
3	$\text{COOH (H}_2\text{L}^- + \text{H}^+ \rightleftharpoons \text{H}_3\text{L)}$	$3.09^{13}, (3.03 \pm 0.01)^a$	$2.75^{13}, (2.94 \pm 0.02)^a$	$1.0^{13}, (1.24 \pm 0.02)^a$
	Cr(III) complexes ( $\log \beta$ )			
4	$\text{Cr}^{+3} + \text{HL}^{-2} \rightleftharpoons \text{Cr(HL)}^+$	$13.07 \pm 0.04$	$11.51 \pm 0.06$	$9.32 \pm 0.06$
5	$\text{Cr(HL)}^+ + \text{OH}^- \rightleftharpoons \text{Cr(HL)(OH)}$	$5.58 \pm 0.03$	$5.59 \pm 0.05$	$5.52 \pm 0.07$
6	$\text{Cr}^{+3} + \text{HL}^{-2} + \text{H}_2\text{L}^- \rightleftharpoons \text{Cr(HL)(H}_2\text{L)}$	$14.91 \pm 0.07$	$14.47 \pm 0.07$	$13.31 \pm 0.07$
7	$\text{Cr(HL)(H}_2\text{L)} + \text{OH}^- \rightleftharpoons \text{Cr(HL)(H}_2\text{L)(OH)}^-$	$5.63 \pm 0.07$	$5.69 \pm 0.07$	$5.77 \pm 0.08$

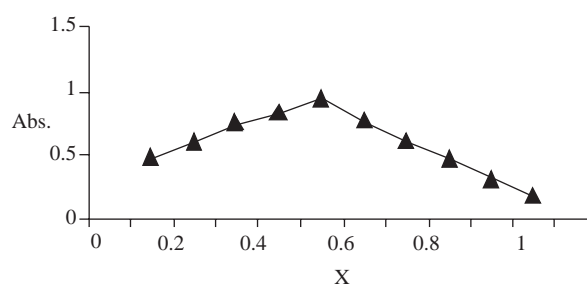
a: This study

**The Formation Curves**

The average number of ligands attached to Cr(III) ions ( $\bar{n}$ ) was found with the help of OSBEP as a function of ( $\bar{n}$ ) values versus  $\log L$  ( $L$  is the free concentration of ligand)<sup>18</sup>. The degree of formation, ( $\bar{n}$ ) values, was evaluated for Cr(III):2,4-DHBA, Cr(III):2,5-DHBA and Cr(III):2,6-DHBA complexes present in 1:1 mol ratios. Then the formation curves were drawn; all of them are similar in appearance up to  $\bar{n} = 1$ . This indicates that only 1 mol of Cr(III) is bound to 1 mol of ligand (only one formation curve is given in Figure 2).



**Figure 2.** Degree of formation,  $\tilde{n}$ , as a function of  $-\log L$  in Cr(III):2,4-DHBA complex.



**Figure 3.** Job's plot for Cr(III):2,4-DHBA system in pH 4.0 at  $\lambda = 320$  nm.

## Spectroscopic investigation

In order to validate the existence of a  $\text{Cr}(\text{HL})^+$  type complex, the stoichiometries of the formed complexes were investigated by a spectrophotometric method. First, the working wavelengths for each ligand were determined. Then Job's method was applied for the Cr(III):2,4-DHBA system at  $\lambda = 320$  nm and pH 4.0, to the Cr(III):2,5-DHBA system at  $\lambda = 360$  nm and pH 4.0 and to the Cr(III):2,6-DHBA system at  $\lambda = 340$  nm and pH 4.0. The coordination of the phenolate oxygen was observed due to the charge transition between this donor and the Cr(III) ion. The spectroscopic data fit very good agreement with the potentiometric results, and Job's plots reflected the formation of  $\text{Cr}(\text{HL})^+$  type complex.

## Conclusion

Cr(III) ions coordinate 2,x-DHBA ligands through the carboxylate ( $\text{COO}^-$ ) and the phenolate oxygen ( $\text{O}^-$ ) being in the ortho position to the carboxylate in acidic medium. The OH groups in  $x = 4, 5$  or  $6$  positions do not take part in the binding to Cr(III). The stabilities of  $\text{Cr}(\text{HL})^+$  type complexes that have a salicylate binding mode depend on the position of x-OH groups. They decrease in the  $x = 4, 5$  and  $6$  order; the strongest complex is formed by 2,4-DHBA. The existence of  $\text{Cr}(\text{HL})^+$  type complex was verified by Job's plot and by formation curves. A further increase in pH leads to the formation of the hydroxo complexes of complex species. In the presence of excess ligand,  $\text{Cr}(\text{HL})(\text{H}_2\text{L})$  type complex is formed. A detailed study is in progress to evaluate the stability of these complexes.

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