

Scientific paper

# Spectroscopic and Potentiometric Study of 2,3-Dihydroxybenzoic Acid and its Complexation with La(III) Ion

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Received: 13-07-2006

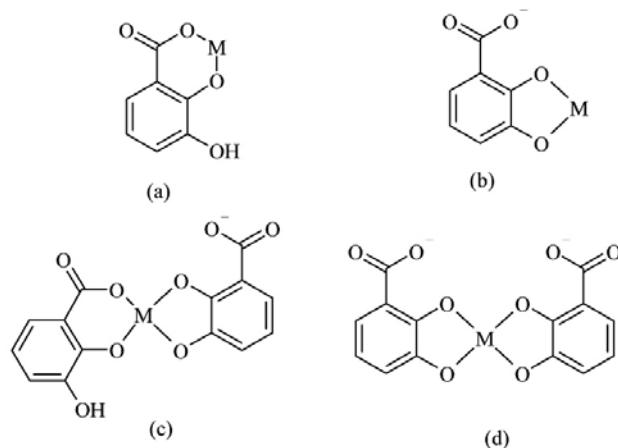
## Abstract

The equilibrium reactions between 2,3-dihydroxybenzoic acid (2,3-DHBA) and Lanthanum(III) ion was investigated in an aqueous medium of 0.1M ionic strength and  $25 \pm 1$  °C by potentiometric and spectrophotometric methods. Formation of complexes of the types ML and  $ML_2H$  were observed and their stability constants were reported. The ligand showed competitive coordination mode in solution: in acidic medium, 2,3-DHBA showed preference to salicylate type whereas catecholate type in basic media.

**Keywords:** Dihydroxybenzoic acid, lanthanum and stability constants.

## 1. Introduction

The aqueous coordination chemistry of lanthanide(III) ions is dominated by their oxophilicity, with most ligands studied containing carboxylato- or phosphonato-oxygen donors.<sup>1</sup> There is little known about the affinity of lanthanide(III) ions towards phenolate and catecholate group as anionic oxygen donor for these metal ions.<sup>2-3</sup> Main reason why the coordination of lone phenol is hindered due to the weak acidity of the hydroxy group ( $pK_a$  of phenol  $\sim 10$ )<sup>2</sup> and since the lanthanide aqueous ions are themselves weak Lewis acids, they generally cannot compete with the hydrogen ion for complexation of phenol in water and precipitate as hydroxides above pH 8. However, coordination of phenol in salicylate type complexes were well characterized with lanthanide(III) ions in aqueous medium, which can be ascribed to the initial condition of the anionic carboxylate oxygen which serves to anchor the ligand while the phenolate moiety coordinates secondarily.<sup>4</sup> But, the solution and synthetic chemistry of the lanthanide catecholates indicate that formation of only 1:1 lanthanide:catecholate complex below pH 7 and at around pH 7, hydrolysis of this complex occurs and an insoluble complex of the stoichiometry  $[Ln(cat)(OH)]4H_2O$  (cat = catecholate) is predominant species, regardless of the amount of excess ligand present.<sup>5-6</sup>



**Figure 1.** (a) Salicylate, (b) catecholate and other possible coordination modes of 2,3-DHBA.

2,3-dihydroxybenzoic acid (2,3-DHBA) is a very interesting ligand because of its potential to form two different kind of complexes, salicylate and catecholate type (Figure 1). The complexation of this ligand has been studied extensively with many transition as well as non-transition elements and formation of both salicylate and catecholate type complexes were depicted.<sup>7-10</sup> Kiss *et al.*, reported that 2,3-DHBA with oxo-vanadium(IV) ion, the

stepwise deprotonation of the salicylic acid takes place in lower pH and than rearrangement occurs from the salicylate type to catechol type coordination at higher pH.<sup>10</sup> Also, the complexes formed by 2,3-DHBA were stable enough to resist its strong hydrolytic tendencies (and consequent precipitation).<sup>9–10</sup>

Keeping in view of the above diversified coordination properties of 2,3-DHBA and lanthanide ions, the complexation reactions between La(III) ion and 2,3-DHBA was investigated by potentiometric and spectrophotometric methods. The equilibrium constants of the various metal complexes were reported.

## 2. Experimental

### 2.1. Materials and Titration Procedure

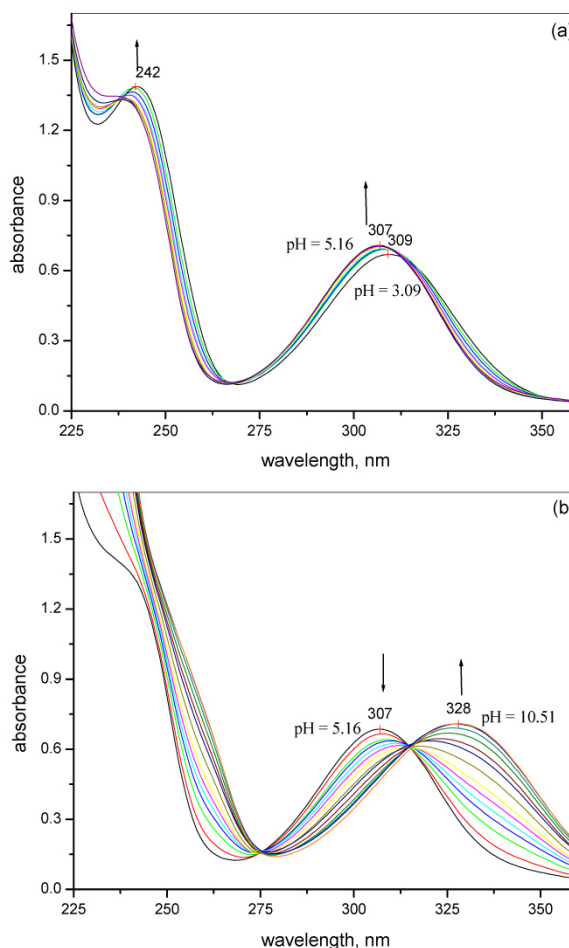
The compound 2,3-DHBA were obtained from Sigma-Aldrich and used directly. Nitrate salt of lanthanum was obtained from Indian Rare Earths Ltd., India. All other chemicals: potassium hydroxide, hydrochloric acid and potassium chloride were obtained from Merck. All solutions were prepared prior to the experiments in double distilled deoxygenated water. KOH solution of 0.1 M was prepared and standardized against potassium hydrogen phthalate. HCl solution (0.1 M) was prepared and standardized against standard KOH. The ionic strength was maintained at 0.1 M by adding appropriate amount of 1 M KCl. Stock solutions of 0.01 M ligand and 0.01 M metal ions were also prepared in deoxygenated water.

The protonation constants of the ligand and the stability constants of the metal complexes were determined by potentiometric and spectrophotometric titrations at  $25 \pm 1$  °C maintained from a double wall glass jacketed titration cell connected to a constant temperature circulatory bath. For all titrations, the observed pH was measured as  $-\log [H^+]$  using a ThermoOrion 720A<sup>+</sup> pH meter equipped with a combined glass electrode. The electrode was calibrated to read pH according to the classical method.<sup>11</sup> A standard hydrochloric acid solution was titrated with a standard KOH solution and the calculated hydrogen ion concentrations ( $pK_w = 13.77 \pm 0.05$ ) was used to convert the pH-meter reading to hydrogen ion concentration. Final concentration of ligand ( $1-2 \times 10^{-3}$  M) and metal ( $1 \times 10^{-3}$  M) were maintained for the different titrations. Following titrations with metal-to-ligand molar ratios:  $C_M/C_L = 0:1$ ;  $C_M/C_L = 1:1$ ,  $1:2$  ( $M = La^{+3}$ ) were carried out. The protonation constants of the ligand and the formation constants of the metal complexes were determined using computer program Hyperquad 2000.<sup>12</sup> The apparatus and method used for the potentiometric and spectrophotometric titrations are very similar except dilute solutions of ligand ( $2.252 \times 10^{-4}$  M) and metal ions ( $1.12-2.252 \times 10^{-4}$  M) were used. After each adjustment of pH, an aliquot was removed and spectra were recorded.

## 3. Results and Discussion

### 3.1. Ligand Protonation Constants

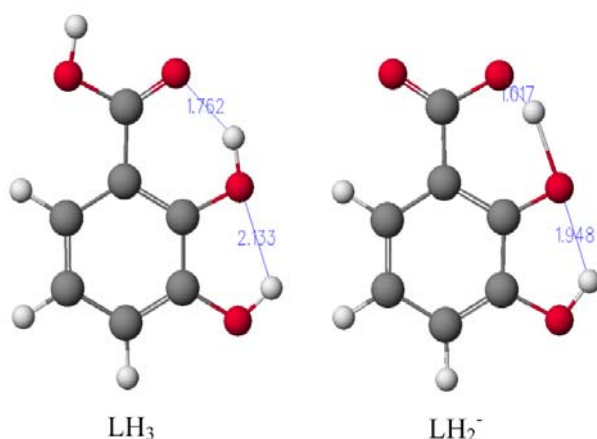
The protonation constants of 2,3-DHBA (L) have been determined earlier<sup>13</sup> and it was repeated again by means of potentiometric and spectrophotometric methods and the results (Table 1) are in well agreement with the values reported by Kiss and his coworkers.<sup>14</sup> The recorded electronic spectra of the ligand at different pH (pH 3.09–10.51) were shown in Figure 2a-b. The whole spectra were presented in two set according to the nature of shifting. In the first set (Figure 2a), the ligand peak at 309 nm (pH = 3.09) shifted hypsochromically to 307 nm whereas with increase in pH from 5.16, the peaks at 307 nm start to shifted bathochromically. The first blue shift happened due to conversion of COOH group into COO<sup>-</sup> ion whereas the red shift assigned for the deprotonation of hydroxyl group. The equilibrium reaction between the protonated and deprotonated species can also be assignable from the isosbestic point. The calculation provided only



**Figure 2.** Experimental electronic spectra of 2,3-DHBA as a function of pH ((a) pH = 3.09–5.16 and (b) pH = 5.16–10.51) during a spectrophotometric titration:  $[2,3\text{-DHBA}] = 1.25 \times 10^{-4}$  M;  $[\text{KCl}] = 0.1$  M and  $T = 25 \pm 1$  °C.

two protonation constants for the carboxylic and hydroxyl groups at 3-position. The dissociation of OH group *ortho* to the carboxylate is not possible due to the strong intramolecular hydrogen bond between carboxylate and phenol (OH) group within the experimental condition adopted here.

Molecular modeling calculation was carried out to obtain the optimized geometries of 2,3-DHBA using DFT with the gradient corrected B3LYP functional and the 6-31+G(d) basis set (Figure 3). The calculated intramolecular H-bond length (OH...O) 1.762 Å in 2,3-DHBA (LH<sub>3</sub>) is much stronger 1.017 Å upon formation of species LH<sub>2</sub><sup>-</sup>. Simultaneously there is a decrease in partial atomic charges of the hydrogen atom (OH...O) from 0.565 to 0.552. This change also indicates that there is an increase in basicity of the hydroxy group because in general it is expected that those substance with the most positive partial charge on the hydrogen will be the most acidic. These results corroborate well with the assignment made here for the release of proton from the hydroxyl group at 2-position.

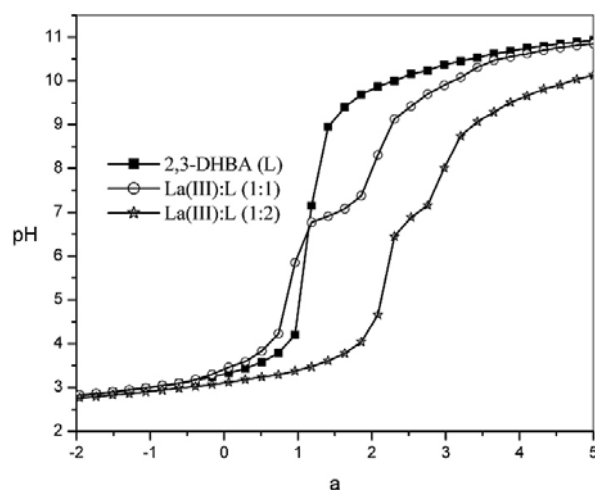
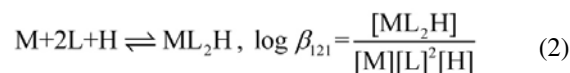
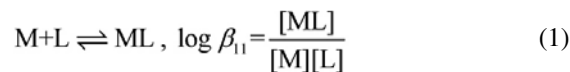


**Figure 3.** Optimized geometry of 2,3-DHBA (LH<sub>3</sub>) and its deprotonated species LH<sub>2</sub><sup>-</sup>.

### 3. 2. Metal complexes

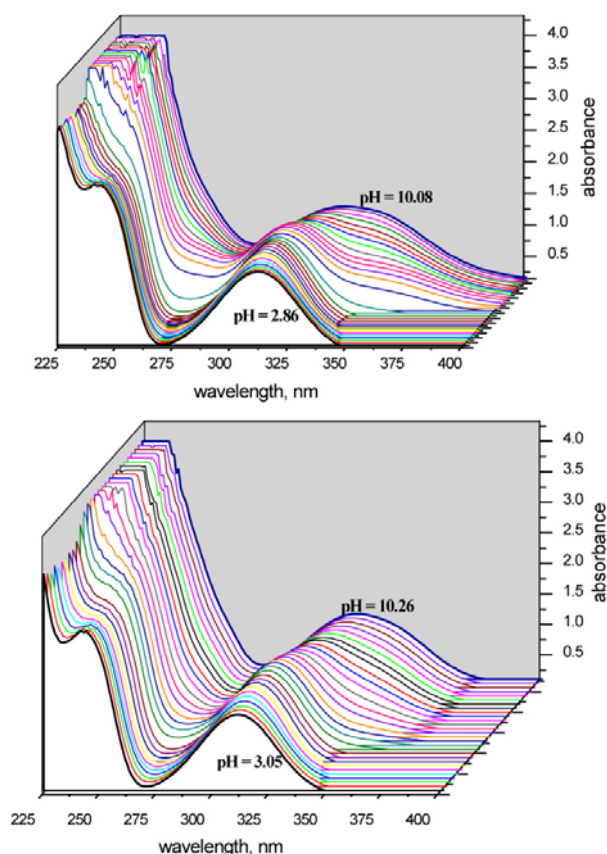
Potentiometric titrations of 2,3-DHBA (L) with La(III) ion were carried out in 1:1 and 1:2 metal-ligand molar ratios at  $\mu = 0.1$  M KCl and  $25 \pm 1$  °C in aqueous medium. The potentiometric titration curves for the 1:1 and 1:2 metal-ligand molar ratio alongwith the free ligand curve are given in Figure 4. The deviation in the metal-ligand titration curves from the free ligand titration curve implies the formation of metal complexes. Keeping in view different possible models were tested in the minimization program and the best-fit model was obtained when formation of species of the types ML and ML<sub>2</sub>H were considered. Formations of any hydroxo species were not considered during minimization. These species are formed in general

due to the release of proton from the coordinated water molecules. The overall formation constants ( $\log \beta$ ) of the species were calculated using Hyperquad 2000 program are summarized in Table 1. The equilibrium reactions for the overall formations of the complexes are given below by the following equations (charges are omitted for clarity):



**Figure 4.** Potentiometric titration curves of 2,3-DHBA in absence and presence of metal ions La(III) in 1:1 and 1:2 ligand-metal molar ratio, where 'a' is moles of base added per mole of ligand present.

The interaction of La(III) ions with 2,3-DHBA (L) was also studied by spectrophotometric method to explain the different possible coordination modes of the species in solution. Spectrometric titrations of 2,3-DHBA was carried out in 1:1 and 1:2 metal-to-ligand ratios with the ligand concentration  $[L] = 2.25 \times 10^{-4}$  M and the metal ion concentrations  $[M(III)] = 2.25 \times 10^{-4}$  M (M:L::1:1) and  $1.12 \times 10^{-4}$  M (M:L::1:2) with increasing pH. The experimental electronic spectra of 2,3-DHBA-La(III) systems are given in Figure 5. Since there is no ligand field interaction with the  $f^{(0)}$  La(III) ion, the peak was assigned for the intra-ligand transition. The shifting of peak as well as variation in the position of the peak in comparison with the free ligand peak indicates the formation of metal complexes. At low pH, the maximum absorbance in 1:1 and 1:2 metal-ligand systems obtained at 311 and 310 nm respectively where free ligand absorbed at 309 nm. Whereas at high pH, the ligand peak (328 nm)



**Figure 5.** Experimental electronic spectra of 1:1 and 1:2 metal-to-ligand ratios with successive increase in pH; (a) pH: 2.86–10.08 and (b) pH: 3.05–10.26.

shifted to 323 and 320 nm in 1:1 and 1:2 metal-to-ligand ratio. The spectral changes also indicate that different complexes were formed in different metal-to-ligand molar ratios.

Stoichiometrically three protons are released from 2,3-DHBA to give the species  $ML_2H$  among which only two protonation constants were calculated within the experimental condition. From the 1:1 metal-ligand titration curve (Figure 3), when the first proton dissociated between a = 0–1 from most acidic carboxyl group, the curve superimposable with the neutralisation curve of 2,3-DHBA alone implies the carboxylate ion not coordinate strongly with the metal ion rather than it promote the coordination or provide an anchoring effect for coordination of hydroxyl group at 2-position whose protonation constant was not known. As pH increases subsequently two more protons are release from catecholic part to give a stable complex  $ML$ . This strongly suggests competitive salicylate type ( $COO^-$ ,  $O^-$ ) coordination in acidic pH range, and then catecholate type ( $O^-$ ,  $O^-$ ) coordination in higher pH range. Similar coordination was suggested earlier for aluminium (III) and oxovanadium (IV) towards 2,3-DHBA.<sup>15</sup> Moreover, Since the five membered chelate rings is more stable than six membe-

red chelate rings for the lanthanide metal ions<sup>16</sup> and the catecholate mode is more preferable. Also, the bathochromic spectral shifting of ligand peak with successive rise in pH assignable to the coordination of chromophoric catecholic oxygens (Figure 5), which results stabilization of the  $\pi^*$  excited state due to charge delocalization and brings the lowest excited state closer to the highest ground state and thus permits a lower energy (longer wavelength) for transition.

**Table 1.** Protonation and stability constants of 2,3-Dihydroxybenzoic acid and La(III) complexes at 0.1 M ionic strength and 25±1 °C.

Equilibrium	log K
$OH (L^{3-} + H^+ \rightleftharpoons HL^{2-})$	
OH at 2-position in 2,3-DHBA	>14 <sup>a</sup>
$OH (HL^{2-} + H^+ \rightleftharpoons H_2L^-)$	9.81 <sup>a</sup>
OH at 2-position in 2,3-DHBA	9.91 <sup>b</sup>
	9.89 ± 0.05
$COOH (H_2L^- + H^+ \rightleftharpoons H_3L)$	3.32 <sup>a</sup>
	2.74 <sup>b</sup>
	3.30 ± 0.05
<b>La(III) complexes</b>	<b>log β</b>
$La^{3+} + L^{3-} \rightleftharpoons LaL$	10.54 ± 0.07
$La^{3+} + L^{3-} + HL^{2-} \rightleftharpoons LaL(HL)^{2-}$	13.57 ± 0.05

<sup>a</sup>Ref. 14; <sup>b</sup>Ref. 13.

Another species  $ML_2H$  was observed from the 1:2 metal-to-ligand ratio, where five protons are released from the two moles of ligand on interaction with one mole of metal ion. This species can be assignable to the formation of complex where both salicylate and catecholate mode are presented (as shown in Figure 1c). At low pH, the two moles of ligand coordinate from salicylate sides assigned from the blue shift of ligand peak (Figure 5) whereas as pH increases rearrangement of complex take place from salicylic acid type to catechol type; while the second moles of 2,3-DHBA remain in the salicylate mode.

## 4. Conclusions

La(III) ion shows competitive coordination mode with 2,3-DHBA where the carboxylate group provide anchoring effect for the coordination of hydroxyl group at 2-position. Formation of species of types  $LaL$  and  $LaL(HL)^{2-}$  were observed. The salicylate mode is effective over the acidic pH range, while catecholate mode acts more efficiently in higher pH range. In all conditions, 2,3-DHBA act as a bidentate ligand. In higher ligand to metal molar ratios (1:2), the coordination may occur through mixed salicylate and catecholate bonding mode.

## 5. References

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## Povzetek

Ravnotežno reakcijo med 2,3-dihidroksibenzojsko kislino (2,3-DHBA) in lantanovim (III) ionom v vodni raztopini smo študirali s potenciometrijo in spektrofotometrijo. V raztopini smo opazili tvorbo kompleksov ML and  $ML_2H$ , katerim smo tudi določili konstante stabilnosti. Ligand 2,3-DHBA se v raztopini koordinira na dva različna načina, v kislem prevladuje salicilatni ligand in v bazičnem mediju kateholatni.