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PREPARATION, COORDINATION AND STRUCTURE OF MIXED LIGAND COBALT (II) COMPLEXES OF HISTIDINE AND HIPPURIC ACID

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Abstract. Mixed ligand cobalt(II) complexes, $Na_2[Co(C_6H_5CONHCH_2COO)(C_6H_8N_3O_2).H_2O].9H_2O$ and $Na_2[Co(C_6H_5CONHCH_2COO)(C_6H_8N_3O_2).H_2O].\ 5H_2O$ formed with histidine and hippuric acid have been synthesized. The mode of coordination and their structure have been determined by elemental analysis, spectral (Infra red and electronic spectra) studies and magneto-chemical measurements. Histidine shows a tridentate behaviour with coordinating through the carboxylate oxygen atom and the two nitrogen atoms of the imidazole and $–NH_2$group. Hippuric acid acts as a bidentate ligand and the coordination occurs through the carboxylate oxygen and the nitrogen of the amido group. The remaining sixth coordination position is satisfied by a water molecule and hence the complexes have been suggested to show an octahedral structure.

Keywords: Co(II) complexes, histidine, hippuric acid, preparation, structure

Introduction

Mixed ligand complexes are well known to play a significant role in biological systems [1]. Synthesis, structural studies and some other properties of mixed ligand transition metal complexes formed with histidine and adenine or guanine [2] and other amino acids have been reported [3-6]. The determination of acid

dissociation constant and binding formation constant of nickel(II) and cobalt(II) complexes of histidine and phosphonoformic acid [7] and the potentiometric studies, synthesis and characterization of mixed complexes of Cu(II), Ni(II) and Mn(II) formed with histidine and N-(2-acetamidoiminodiacetic)acid have also been studied [8]. In earlier publications, the synthesis and characterization of some bivalent simple and mixed ligand transition metal complexes of hippuric acid and nitrilotriacetic acid and iminodiacetic acid have been reported [9-11]. Literature survey shows that no studies on the synthesis and characterization of mixed ligand complexes of histidine and hippuric acid have been reported. Hence the present paper reports the preparation, coordination and structure of new mixed ligand cobalt(II) complexes formed with histidine and hippuric acid.

Experimental

Solutions of histidine (Fluka) and hippuric acid (Fluka) were prepared by dissolving them in one equivalent of sodium hydroxide. The solution of cobalt(II) chloride (Fluka) was prepared in one equivalent of hydrochloric acid. To prepare the metal complex, the two ligands were mixed with 0.1M metal ion solution in 1:1:1 molar ration at room temperature. At first histidine solution was mixed with metal ion solution followed by the hippuric acid solution and the pH of the resulting mixture was adjusted to ~ 5.43 by adding sodium hydroxide solution. On the addition of histidine to the metal ion solution followed by the hippuric acid solution, a clear pink solution was obtained with the pH ~ 3.6. The pH of this resulting solution was adjusted to ~ 5.43 by the addition of sodium hydroxide. The clear pink solution was then concentrated over a steam bath and allowed to crystallize. The product was then filtered and washed with 50% ethanol-water mixture followed by acetone and dried in a vacuum desicator. On heating the pink crystalline product in an air oven at 100-110^{0}C for about two hours, the colour of the complex changes to deep violet, indicating the lose of the water molecule from the complex.

The infra-red spectra of the ligands and the metal complexes were recorded on a Perkin-Elmer FT-IR 2000 spectrophotometer in 4000 — 400 cm^{-1} range in KBr disc. Shimiadzu UV-vis 2501 PC spectrophotometer model TCC-240A was used to record the electronic spectra of the complexes in methanol in 190-1100 nm range. The magnetic susceptibility of the complexes was measured at room temperature using Johnson Matthew Alfa Product magnetic susceptibility balance. The VarioEL CHNO/S elemental analyzer was used to determine the elemental (CHN) analysis. The content of the metal present in the complexes was determined using Atomic Absorption Spectrophotometer 220FS.

Results and Discussion

Elemental Analysis:

Analytical data are as follows:

1. Disodium(hippurato)(histidino)(monoaqua)cobalt(II)nonahydrate. Pink crystalline. Anal.

Calcd for $Na_2[Co(C_6H_5CONHCH_2COO)(C_6H_8N_3O_2).H_2O].9H_2O$: Co = 9.54%, C = 29.17%,

H = 5.88%, N = 9.06%; Found: Co = 9.22%, C = 29.34%, H = 5.69%, N = 9.10%.

2. Disodium(hippurato)(histidino)(monoaqua)cobalt(II)pentahydrate. Deep violet crystalline. Anal. Calcd for $Na_2[Co(C_6H_5CONHCH_2COO)(C_6H_8N_3O_2).H_2O].5H_2O$: Co = 10.80%, C = 33.03%, H = 5.19%, N = 10.27%; Found: Co= 10.92%, C = 33.23%, H = 5.34%, N = 10.21%.

NOTE: In further discussion in the text for convenience the two complexes are referred to as decahydrate and hexahydrate respectively.

IR Studies

In amino acid νNH_3^+ appears in 3130-3030 cm^{-1} region [12]. In the ir spectrum of histidine it appears at ~ 3082 cm^{-1} but overlaps with other vibrations such as νNH (imidazole group), and νCH (heterocyclic + νCH_2 group ~ 3016 cm^{-1}). Theoretically νNH_3^+ should vanish on coordination. In metal complexes, however, some broad band appears at ~ 3300 cm^{-1}, which must be arising from other vibrations appearing in this region. In histidine δNH_3^+ appears at 1560 cm^{-1} which vanishes in the metal complexes. The $\nu_{as}COO^-$ and ν_sCOO^- absorptions appear in histidine at 1633 and 1418 cm^{-1} respectively [13]. In imidazole [14], the νNH absorption appears at 3125 cm^{-1}. In histidine, it gets mixed with other absorptions in this region and a broad band at 3082-2866 cm^{-1} is visible. In case of the complexes it is absent since no band is observed in this region. Hippuric acid shows characteristic ν(C = 0) absorption bands for the COOH group at 1750 cm^{-1} which vanishes in case of cobalt(II) complexes. Instead, asymmetric and symmetric COO^- stretching frequencies are obtained. The decahydrate complex shows $\nu_{as}COO^-$ and ν_sCOO^- frequencies at 1634 and 1428 cm^{-1} respectively whereas in hexahydrate complex these frequencies are observed at 1607 and 1413 cm^{-1} respectively. The ν(NH) absorptions in hippuric acid are observed at 3343 cm^{-1} which in the complexes is mixed with ν(OH) and is observed at 3333 cm^{-1}. Hippuric acid shows amide I ν(C = 0) band at 1608 cm^{-1}, amide II [δ(NH) + ν(CN)] with benzene ring vibrations in the range 1559 — 1412 cm^{-1} range, amide III [ν(CN) + δ(NH)] band at 1310 cm^{-1}. In decahydrate and hexahydrate complexes, amide I band together with $\nu_{as}COO^-$ is obtained at 1634 and 1607 cm^{-1} respectively. Amide II band along with benzene ring and ν_sCOO^- vibrations

are obtained at 1428 and 1413 cm^{-1} in decahydrate and hexahydrate complexes respectively. In decahydrate complex amide III band is observed at 1318 cm^{-1} whereas in hexahydrate complex it is obtained at 1297 cm^{-1}. Besides, both the complexes show additional band at ~ 3333 cm^{-1} attributable to water molecules [13]. The appearance of rocking ρ_r (HOH) frequency [15] at 716 and 706 cm^{-1} in case of decahydrate and hexahydrate complexes respectively shows that the water molecules are also coordinated. The ir frequencies of the ligands and the metal complexes are listed in Table 1. Thus the ir studies suggest that in cobalt(II) complexes, histidine coordinates through the carboxylate oxygen atom and two nitrogen atoms of imidazole and $—NH_2$ group, hence acts as a tridentate ligand. Hippuric acid shows bidentate behaviour and the coordination occurs through the carboxylate oxygen atom and the nitrogen of the amido group.

Table 1. IR Frequencies (cm^{-1}) of Histidine, Hippuric Acid and Their Mixed Cobalt(II) Complexes

Histidine	Band Assignment	Hippuric Acid	Band Assignment	Na_2[{Co(II)-His –HA }. H_2O] . $9H_2O$]	Na_2[{Co(II) - His- HA}. H_2O] . $5H_2O$	Band Assignment
3082-2866	ν(NH)(imidazole) + ν CH (Heterocyclic) +ν NH_3^+ + ν CH(-CH_2)	1750	ν (C=O) Carboxylic group	3333	3333	ν (OH) water molecules mixed with ν(NH)
1633	$\nu_{as}COO^-$	3085	ν (CH)	3010	3059	ν(NH)+ ν(CH)
1418	ν_sCOO^-	3343	ν(NH)	1634	1607	$\nu_{as}COO^-$ +ν (C=O) amide I
1560	δNH_3^+	1608	ν(C=O) amide I	1428	1413	ν_sCOO^- + benzene ring + (δNH+νCN) amide II
1457	Ring Structure (imidazole)	1559,1487, 1412	Benzene ring + (δNH+νCN) amide II	1318	1297	νCN+(νCN+δ NH) amide III
1336	νCN	1310	(νCN + δ N H) amide III	716	706	P_r(HOH) Coordinated water molecule

* His and HA stand for anion of Histidine and hippuric acid respectively.

Magnetic measurements and Electronic Spectra.

The magnetic moment of cobalt(II) complexes,

$Na_2[Co(C_6H_5CONHCH_2COO)\ (C_6H_8N_3O_2).H_2O].9H_2O$: μ_{eff} = 4.94 BM

and $Na_2[Co(C_6H_5CONHCH_2COO)\ (C_6H_8N_3O_2).H_2O].5H_2O$: μ_{eff} = 4.52 BM

suggest a six fold octahedral structure [16] for both the complexes. These values are higher than required for a free spin d^7 state (three unpaired electrons) and it can be ascribed to orbital contribution. The magnetic measurements are given in Table 2. The octahedral cobalt(II) is known to have the following three spin allowed transitions.

1. $(\nu_1)^4 T_{1g}(F) \rightarrow {}^4 T_{2g}(F)$
2. $(\nu_2)^4 T_{1g}(F) \rightarrow {}^4 A_{2g}(F)$
3. $(\nu_3)^4 T_{1g}(F) \rightarrow {}^4 T_{2g}(P)$

Table 2. Magnetic Measurements of Cobalt(II) Complexes

Compound	Temp (K)	χ_g x 10^{-6} c.g.s	χ_M x 10^{-6} c.g.s	χ_M' x 10^{-6} c.g.s	μ_{eff} (BM)
Na_2[{Co(II)-His-HA}.H_2O]. $9H_2O$	296.5	16.5149	10197.45	10305.04	4.94
Na_2[{Co(II)-His-HA}.H_2O].$5H_2O$	292.0	8655.07	8762.66	9019.9	4.52

* His and HA stand for anion of Histidine and hippuric acid respectively.

Out of these, the first transition (ν_1) usually occurs at lower frequencies and is expected to appear beyond 1000 nm in the near infrared region. For the (ν_2) transition, since the $^4A_{2g}$ state is derived mainly from a $^5t_{2g}$. ^2e_g configuration, this transition would involve a two electron process and hence should be weaker by about a factor of 10^{-2} than other transition [17]. The position of ν_2 transition in cobalt(II) complexes may, however be ambiguous and is rather difficult to locate with certainty [18]. Sometimes it appears as a shoulder on either side of the main absorption band (ν_3 transition) or in some cases it may not be observed at all. Thus in the present study of cobalt(II) complexes, the transition obtained at 1081 nm in both the complexes can be assigned as ν_1 transition. The main absorption band observed at 516 nm and 522 nm in decahydrate and hexahydrate complexes respectively can safely be assigned as transition (ν_3). The position of ν_2 transition in both the complexes is however not clear. The other bands observed at 231 nm (decahydrate) and 230 nm (hexahydrate) can be regarded as charge transfer bands.

Conclusion

Thus the evidences obtained from IR spectra, electronic spectra and magneto chemical measurements suggest an octahedral structure (Fig. 1) for cobalt(II) complexes in which histidine acts as a tridentate ligand and hippuric acid behaves as a bidentate ligand. The sixth coordination position is satisfied by a water molecule.

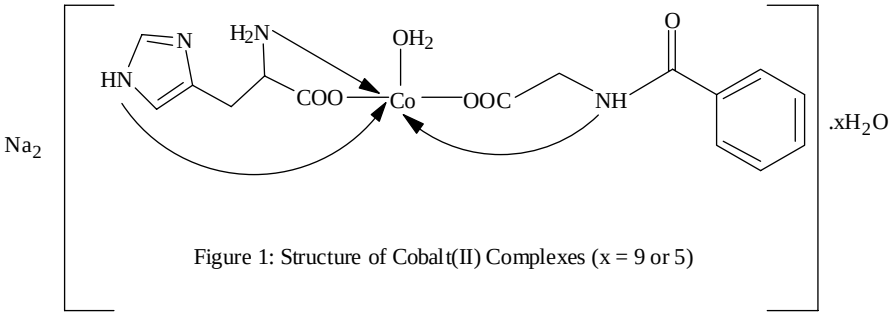

Figure 1: Structure of Cobalt(II) Complexes (x = 9 or 5)

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СМЕСЕНИ КОБАЛТ (II) КОМПЛЕКСИ НА ХИСТИДИН И ХИПУРОВА КИСЕЛИНА

Резюме. Синтезирани са комплексите
$Na_2[Co(C_6H_5CONHCH_2COO)(C_6H_8N_3O_2).H_2O].9H_2O$
$Na_2[Co(C_6H_5CONHCH_2COO)(C_6H_8N_3O_2).H_2O].5H_2O$.
Тяхната структура е определена чрез елементен анализ и спектрални (инфрачервени и електронни спектри) и магнито-химични измервания.

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