

Synthesis and Characterization of Mixed Ligand Complexes of Nickel(II) with Histidine and Hippuric Acid

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Mixed ligand complexes of nickel(II) with the composition $\text{Na}_2[\text{Ni}\{(\text{C}_6\text{H}_5\text{CONHCH}_2\text{COO})(\text{C}_6\text{H}_8\text{N}_3\text{O}_2)\cdot\text{H}_2\text{O}\}]\cdot 7\text{H}_2\text{O}$ and $\text{Na}_2[\text{Ni}\{(\text{C}_6\text{H}_5\text{CONHCH}_2\text{COO})(\text{C}_6\text{H}_8\text{N}_3\text{O}_2)\cdot\text{H}_2\text{O}\}]\cdot \text{H}_2\text{O}$ formed with histidine and hippuric acid have been synthesized. The mode of coordination and their structures have been examined by elemental analysis, infrared, electronic spectra and magnetic measurements. Histidine has shown a tridentate behaviour with the coordination occurring through the carboxylate oxygen atom and two nitrogen atoms of the imidazole and $-\text{NH}_2$ groups. Hippuric acid has been found to act as a bidentate ligand coordinating through carboxylate oxygen atom and the nitrogen of the amido group.

Key Words: Synthesis, Characterization, Nickel(II) complexes, Histidine and Hippuric acid.

INTRODUCTION

Mixed ligand complexes are known to play a vital role in biological systems¹ and have received a considerable attention in recent years. Synthesis, characterization and some other properties of mixed ligand transition metal complexes formed with histidine and adenine/guanine² and other amino acids (glycine, alanine, valine, glutamine, methionine, serine and lysine) have been reported³⁻⁷. In earlier publications^{8,9}, the synthesis and characterization of mixed ligand Cu(II), Co(II), Ni(II) complexes formed with hippuric acid and nitrilotriacetic acid and imino-diacetic acid have also been reported. Literature survey reveals that the preparation, mode of coordination and the structures of mixed ligand transition metal complexes formed with hippuric acid and histidine have not been reported. Hence, the present paper describes the synthesis and characterization of some mixed ligand complexes of nickel(II) formed with hippuric acid and histidine.

EXPERIMENTAL

Solutions of histidine (Fluka) and hippuric acid (Fluka) were prepared in one equivalent of sodium hydroxide. The solution of nickel(II) chloride (Rochelle Chemicals) was prepared in one equivalent of hydrochloric acid. To prepare the metal complex, the two ligands were mixed with 0.1 M metal ion solution in 1:1:1 molar ratio at

room temperature. At first, histidine solution was mixed with nickel(II) ion solution followed by hippuric acid solution. A clear light blue solution was obtained with pH *ca.* 4.71 which was raised to *ca.* 5.03 by adding sodium hydroxide solution. The clear blue solution was then concentrated over a steam bath and allowed to crystallize overnight. The green crystalline product was washed first with 50 % ethanol-water mixture followed by acetone and dried in a vacuum desiccator. On heating the green product in an air oven at 100-110 °C for *ca.* 2 h, the colour of the product changed to light green indicating the loss of water molecules from the complex.

The electronic spectra of the complexes was recorded in methanol in 190-1100 nm range on a Shimidazu UV-Vis-2501 spectrophotometer model TCC-240A. The infrared spectra of the ligands and metal complexes were recorded on a Perkin-Elmer FTIR2000 spectrophotometer in 4000-400 cm^{-1} range in KBr disc. Johnson Matthey Alfa Product magnetic susceptibility balance was used to measure magnetic susceptibility at room temperature. Elemental analysis (CHN) of the complexes was carried out using VarioEL CHNO/S elemental analyzer. The metal content in the complexes was determined by atomic absorption spectrophotometer model 220FS.

RESULTS AND DISCUSSION

Elemental analysis: Analytical data are as follows.

(1) **Disodium(monoaquo)(hippurato)(histidino)nickel(II)heptahydrate:** Green crystalline. Anal. calcd. for $\text{Na}_2[\text{Ni}\{(\text{C}_6\text{H}_5\text{CONHCH}_2\text{COO})(\text{C}_6\text{H}_8\text{N}_3\text{O}_2)\cdot\text{H}_2\text{O}\}]\cdot 7\text{H}_2\text{O}$ (%): Ni = 10.10; C = 30.99; H = 5.56; N = 9.64; Found (%): Ni = 10.47; C = 31.34; H = 5.57; N = 9.53.

(2) **Disodium(monoaquo)(hippurato)(histidino)nickel(II)monohydrate:** Light green crystalline. Anal. calcd. for $\text{Na}_2[\text{Ni}\{(\text{C}_6\text{H}_5\text{CONHCH}_2\text{COO})(\text{C}_6\text{H}_8\text{N}_3\text{O}_2)\cdot\text{H}_2\text{O}\}]\cdot\text{H}_2\text{O}$ (%): Ni = 12.41 ; C = 38.08; H = 4.27; N = 11.84. Found: Ni = 12.49; C = 38.18; H = 4.03; N = 11.45.

Note: In further discussion in the text for convenience the two complexes are refereed to as octahydrate and dihydrate, respectively.

IR Studies: In amino acids, $\nu(\text{NH}_3^+)$ appears in 3130-3030 cm^{-1} range¹⁰. In the IR spectra of histidine it appears at *ca.* 3082 cm^{-1} but overlaps with other vibrations such as $\nu(\text{NH})$ (imidazole group) and $\nu(\text{CH})$ (heterocyclic + $\nu(\text{CH}_2)$ group *ca.* 3016 cm^{-1}). Theoretically, $\nu(\text{NH}_3^+)$ should vanish on coordination. In metal complexes, however, a broad band appears at *ca.* 3300 cm^{-1} which must be arising from other vibrations appearing in this region. In histidine, $\delta(\text{NH}_3^+)$ appears at 1560 cm^{-1} which disappears in metal complexes. The $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ absorptions appear in histidine at 1633 and 1418 cm^{-1} , respectively¹¹. In imidazole¹², the $\nu(\text{NH})$ 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 metal complexes it is absent since no band is observed in this region. Hippuric acid shows characteristic $\nu(\text{C}=\text{O})$ absorption band for the COOH group at 1750 cm^{-1} which disappears in case of nickel(II) complexes. Instead, asymmetric and symmetric COO^- stretching

frequencies are observed. The octahydrate complex shows $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ frequencies at 1637 and 1436 cm^{-1} , respectively whereas in dihydrate complex these frequencies are obtained at 1608 and 1414 cm^{-1} , respectively. The $\nu(\text{NH})$ absorptions in hippuric acid are observed at 3343 cm^{-1} which in the complexes is mixed with $\nu(\text{OH})$ and is observed at 3315 and 3335 cm^{-1} in octahydrate and dihydrate complexes, respectively. Hippuric acid shows amide I, $\nu(\text{C}=\text{O})$ band at 1608 cm^{-1} , amide II [$\delta(\text{NH}) + \nu(\text{CN})$] with benzene ring vibrations in 1559-1412 cm^{-1} range, amide III [$\nu(\text{CN}) + \delta(\text{NH})$] band at 1310 cm^{-1} . In octahydrate and dihydrate complexes, amide I band together with $\nu_{as}(\text{COO}^-)$ is obtained at 1637 and 1608 cm^{-1} , respectively. Amide II band along with benzene ring vibrations is mixed with $\nu_s(\text{COO}^-)$ and is obtained at 1436 and 1414 cm^{-1} in octahydrate and dihydrate complexes, respectively. In octahydrate complex amide III band together with $\nu(\text{CN})$ vibrations is observed at 1322 cm^{-1} whereas in dihydrate complex it appears at 1298 cm^{-1} . Besides, octahydrate and dihydrate complexes show additional bands at 3315 and 3335 cm^{-1} , respectively attributable to water molecules¹¹. The appearance of rocking $\nu(\text{HOH})$ frequencies¹³ at 722 and 708 cm^{-1} in case of octahydrate and dihydrate complexes, respectively shows the presence of coordinated water molecules. The IR frequencies of the ligands and nickel(II) complexes are given in Table-1.

Thus the IR studies suggest that in nickel(II) complexes, histidine coordinates through carboxylate oxygen atom and two nitrogen atoms of imidazole and $-\text{NH}_2$ groups, 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 groups.

Magnetic studies and electronic spectra: The magnetic moment of nickel(II) complexes, $\text{Na}_2[\text{Ni}\{(\text{C}_6\text{H}_5\text{CONHCH}_2\text{COO})(\text{C}_6\text{H}_8\text{N}_3\text{O}_2)\cdot\text{H}_2\text{O}\}]\cdot 7\text{H}_2\text{O}$: $\mu_{\text{eff}} = 3.14$ BM and $\text{Na}_2[\text{Ni}\{(\text{C}_6\text{H}_5\text{CONHCH}_2\text{COO})(\text{C}_6\text{H}_8\text{N}_3\text{O}_2)\cdot\text{H}_2\text{O}\}]\cdot \text{H}_2\text{O}$: $\mu_{\text{eff}} = 3.39$ BM suggest a six coordinate octahedral structure¹⁴ for both the complexes which is supported by their electronic spectra¹⁵. The magnetic measurements are given in Table-2. In six coordinate octahedral nickel(II) complexes, three spin allowed transitions (ν_1) ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$; (ν_2) ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and (ν_3) ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ generally fall in the ranges 7000-13000, 11000-20000 and 19000-27000 cm^{-1} , respectively¹⁵. In case of octahydrate complex these transitions are observed at 9643, 11235 and 25063 cm^{-1} , respectively where as in case of dihydrate complex these transitions are obtained at 10917, 11891 and 25000 cm^{-1} , respectively. The other bands obtained at 43103 and 43290 cm^{-1} in octahydrate and dihydrate complexes, respectively can be assigned as charge transfer from ligand to metal ion.

Conclusion

Thus the evidences obtained above suggest a six coordinated structure for both nickel(II) complexes in which histidine acts as a tridentate ligand and hippuric acid shows a bidentate behaviour. The sixth coordination position is satisfied by a water molecule in both the complexes (Fig. 1).

TABLE-1
IR FREQUENCIES (cm⁻¹) OF HISTIDINE, HIPPURIC ACID AND THEIR MIXED LIGAND Ni(II) COMPLEXES

| Histidine | Band assignment | Hippuric acid | Band assignment | Na ₂ [[Ni(II)-His-HA].H ₂ O].7H ₂ O | Na ₂ [[Ni(II)-His-HA].H ₂ O].H ₂ O | Band assignment |
|-----------|---|------------------|---|--|---|--|
| 3082-2866 | v(NH)(imidazole) + v(CH) (Heterocyclic) + v(NH ₃ ⁺) + v(CH(-CH ₂)) | 1750 | v(C=O) carboxylic group | 3315 | 3335 | v(OH) water molecules mixed with v(NH) |
| 1633 | v _{as} (COO ⁻) | 3085 | v(CH) | 3150 | 3060 | v(NH) + v(CH) |
| 1418 | v _s (COO ⁻) | 3343 | v(NH) | 1637 | 1608 | v _{as} (COO ⁻) + v(C=O) amide I |
| 1560 | δ(NH ₃ ⁺) | 1608 | v(C=O) amide I | 1436 | 1414 | v _s (COO ⁻) + benzene ring + [δ(NH) + v(CN)] amide II |
| 1457 | Ring structure (imidazole) | 1559, 1487, 1412 | Benzene ring + [δ(NH) + v(CN)] amide II | 1322 | 1298 | v(CN) + [v(CN) + δ(NH)] amide III |
| 1336 | v(CN) | 1310 | [v(CN) + δ(NH)] amide III | 722 | 708 | P _i (HOH) Coordinated water molecule |

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

TABLE-2
MAGNETIC MEASUREMENTS OF Ni(II) COMPLEXES

| Complex | Temp (K) | χ _g × 10 ⁻⁶ c.g.s | χ _M × 10 ⁻⁶ c.g.s | χ _M ' × 10 ⁻⁶ c.g.s | μ _{eff} (BM) |
|--|----------|---|---|---|-----------------------|
| Na ₂ [[Ni(II)-His-HA].H ₂ O].7H ₂ O | 295.5 | 7.0086 | 4073.12 | 4180.71 | 3.14 |
| Na ₂ [[Ni(II)-His-HA].H ₂ O].H ₂ O | 296.0 | 10.0497 | 4753.58 | 4861.17 | 3.39 |

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

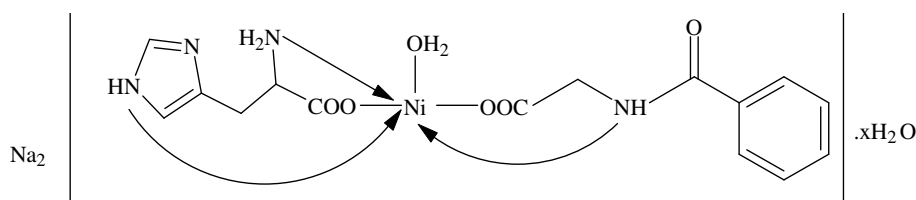


Fig. 1. Structure of nickel(II) complexes ($x = 7$ or 1)

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