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

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Mixed ligand nickel(II) complexes, $Na[Ni\{NH(CH_2COO)_2\}(C_6H_5CONHCH_2COO)\cdot H_2O]\cdot 6H_2O$ and $Na[Ni\{NH(CH_2COO)_2\}(C_6H_5CONHCH_2COO)\cdot H_2O]$ formed with iminodiacetic acid and hippuric acid have been synthesized. Their mode of coordination and the structures have been investigated using infra-red spectra, electronic spectra and magnetic measurements. Iminodiacetic acid has been found to act as a tridentate ligand with the coordination occurring through the carboxylate oxygen atoms and the nitrogen atom. Hippuric acid behaves as a bidentate ligand coordinating through the carboxylate oxygen atom and the nitrogen of the amido group. The sixth coordination position is satisfied by the water molecule.

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

INTRODUCTION

Mixed ligand complexes are well known to play an important role in biological systems[1]. Synthesis, equilibrium and spectral studies on the transition metal complexes of iminodiacetic acid and its derivatives and mixed ligand complexes have been reported[2-4]. Ahmad and Boracei[5] have also reported the synthesis and spectral characterization of six coordinate mixed ligand complexes of some bivalent transition metals formed with 5-methyl uracil, amino acids and N-(2-acetamido)iminodiacetic acid. Some binary and ternary transition metal complexes of hippuric acid have been studied[6-8]. In recent publications[9-11] mixed ligand six fold octahedral Co(II), Cu(II) and Ni(II) complexes formed with hippuric acid and nitrilotriacetic acid have been reported. The present paper reports the synthesis and characterization of nickel(II) complexes formed with iminodiacetic acid (IDA) and hippuric acid (HA).

EXPERIMENTAL

Solutions of hippuric acid (Fluka) and iminodiacetic acid (Aldrich) were prepared by dissolving them in one equivalent of sodium hydroxide. The solution of nickel(II) chloride (Roschelle 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 a 1:1:1 molar ratio at room temperature. At first iminodiacetic acid was mixed with nickel(II) chloride solution followed by hippuric acid solution and the pH of the solution was adjusted to *ca.* 5.0 by adding sodium hydroxide. On adding iminodiacetic acid to the metal ion solution, it gave a clear green solution of pH 2.9 which was raised to *ca.* 4.0 by the addition of sodium hydroxide. On the addition of hippuric acid to this solution, the pH of the resulting green solution was adjusted to *ca.* 5.0 by adding sodium hydroxide. The clear green solution was then concentrated over a steam bath and allowed to crystallize. The green crystalline product was then filtered and washed first with 50 % ethanol-water mixture followed by acetone and dried in a vacuum desicator. The green crystalline product was also heated in an air oven for about 2 h at 110 ºC, the colour of the product changed to light green which indicates the loss of water molecules.

The IR spectrum of ligands and metal complexes were recorded on a Perkin-Elmer FT-IR 2000 spectrophotometer in 4000-400 cm^{-1} range in KBr discs. The magnetic susceptibility of the complexes was measured at room temperature using Johnson Matthey Alfa Product magnetic susceptibility balance. Shimadzu UV-Vis 2501 PC spectrophotometer model TCC-240A was used to record the electronic spectra of the complexes in methanol in 200-1100 nm range. The elemental analysis (CHN) was carried out on a VarioEL CHNO/S elemental analyzer. The content of the metal present in complexes was determined by using atomic absorption spectrophotometer 220FS.

RESULTS AND DISCUSSION

The analytical data of the Ni(II) complexes are given below:

Sodium(hippurato)(iminodiacetato)(monoaqua)nickel(II) hexahydrate green crystalline, Anal. (%) calcd. for Na $[Ni(C_6H_5CONHCH_2COO)\{NH(CH_2COO)_2\}H_2O]\cdot6H_2O$: Ni =11.35, C = 30.20, H = 5.27, N = 5.41. Found: Ni = 11.51, C = 30.18, H = 5.58, N = 5.41.

Sodium(hippurato)(iminodiacetato)(monoaqua)nickel(II) light green crystalline, Anal. (%) calcd. for $Na[Ni(C_6H_5CONHCH_2COO)\{NH(CH_2COO)_2\cdot H_2O]$: Ni = 14.35, C = 38.17, H = 3.70, N = 6.85. Found: Ni = 14.68, C = 38.20, H = 3.75, N = 6.82.

Note: In further descriptions in the text for convenience the two complexes are referred to as heptahydrate and monohydrate, respectively.

Iminodiacetic acid and hippuric acid show characteristic ν(C=O) absorption bands for the COOH group at 1747 and 1715 cm^{-1}, respectively, which vanishes in case of metal complexes. Instead, asymmetric and symmetric stretching frequencies are obtained. The heptahydrated complex shows $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ frequencies at 1635 and 1410 cm^{-1}, respectively whereas in the monohydrate complex these frequencies are observed at 1607 and 1414 cm^{-1}, respectively. In iminodiacetic acid, ν(CN) absorption band is observed at 1328 cm^{-1}, which lowers on coordination in the metal complexes. The ν(NH) absorptions in hippuric acid are observed at 3342 cm^{-1}. Hippuric acid shows amide I ν(C=O) band at 1605 cm^{-1}, amide II [δ(NH) + ν(CN)] with benzene ring vibrations in 1556-1416 cm^{-1} range and amide (III) [(νCN) + δ(NH)] band at 1334, 1314 cm^{-1}. In the heptahydrated complex, amide I, amide II and benzene ring vibrations are mixed together to give a composite broad band at 1566 cm^{-1}, whereas in monohydrate complex these vibrations together with $\nu_{as}(COO^-)$ and δ(HOH) are observed at 1607 cm^{-1}. Amide III band is mixed with ν(CN) absorptions and is observed at 1323 and 1298 cm^{-1} in the heptahydrate and monohydrate complexes, respectively. δ(HOH) vibrations are mixed with $\nu_{as}(COO^-)$ vibrations and are observed at 1635 and 1607 cm^{-1} in heptahydrate and monohydrate complexes, respectively. Besides, both the complexes show additional bands in 3450-3320 cm^{-1} range attributable to water molecules[12]. The appearance of rocking ρ_r(HOH) frequency[13] at 717 and 751 cm^{-1} in the heptahydrate and monohydrate complexes, respectively shows the presence of coordinated water molecule. The IR frequencies of the ligands and the metal complexes are given in Table-1.

TABLE 1
IR FREQUENCIES (cm^{-1}) OF IMINODIACETIC ACID, HIPPURIC ACID AND THEIR HEPTAHYDRATE AND MONOHYDRATE MIXED LIGAND NICKEL(II) COMPLEXES

Imino diacetic acid	Hippuric acid	Na[Ni(IDA)(HA)·H_2O]·6H_2O	Na[Ni(IDA)(HA).H_2O]	Band assignments
-	-	3450	3407 (b)	ν(OH) for water
1715	1747	-	-	ν(C=O) for COOH group
3022, 2972	3079	2970	2918	ν(CH)
-	-	1635	1607	ν_{as} COO^-
-	-	1410	1414	ν_s COO^-
3099	3342	3320 (b), 3100 (sh)	3052	ν(NH)
-	1605	-	-	ν(C=O)amide I band
-	1556, 1489 1416	1556, 1434, 1410	1607	(δNH + νCN) amide II band + benzene ring
1328	1334, 1314	1323	1298	ν(CN) for IDA + (νCN + δNH) amide III band
-	-	717	751	$\rho_r(H_2O)$

It may thus be inferred that in the nickel(II) complexes, both the protons of iminodiacetic acid are liberated and acts as a tridentate ligand by coordinating through the nitrogen atom and the carboxylate oxygen atoms. Hippuric acid shows bidentate behaviour and the coordination takes place through its carboxylate oxygen atom and the nitrogen of the amido group.

The magnetic moments of nickel(II) complexes are: $Na[Ni(C_6H_5CONHCH_2COO)\{NH(CH_2COO)_2 \cdot H_2O]\cdot 6H_2O$: $\mu_{eff} = 2.85$ BM; $Na[Ni(C_6H_5CONHCH_2COO)\{NH(CH_2COO)_2 \cdot H_2O]$: $\mu_{eff} = 3.20$ BM. It suggests a six fold octahedral structure[14] which is supported by their electronic spectra[15]. The magnetic measurements for the complexes are given in Table-2. The three spin allowed transitions[16] for the complexes are given in Table-3.

TABLE-2
MAGNETIC MEASUREMENTS OF Ni(II) COMPLEXES

Complex	Temp. (K)	$\chi_g \times 10^{-6}$ (cgs)	$\chi_M \times 10^{-6}$ (cgs)	$\chi_{M'} \times 10^{-6}$ (cgs)	μ_{eff} (BM)
$Na[(Ni\text{-}IDA\text{-}HA)H_2O]\cdot 6H_2O$	300	6.3638	3290.78	3382.50	2.85
$Na[(Ni\text{-}IDA\text{-}HA)H_2O]$	300	10.217	4178.65	4270.37	3.20

IDA and HA stand for the anions of iminodiacetic acid and hippuric acid, respectively.

TABLE-3
ELECTRONIC SPECTRAL BANDS OF NICKEL(II) COMPLEXES

Bands	$Na[(Ni\text{-}IDA\text{-}HA)H_2O]\cdot 6H_2O$ (cm^{-1})	$Na[(Ni\text{-}IDA\text{-}HA)H_2O]$ (cm^{-1})
$(\nu_1)\ ^3A_{2g} \rightarrow {}^3T_{2g}$	10560	10141
$(\nu_2)\ ^3A_{2g} \rightarrow {}^3T_{1g}(F)$	12722	13123
$(\nu_3)\ ^3A_{2g} \rightarrow {}^3T_{1g}(P)$	25062	25160
Charge transfer[14] L → M	43103	43290

Conclusion

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

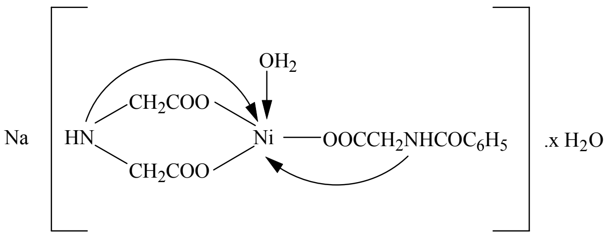

Fig. 1. Structure of Ni(II) complexes (x = 6 or 0)

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