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SYNTHESIS, COORDINATION AND STRUCTURE OF MIXED LIGAND COPPER (II) COMPLEXES OF IMINODIACETIC ACID AND HIPPURIC ACID

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Abstract. Mixed ligand copper(II) complexes, $Na[Cu(C_6H_5CONHCH_2COO)\{NH(CH_2COO)_2\}.H_2O]H_2O$ and $Na[Cu(C_6H_5CONHCH_2COO)\{NH(CH_2COO)_2\}.H_2O]$ formed with iminodiacetic acid and hippuric acid have been synthesized. The mode of coordination and structural investigations have been done by their elemental analysis, spectral (IR and electronic spectra) and magnetic measurements studies. Iminodiacetic acid acts as a tridentate ligand and the coordination occurs with two carboxylate oxygen atoms and the nitrogen atom. Hippuric acid shows a bidentate behavior coordinating through the carboxylate oxygen atom and the nitrogen of the amido group. The sixth coordination position is satisfied by one water molecule. Thus both the Cu(II) complexes have been suggested to show a six fold octahedral structure.

Keywords: synthesis, coordination, structure, Cu(II) compexes, hippuric acid, iminodiacetic acid

Introduction

It is well known that mixed ligand coordination complexes play an important role in biological systems [1]. Hippuric acid (N-benzoylglycine) is an α-amido acid (Fig. 1) containing an acidic COOH, basic NH and a substituent benzoyl group. It is thus capable of forming metal chelates. It has a special biological significance as it is found in the urine of camel. Its alkali, calcium and magnesium salts have also been used as solubilizers in the preparation of aqueous solutions of some sparingly soluble medicinal compounds [2]. Several binary and ternary metal complexes of hippuric acid and its derivatives have been reported. [3-11]. It can coordinate with metal ions through the only carboxylate oxygen atom acting as a monodentate ligand

or bidentate; or it may also coordinate through both the carboxylate oxygen atom and the nitrogen of the amido group and thus acts as a bidentate ligand.

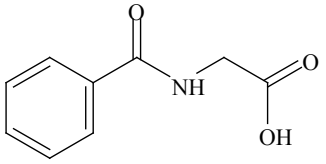

Figure 1: Structure of hippuric acid

Iminodiacetic acid (Fig. 2) is a tridentate ligand containing two carboxylate groups and a NH group. Synthesis, equilibrium and structural studies on the transition metal complexes of iminodiacetic acid and its derivatives and mixed ligand complexes have been reported [12-16]. Abdalla and Said [17] have also reported thermal studies on Co(II), Ni(II) and Cu(II) ternary complexes of N-(2-acetamido) iminodiacetic acid and imidazoles.

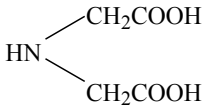

Figure 2: Structure of iminodiacetic acic

In earlier publications [18] mixed ligand six fold octahedral Co(II), Cu(II) and Ni(II) complexes formed with hippuric acid and nitrilotriacetic acid have been reported. Literature reveals that the studies on the mixed ligand transition metal complexes formed with iminodiacetic acid and hippuric acid have not been studied. Hence the present paper describes the synthesis, mode of coordination and the structural investigations of Cu(II) complexes formed with iminodiacetic acid and hippuric acid.

Experimental

Solutions of hippuric acid (Fluka) and iminodiacetic acid (Aldrich) were prepared by dissolving them in one equivalent of sodium hydroxide. The solution of anhydrous copper(II) chloride (BDH) 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 a 1:1:1 molar ratio at room temperature. At first iminodiacetic acid was mixed with copper(II) chloride solution followed by hippuric acid solution and the pH of the solution was adjusted to ~ 5 by adding sodium hydroxide. On adding iminodiacetic acid to the metal ion solution, a clear light blue solution was obtained with a pH of 2.3 which was raised to ~ 3.5 by the addition of sodium hydroxide. On the addition of hippuric acid to this solution, the pH of the resulting dark blue solution was adjusted to ~ 5 by adding sodium hydroxide solution. The clear dark

blue solution was then concentrated over a steam bath and allowed to crystallize. The dark blue crystalline product was then filtered and washed first with 50% ethanol-water mixture followed by acetone and dried in a vacuum desicator. The dark blue crystalline product was also heated in an air oven for about two hours at 110 ^{0} C, the colour of the product changed to light blue indicating the loss of water molecules. The IR spectra 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 copper content of the complexes was determined by the Atomic Absorption Spectrophotometer 220 FS.

Results and discussion

Elemental analysis.

Sodium(hippurato)(iminodiacetato)(monoaqua)copper(II) mono hydrate. Dark blue crystal. Anal. Calcd. for $Na[Cu\ (C_6H_5\,CO\ NH\ CH_2\,COO)\ \{NH\ (CH_2\,COO)_2\}.\ H_2O].H_2O$: Cu=14.72%, C=36.15% ,H = 3.98%, N = 6.48%. Found: Cu = 14.80%, C = 35.96%, H = 4.09%, N = 6.26%

Sodium(hippurato)(iminodiacetato)(monoaqua)copper(II). Light blue crystal. Anal. Calcd. for $Na[Cu\,(C_6H_5CONHCH_2COO)\{NH\,(CH_2COO)_2\}.\,H_2O]$. Cu=15.35%, C=37.73%, H=3.66%, N=6.77% ; Found: Cu=15.40%, C= 37.91 % , H=3.50%, N=6.67% .

NOTE: *In further descriptions in the text for convenience the two complexes are refereed to as dihydrate and monohydrate respectively.*

IR studies

Iminodiacetic acid and hippuric acid show characteristic ν (C=O) absorption band for the COOH group at 1715 cm^{-1} and 1748 cm^{-1} respectively, which vanishes in case of metal complexes. Instead, asymmetric and symmetric stretching COO^- frequencies are observed. The dihydrate complex shows $\nu_{as}COO^-$ and ν_sCOO^- frequencies at 1576 and 1395 cm^{-1} respectively, whereas in mono hydrate complex these frequencies are observed at 1590 cm^{-1} and 1404 cm^{-1} respectively. In iminodiacetic acid ν(CN) absorption band is obtained at 1328 cm^{-1} which is lowered in case of metal complexes. The ν(NH) absorption band in iminodiacetic acid and hippuric acid is observed at 3099 cm^{-1} and 3342 cm^{-1} respectively. This appears at 3262 cm^{-1} and 3205 cm^{-1} in dihydrate and monohydrate complex respectively. In hippuric acid amide I (ν C=O), amide II (δ NH + ν CN) along with benzene ring vibrations and amide III (ν CN + δ NH) bands are obtained at 1605 cm^{-1} (1556, 1489, 1416) cm^{-1} and (1334, 1314) cm^{-1} respectively. In dihydrate complex amide I ,

$\nu_{as}COO^-$ and δ (HOH) frequencies are mixed together to give a composite band at ~ 1576 cm^{-1} whereas in monohydrate complex, the composite band is observed at 1590 cm^{-1}. Amide II band and benzene ring vibrations are also mixed together, appearing at ~ 1480 cm^{-1} and 1470 cm^{-1}. Amide III band mixed with ν (CN) vibrations is obtained at 1318 cm^{-1} and 1313 cm^{-1} in dihydrate and monohydrate complexes respectively. Besides, both the complexes show additional bands at ~ 3416 cm^{-1} attributable to water molecules [19]. The appearance of rocking ρ_r (HOH) frequency [20] at 750 cm^{-1} and 741 cm^{-1} in case of dihydrate and monohydrate omplexes respectively shows that water molecules are also coordinated. The IR frequencies of the ligands and the metal complexes are given in Table 1.Thus the IR studies suggest that in copper(II) complexes, iminodiacetic acid coordinates through both carboxylate oxygen atoms and the nitrogen atom, hence acts as a tridentate ligand. Hippuric acid shows bidentate behaviour and the coordination occurs through carboxylate oxygen atom and the nitrogen of the amido group.

Magnetic measurements and electronic spectra

The observed magnetic moments of copper (II) complexes: Sodium (hippurato) (iminodiacetato) (monoaqua) copper(II) monohydrate. μ_{eff} = 1.86 BM and Sodium (hippurato) (iminodiacetato) copper (II) (monoaqua) , μ_{eff} = 1.74 BM suggest a spin free octahedral structure for the complexes [21], which is supported by their electronic spectra [22]. The band observed at 13736 cm^{-1} in both the copper (II) complexes can be regarded as the d-d transition. The complexes also show a band at 42016 cm^{-1} which may be assigned as a charge transfer band from carboxylate group to the metal. The magnetic measurements and the electronic spectra data are given in Table 2.

Conclusion

Thus the evidences obtained from the above studies suggest a six fold octahedral structure for the mixed ligand copper (II) complexes in which iminodiacetic acid and hippuric acid act as tridentate and bidentate ligands, respectively. The sixth coordination position is satisfied by a water molecule.

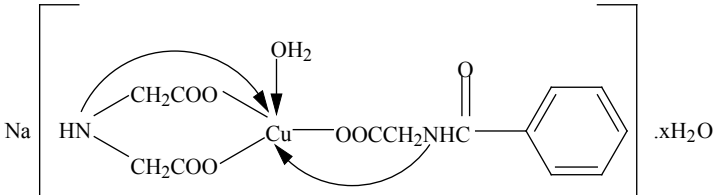

Figure 3: Structure of copper(II) complexes (x = 1 or 0)

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

Iminodiactic acid	Hippuric acid	$Na[Cu(IDA)(HA).H_2O]H_2O$	$Na[Cu(IDA)(HA).H_2O]$	Band assignment
-	-	3416	3416	ν (OH) water
3099	3342	3262	3205	ν (NH)
1715	1748	-	-	ν(C=O),COOH group
-	-	1576 [@]	1590 [@]	ν_{as} COO^-
-	-	1395	1404	ν_{s} COO^-
3022	3079	2926	2940	ν(CH)
-	1605	1576 [@]	1590 [@]	ν(C=O) amide I band
-	1556,1489, 1416	1480	1470	(δNH + νCN) amide II band + benzene ring
1328	1334, 1314	1318 [⊗]	1313 [⊗]	ν (CN) and (νCN + δNH) amide III band
-	-	750	741	ρ_r (HOH)

[@] Amide I, ν_{as} COO^- and δ(HOH) vibrations are mixed together.
[⊗] ν (CN) is mixed with amide III band.
NOTE: *IDA and HA stand for the anion of iminodiacetic acid and hippuric acid respectively.*

Table 2. Magnetic Measurements and Electronic Spectra of Copper (II) Complexes

Complex	Magnetic measurements					Electronic spectra	
	T (K)	χ_g x 10^{-6} (cgs)	χ_M x 10^{-6} (cgs)	$\chi_{M'}$ x 10^{-6} (cgs)	μ_{eff} (BM)	d-d transition (cm^{-1})	CT from L→ M (cm^{-1})
$Na[Cu(IDA)(HA).H_2O]H_2O$	291	3.2263	1393.34	1485.06	1.86	13736	42016
$Na[Cu(IDA)(HA).H_2O]$	291	2.9070	1203.06	1294.78	1.74	13736	42016

NOTE: *IDA and HA stand for the anion of iminodiacetic acid and hippuric acid respectively.*

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СИНТЕЗ, КООРДИНАЦИЯ И СТРУКТУРА НА СМЕСЕНИ ЛИГАНДНИ МЕД (II) КОМПЛЕКСИ НА ИМИНОДИОЦЕТНАТА И ХИПУРОВАТА КИСЕЛИНИ

Резюме. С иминодиоцетна и хипурова киселини са синтезирани комплексите

$Na[Cu(C_6H_5CONHCH_2COO)\{NH(CH_2COO)_2\}.H_2O]H_2O$

$[Cu(C_6H_5CONHCH_2COO)\{NH(CH_2COO)_2\}.H_2O].$

Степента на координация и структурните изследвания са проведени с елементен анализ, спектрални (инфрачервени и електронни спектри) и магнитни методи. Иминодиоцетната киселина действа като триденттантен лиганд. Хипуровата киселина действа като бидентантен лиганд. Шестата кординацианна позиция е заета от една водна молекула.

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