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SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND Cu(II) AND Co(II) COMPLEXES OF L-PHENYLALANINE AND IMINODIACETIC ACID

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Abstract. Mixed ligand complexes, $Na[M\{(C_6H_5\ CH_2\ CH(NH_2)\ COO)\}\{NH(CH_2COO)_2\}.H_2O]$, where M = Cu(II) and Co(II), formed with phenylalanine and iminodiacetic acid were synthesized and characterized by their elemental analysis, spectral (IR and UV) and magneto chemical studies. In both complexes, phenylalanine was found to act as a bidentate ligand coordinating through the carboxylate oxygen and the nitrogen atom of the amino group. The iminodiacetic acid, however, coordinated through the two carboxylate oxygen atoms and the nitrogen of the NH group, hence acted as a tridentate ligand. The remaining coordination position is satisfied by one water molecule. Thus both complexes have been suggested to show six fold octahedral structures.

Keywords: phenylalanine, iminodiacetic acid, Cu(II) and Co(II) complexes, synthesis, characterization, structure

Introduction

Some transition metal ions play an important role in various biological systems and hence can form simple and mixed ligand complexes with biologically active ligands (Choudhary et al., 2011). Mixed ligand complexes have been found to be biologically active against pathogenic microorganisms (Patil et al., 2011; Thakkar & Thakkar, 2000) and can act as active catalysts in industrially useful reactions (Patil et al., 2012). Amino acids are biologically active ligands and have the ability to form various types of metal complexes. Amino acids involved mixed ligand complexes may give a better understanding about the reactions of various drugs that may undergo in the body (Iakovidis & Hadjiliadis, 1989) and are also significant potential model for enzyme metal ion substrate complex (Choudhary et al., 2011; Thakkar & Thakkar, 2000). Patel & Joshi (1997) have reported the formation and the stability constants of mixed ligand

Ni(II), Zn(II) or Cd(II) complexes potentiometrically in aqueous solution involving iminodiacetic acid and phenylalanine. Mixed Al^{3+} complex in aqueous solution with β-phenylalanine and iminodiacetic acid has also been identified (Petrosyants et al., 1996). Synthesis, characterization, antibacterial and antimicrobial studies of some transition metal mixed ligand complexes formed with phenylalanine and pyrimidine nucleoside (uridine) (Reddy & Reddy, 2000), 8-ydroxyquinoline (Patil et al., 2011), 1-nitroso-2 naphthol (Fayad et al,, 2012) or 5-flurouracil (Choudhary et al., 2011; Shobana et al., 2012) have been earlier reported. In earlier publications (Kumar, 2007; Kumar & Kiremire, 2007; Kumar, 2008) mixed ligand octahedral complexes of some transition metals formed with iminodiacetic acid and hippuric acid have been studied. Literature is lacking on the studies of mixed ligand transition metal complexes formed with phenylalanine and iminodiacetic acid. Hence this paper describes the synthesis and characterization of mixed ligand Cu(II) and Co(II) complexes of iminodiacetic acid and phenylalanine.

Experimental

Solutions of L-phenylalanine (Aldrich) and iminodiacetic acid (Aldrich) were prepared in one equivalent of sodium hydroxide. Solutions of metal ions, $CuCl_2.2H_2O$ (BDH) and $CoCl_2$ (Rochelle Chemicals) were prepared in one equivalent of hydrochloric acid.

Synthesis of Cu(II) complex

Two ligands solutions (0.1M) were mixed with 0.1 M metal ion solution in 1:1:1 volume ratio at room temperature. At first phenylalanine solution was mixed with $CuCl_2.2H_2O$ solution followed by iminodiacetic acid solution and the pH of the solution was adjusted to ~ 4.24 by adding sodium hydroxide. On adding phenylalanine solution to metal ion solution, a light blue solution was obtained with pH 0.51. On the addition of iminodiacetic acid to this solution, the pH of the resulting dark blue solution was adjusted to ~ 4.24 by adding sodium hydroxide. The dark blue solution was then concentrated between 20-25 ml over a steam bath and allowed to crystallize. Dark blue crystalline product was then filtered and washed first with 50% water – ethanol mixture followed by acetone and dried in a vacuum desiccator.

Synthesis of Co(II) complex

Two ligands solution (0.1M) were mixed with anhydrous Co(II) chloride solution in 1:1:1 volume ratio at room temperature. At first phenylalanine solution was added to the metal ion solution followed by iminodiacetic acid solution and the pH of the solution was adjusted to ~ 5.12 by adding sodium hydroxide solution. On the addition of phenylalanine to the metal ion solution, a pink solution with pH 2.92 was obtained. On the addition of iminodiacetic acid solution to this solution, a clear pink solution was obtained with pH 2.56 which was raised to ~ 5.12 by adding sodium hydroxide. The clear pink solution was then concentrated over a steam bath between 20 to 25 ml and allowed to crystallize. The dark violet crystalline product was then filtered and washed with 50% water – ethanol mixture followed by acetone.

The IR spectra of the ligands and metal complexes were recorded on a Perkin Elmer FT-IR 2000 spectrophotometer in 4000-400 cm^{-1} range using KBr disc. The magnetic susceptibility of the complexes was measured at room temperature using Johnson Matthey Alfa product magnetic susceptibility balance. Schimadzu UV-vis 2501 model TCC-240A was used to record the electronic spectra of the complexes in 200-1100 nm range. The elemental analysis (CHN) was carried out on a Vario EL CHNO/S elemental analyzer.

Results and discussion

Elemental analysis

(1) Sodium(phenylalaninato)(iminodiacetato)(monoaqua)copper(II). Dark blue crystals. Anal. Calcd for $Na[Cu(C_6H_5CH_2CH(NH_2)COO)\{NH(CH_2COO)_2\}.H_2O]$: C= 39.05% ; H= 4.29% ; N = 7.00%. Found C = 38.61%; H = 3.98%; N = 6.87%.

(2) Sodium(phenylalaninato)(iminodiacetato)(monoaqua)cobalt(II). Pink powder. Anal. Calcd for $Na[Co(C_6H_5CH_2CH(NH_2)COO)\{NH(CH_2COO)_2\}.H_2O]$: C = 39.70%; H = 4.36% ; N = 7.12%. Found C = 39.40%; H = 4.35%; N = 6.84%.

IR studies

Iminodiacetic acid shows characteristic ν (C=O) adsorption band for COOH group at 1702 cm^{-1} which does not appear in case of metal complexes. Instead, asymmetric and symmetric stretching COO^- frequencies are observed. The Cu(II) complex shows $\nu_{as}COO^-$ and ν_sCOO^- frequencies at 1615 cm^{-1} and 1382 cm^{-1} respectively whereas in Co(II) complex these bands are observed at 1558 cm^{-1} and 1404 cm^{-1} respectively. The ν(CN) absorption band in iminodiacetic acid is observed at 1330 cm^{-1} which is lowered in metal complexes. The ν(NH) absorption band in iminodiacetic acid appears at 3092 cm^{-1}. This band appears at 3247 cm^{-1} and 3275 cm^{-1} in Cu(II) and Co(II) complexes respectively. Therefore, it can be concluded that iminodiacetic acid in both the complexes act as a tridentate ligand coordinating through the carboxylate oxygen atoms and nitrogen of the NH group. Phenylalanine is an amino acid and therefore as a zwitter ion it may be written as [$C_6H_5CH_2CH(N^+H_3)COO^-$]. Thus it should show characteristic bands (N^+H_3 and COO^-) of amino acids (Srivastava & Srivastava, 1977). Free amino acids show $\nu(N^+H_3)$ band in 3130 cm^{-1} – 3030 cm^{-1} region. In the formation of metal complexes, N^+H_3 is deprotonated and coordinates to the metal through the neutral NH_2 group. This should be supported by an increase in $\nu(NH_2)$ absorption frequency and a characteristic band should appear in 3500-3300 cm^{-1} region (Reddy & Reddy, 2000). In the present study, the IR spectra of phenylalanine shows a characteristic band at 3068 cm^{-1} attributable to the N^+H_3 and is not present in case of metal complexes indicating the deprotonation of N^+H_3 to NH_2 group (Reddy & Reddy, 2000). Instead new bands at 3180 cm^{-1} and 3275 cm^{-1} in case of Cu(II) and Co(II) complexes respectively are observed lower than in $\nu(NH_2)$ group region. Thus it appears that in metal complexes nitrogen of the amino group is involved in the coordination (Reddy & Reddy, 2000). The IR spectra of phenylalanine also shows characteristic ν_{as} COO^- and ν_s COO^- bands

Table 1. IR frequencies (cm^{-1}) of ligands and their metal complexes

Phenylalanine	Iminodiacetic acid	Na[Cu(Phe)(IDA).H_2O]	Na[Co(Phe)(IDA).H_2O]	Band assignment
--	--	3518	3499	ν(OH) water molecule
3068	--	--	--	ν (N^+H_3) amino acid
--	--	3180	3275	$\nu(NH_2)$ coordinated
1623	--	1615	1558	$\nu_{as}COO^-$
1408	--	1383	1404	ν_sCOO^-
--	1702	--	--	ν(C=O) COOH group
--	3092	3247	3275	ν(NH)
--	3020	2942	2962	ν(CH)
--	--	833	848	$\rho_r(H_2O)$ coordinated
--	--	556	524	ν(M-N)

Note: *Ph and IDA stand for the anion of phenyalalanine and iminodiacetic acid respectively in Tables 1 and 2.*

at 1623 cm^{-1} and 1408 cm^{-1} respectively. Cu(II) complex shows these bands at 1615 cm^{-1} and 1385 cm^{-1} respectively. However these bands in Co(II) complex are observed at 1558 cm^{-1} and 1404 cm^{-1}, respectively. The difference ($\Delta\nu_{as}$ - ν_s) of 230 cm^{-1} and 154 cm^{-1} supports the monodentate coordination of the carboxylate group (Mitic et al., 2009; Devereux et al., 1998). Besides Cu(II) and Co(II) complexes also show additional bands at 3518 cm^{-1} and 3499 cm^{-1} attributable to water molecules (Nakamoto, 1970). The presence of $\rho_r(H_2O)$ frequency at 833 cm^{-1} and 848 cm^{-1} in case of Cu(II) and Co(II) complexes, respectively, confirms the presence of coordinated water molecules (Nakagawa & Shimanouchi, 1964). The main IR frequencies of ligands and the metal complexes are listed in Table 1.

Magnetic measurements and electronic spectra

The observed magnetic moment for Cu(II) complex, sodium(phenylalaninato) (iminodiacetato)(monoaqua) copper complex, μ_{eff} = 1.90 BM suggests a spin free octahedral structure for the complex (Figgis & Lewis, 1960) which is supported by its electronic spectra (Lever, 1986). The band observed at 14925 cm^{-1} can be regarded as d-d transition band. The complex also shows a band at 31879 cm^{-1} which can be assigned as a charge transfer band from ligand to metal. For the Co(II) complex, sodium (phenylalaninato) (iminodiacetato)(monoaqua) cobalt(II), a spin free octahedral structure is also suggested on the basis of the observed magnetic moment (μ_{eff}) of 5.11 BM (Figgis & Lewis, 1960) which is supported by its electronic spectra. In this complex the band, observed at 19120 cm^{-1} can be regarded as a ν_3 transition. The position of ν_2 transition in case of octahedral Co(II) complexes may, however, be ambiguous (Lever, 1986) and is rather difficult to

Table 2. Magnetic measurements and electronic spectra of Cu(II) and Co(II) complexes

Complex	Magnetic measurements					Electronic spectra	
	Temp (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(Ph)(IDA).H_2O]	300	3.5240	1406.076	1505.386	1.90	14925	31879
Na[Co(Ph)(IDA).H_2O]	299	27.881	10963.19	11062.49	5.11	19120	34843

observe with certainty. The ν_1 transition occurs at lower frequencies and is expected to be observed beyond 1000 nm in the near infra red region. Thus in the present complex, a band observed at 9302 cm^{-1} (1075 nm) can be assigned as ν_1 transition (Cotton et al., 1999). The band observed at 34847 cm^{-1} can be regarded as a charge transfer band for the Co(II) complex. The observed magnetic measurements and the electronic spectra data are given in Table 2.

Conclusion

Thus data obtained above suggest spin free octahedral structures for both the complexes. In both the complexes iminodiacetic acid acts as a tridentate ligand. However, phenylalanine acts as a bidentate ligand and the sixth coordination position is satisfied by one water molecule.

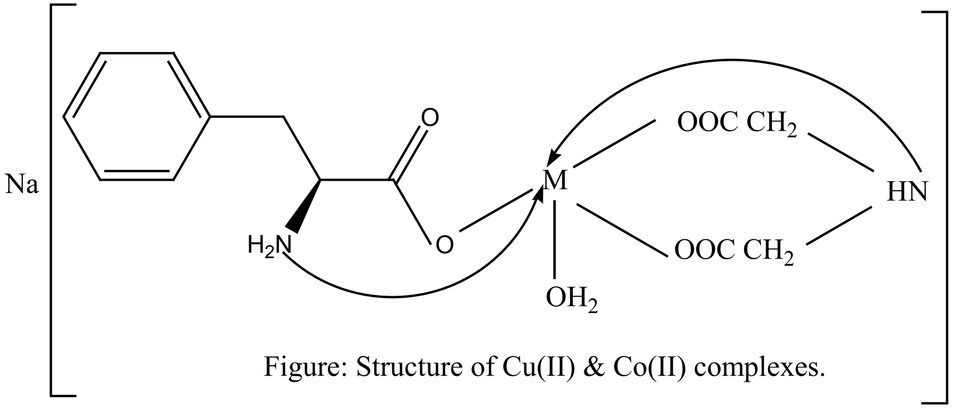

Figure: Structure of Cu(II) & Co(II) complexes.

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NOTES

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