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SYNTHESIS AND CHARACTERIZATION OF MIXED LIGAND CO(II) AND NI(II) COMPLEXES WITH L- PHENYLALANINE AND HIPPURIC ACID

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Abstract. The mixed ligand complexes, $[M(HA)(Phe).2H_2O].2H_2O$, where HA and Phe are the anions of hippuric acid and phenylalnine respectively and M=Co(II) and Ni(II) ions, were synthesized and characterized by FTIR, UV-vis, elemental analysis, TGA and magnetic measurements. Both the ligands act as bidentate, coordinating through carboxylate oxygen and nitrogen atoms. The two coordination positions are occupied by water molecules, hence six fold octahedral geometry has been suggested to both the complexes.

Keywords: hippuric acid, phenylalanine, Co(II), Ni(II) complexes, synthesis, characterization

Introduction

Mixed ligand complexes play a vital role in several chemical systems, e.g. electroplating, ion exchange resins, water softening (Sanap & Patil, 2013). Study of such complexes has also become important because of their role in biological systems as they serve as models for many metalloenzymes (Reddy & Reddy, 2002; Sigel, 1973). Amino acids with many different functional groups are capable of forming metal complexes via carboxylate and amino groups (Shamsi et al., 2014). Phenylalanine is an aromatic essential glucogenic and ketogenic amino acid and is capable of forming simple and mixed ligand transition metal complexes. Study on the formation and characterization including biological activities of mixed ligand complexes of some transition metals with phenylalanine and N,N-bis(2-hydroxyethyl)glycine have been reported (Taha & Khalil, 2005). Literature survey has not revealed the studies on the mixed ligand transition metal complexes formed with phenylalanine and hippuric acid. Thus the present paper describes the synthesis and characterization of Co(II) and Ni(II) complexes of L-phenylalanine and hippuric acid.

Experimental

The two ligands, L-phenylalanine (Aldrich) and hippuric acid (Fluka) were dissolved in one equivalent of sodium hydroxide and metal ions, $CoCl_2$ (Rochelle chemical) and $NiCl_2$ (Rochelle chemical) solutions were prepared in one equivalent of hydrochloric acid.

Vario EL CHNO/S elemental analyzer (UB) was used to carry out elemental analysis (C H N) of the complexes. The magnetic susceptibility of the complexes at room temperature was measured using Johnson Matthey Alfa Product susceptibility balance (UB). IR spectra of the ligands and the complexes were recorded on a Perkin Elmer FT-IR 2000 spectrophotometer in 400-4000 cm^{-1} range using KBr disc (UB). Perkin Elmer UV/VIS/NIR Spectrometer Lambda 750 (IISc) was used to record electronic spectra of metal complexes in solid state in 200-1300 nm range. Thermogravimetric analysis (TGA) was done on a Mettler Toledo TGA/SDTA 851^{e} instrument (IISc) at a heating rate of 10^{o}C/min under nitrogen atmosphere.

Synthesis of Co(II) complex

The ligand solutions (0.1M) were mixed with 0.1M $CoCl_2$ solution in 1:1:1 volume ratio at room temperature. At first phenylalanine solution was added to $CoCl_2$ solution followed by hippuric acid solution and the pH of the resulting mixture solution was adjusted to ~5.08 by adding sodium hydroxide solution. The color of the solution remained pink throughout the experiment. The light pink solution was then concentrated over a steam bath to reduce the volume between 20-25 ml and allowed to crystallize overnight. Light pink crystalline product was then filtered and washed first with 50% alcohol-water mixture followed by acetone and dried in a vacuum desiccator.

Synthesis of Ni(II) complex

Solutions of both ligands (0.1M) were mixed with 0.1M $NiCl_2$ solution in 1:1:1 volume ratio at room temperature. Phenylalanine solution was first mixed with $NiCl_2$ solution followed by hippuric acid solution and the pH of the resulting mixture was adjusted to ~ 5.5 by adding sodium hydroxide solution. This resulting mixture solution was then concentrated over a steam bath to reduce the volume of the solution between 20-25 ml. and allowed to crystallize overnight. The light blue powder product was then filtered and washed with 50% water alcohol mixture followed by acetone and dried in a vacuum desiccator.

Results and discussion

Elemental analysis

(1) [(Diaqua) (hippurato) (phenylalaninato) cobalt(II) dihydrate]. Light pink

crystals. Anal. Calcd for [Co($C_6H_5CONHCH_2COO$)($C_6H_5CH_2CH(NH_2)$) COO.$2H_2O$].$2H_2O$; C=45.67 % ; H=5.55% ; N=5.91%. Found C=45.12% ; 5.23% ; N=5.83%.

(2) [(Diaqua) (hippurato) (phenylalaninato) nickel(II) dihydrate]. Light blue powder. Anal. Calcd for [Ni($C_6H_5CONHCOO$)($C_6H_5CH_2CH(NH_2)$) COO.$2H_2O$].$2H_2O$; C=45.69%; H=5.55% ; N=5.92% . Found C=45.31%; H=5.15%; N=6.04%.

IR studies

In hippuric acid, the characteristic ν(C = O) absorption band for the COOH group is observed at 1740 cm^{-1} which vanishes in metal complexes. Instead, complexes show asymmetric and symmetric stretching frequencies. Both Co(II) and Ni(II) complexes show $\nu_{as}COO^-$ and ν_sCOO^- bands at 1603 cm^{-1} band at ~ 1400 cm^{-1} respectively. ν(NH) absorption band in hippuric acid appears at 3336 cm^{-1} which is lowered in both the complexes. The presence of these absorption bands in the complexes confirm that hippuric acid acts as a bidentate ligand, coordinating through the carboxylate oxygen and the nitrogen atom of the amido group. Phenylalanine being an amino acid shows characteristic $\nu(NH_3^+)$ zwitter ion band at 3068 cm^{-1} which does not appear in both the complexes indicating the deprotonation of $\nu(NH_3^+)$ to NH_2 group. The presence of new bands in both the complexes at lower frequencies than NH_2 group region confirm that the nitrogen atom of the amino group of the phenylalanine is involved in the coordination (Reddy & Reddy, 2000). Phenylalanine also shows $\nu_{as}COO^-$ and ν_sCOO^- absorption bands at 1623 cm^{-1} and 1408 cm^{-1} respectively as was reported in earlier publication (Kumar et al., 2013). Both the complexes show these bands at ~ 1600 cm^{-1} and 1400 cm^{-1} respectively confirm the coordination through the carboxylate oxygen of the phenylalanine (Shamsi et al., 2014).Thus it can be concluded that the phenylalanine also acts as a bidentate ligand in both the complexes coordinating through carboxylate oxygen and nitrogen atoms. Besides both Co(II) and Ni(II) complexes also show additional bands at 3468 cm^{-1} and 3352 cm^{-1}respectively attributable to water molecules. The absorption bands at 717-843 cm^{-1} and 723-850 cm^{-1} in Co(II) and Ni(II) complexes respectively confirm the presence of coordinated water (Shamsi et al., 2014 , Nakamoto, 1970). In view of the above IR discussion, the structure of Co(II) and Ni(II) complexes is proposed in Fig. 1. The main IR frequencies of ligands and the metal complexes are given in Table 1.

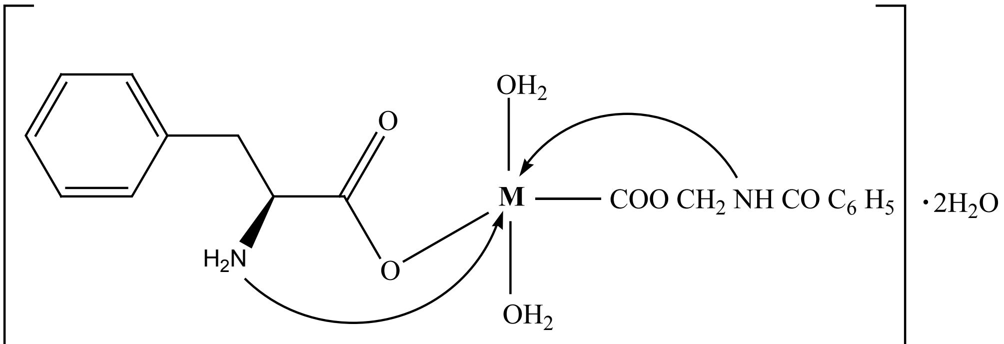

Figure 1: Structure of M(HA)(Phe) complexes ; M = Co (II) and Ni(II)

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

Phenyl-alanine	Hippuric acid	[Co(HA)(Phe).2H$_2$O].2H$_2$O	[Ni(HA)(Phe).2H$_2$O].2H$_2$O	Band assignment
3068	--	--	--	ν(NH$_3^+$) amino acid
--	--	3468	3352	ν(OH) water molecule
--	--	3155	3174	ν(NH$_2$) coordinated
--	1740	--	--	ν(CO) COOH group
1623	--	1603	1603	ν$_{as}$(COO$^-$)
1408		1397	1400	ν$_s$(COO$^-$)
--	3336	3286	3293	ν(NH)
--	3071	2967	3027	ν(CH)
--	--	717	723	ρ(H$_2$O) coordinated

Magnetic measurements and electronic spectra

The observed magnetic moment of cobalt(II) complex, [Co(C$_6$H$_5$CONHCH$_2$COO)(C$_6$H$_5$CH$_2$CH(NH$_2$) COO.2H$_2$O].2H$_2$O , μ_{eff} = 4.20 BM, higher than the free spin value of magnetic moment for three unpaired electrons due to the orbital contribution, suggests a spin free octahedral geometry around the metal (Figgis & Lewis, 1960). Octahedral cobalt(II) has d^{7}configuration and are generally expected to show three spin

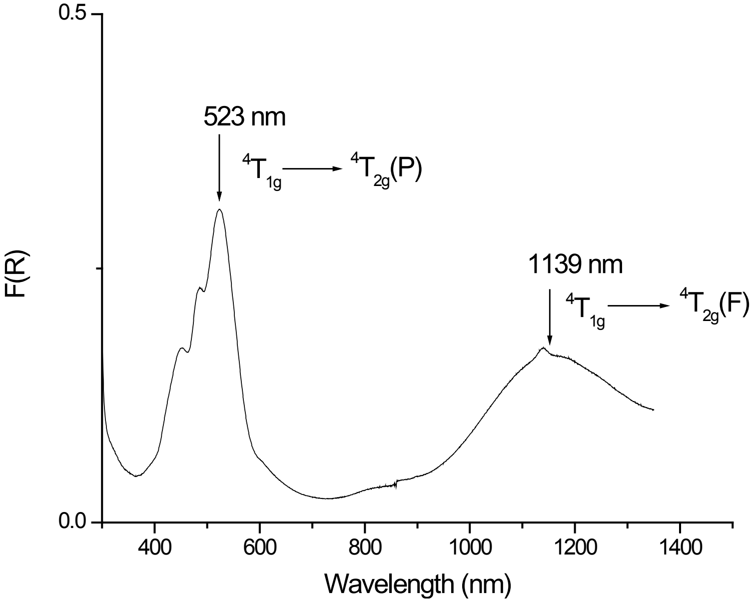

Fig. 2(a). Electronic spectra of Co(II) complex

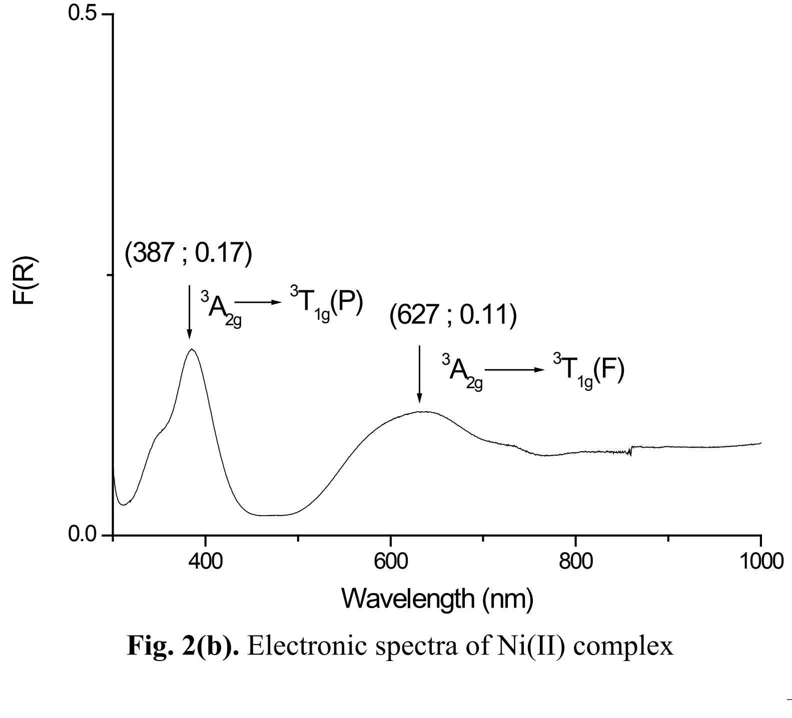

Fig. 2(b). Electronic spectra of Ni(II) complex allowed transitions: (ν_1) $^4T_{1g}\rightarrow{}^4T_{2g}(F)$; (ν_2) $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ and (ν_3) $^4T_{1g}\rightarrow{}^4T_{2g}(P)$. The electronic spectra of cobalt(II) complexes showed main absorption band observed at 523 nm (19120 cm^{-1}) assignable to ν_3 transition whereas band observed at 1139 nm (8780 cm^{-1}) can be assigned to ν_1 transition (Lever, 1986). The position of ν_2 is however ambiguous and is not observed clearly (Raman et al., 2004; Cotton et al., 1999). For Ni(II) complex, $[Ni(C_6H_5CONHCH_2COO)(C_6H_5CH_2CH(NH_2)COO.2H_2O].2H_2O$, the observed magnetic moment, μ_{eff} = 2.9 B M suggests a high spin octahedral geometry around the metal (Figgis & Lewis, 1960). Octahedral nickel(II) has d^{8}configuration and generally show three allowed transitions: (ν_1) $^3A_{2g}\rightarrow{}^3T_{2g}$; ($\nu_2$) $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and (ν_3) $^3A_{2g}\rightarrow{}^3T_{1g}(P)$. The electronic spectra of nickel(II) complex shows two bands at 627 nm (15949 cm^{-1}) and 387 nm(25840 cm^{-1}) attributable to ν_2 and ν_3 transitions respectively (Lever, 1980, Raman et al., 2004).The UV-vis spectra of Co(II)and Ni(II) complexes in solid state are given in Figs 2(a) and 2(b), respectively.

Thermogravimetric analysis (TGA)

In order to understand the fragmentation patterns, information about the structure of the compounds is necessary. We are going to use the structure of Co(II) and Ni(II) complexes presented in figure 1 to discuss the TGA results. TGA analysis allows understanding the fragmentation process and the thermal stability of compounds (Badea et al., 2003).

Cobalt(II) complex

The complex is thermally stable up to 72°C and then loses two uncoordinated water molecules. A fast and continuous decomposition of the complex follows to afford a 12 % residue corresponding to Co metal. The TGA plot of cobalt(II) complex is shown in Fig. 3(a).

Nickel(II) complex

The complex is stable up to 74°C and then loses two uncoordinated molecules. After this step, a fast and continuous decomposition of the complexes takes place to afford a 23 % residue corresponding to Ni-CO_2. The TGA plot of this complex is given in Fig. 3(b).

After losing the uncoordinated water molecules, both complexes displayed fast and continuous decomposition emphasizing that all the intermediate fragments are not stable. This behavior has been observed with other systems reported previously (Masoud et al., 2013; Baran et al., 2012). The two complexes have similar thermal stability (~ 70 °C). Each of the metal complexes has a final residue different from the other. The cobalt

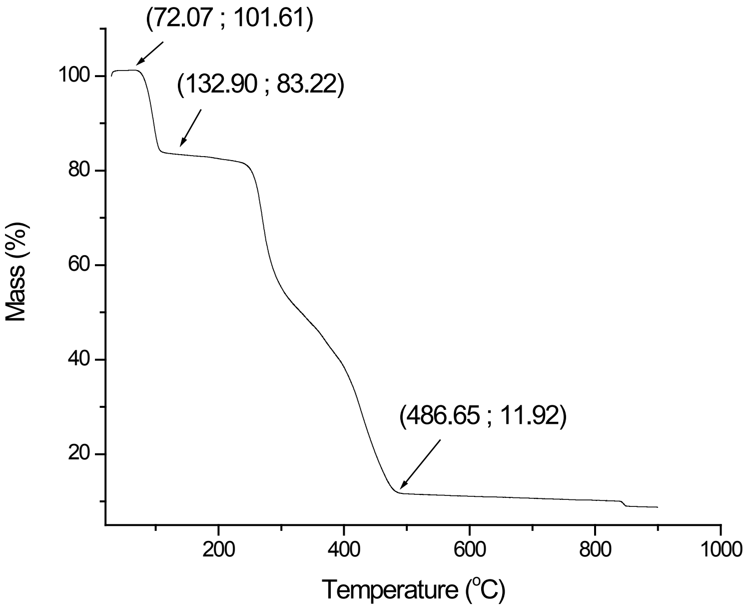

Fig. 3(a). TGA graph of cobalt(II) complex

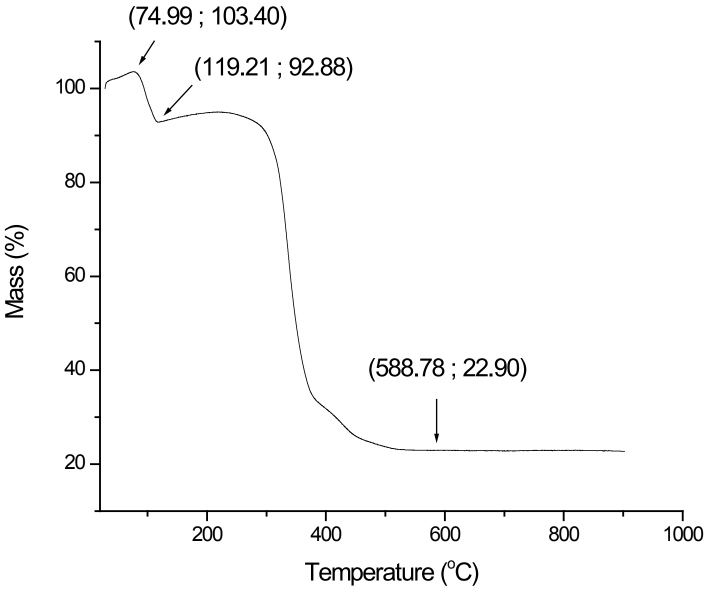

Fig. 3(b). TGA graph for Ni(II)-Ph-HA complex ends up with cobalt metal while the nickel complex residue is of Ni-CO_2. Both cobalt and nickel complexes loose uncoordinated water molecules before decomposition is completed.

The decomposition patterns obtained from TGA are in good agreement with the proposed structures of the complexes. The TGA results of the two complexes are summarized in Table 2.

Table 2. Summary of TGA results for the Co(II) and Ni(II) complexes

Complex	Stability (°C)	Fragment lost/Remaining residue	Temperature range (°C)	Calculated %	TGA (found) %
Co(II)-Ph-HA	72	2 H_2O	72-132	7.61	6.88
		Total decomposition	240-486	81.55	82.08
		Co residue	486	12.45	11.92
Ni(II)-Ph-HA	74	2 H_2O	74-119	7.60	7.12
		Total decomposition	287-588	78.29	77.10
		Ni-CO_2 residue	588	21.71	22.90

Conclusion

Thus the above studies suggest spin free octahedral structures for both Co(II) and Ni(II) complexes in which both phenylalanine and hippuric acid act as a bidentate ligands. The remaining two coordination positions are satisfied by two water molecules.

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