

Research Article

Study on the Coordination Behavior of Amide Derivatives of Copper (II) Complexes

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Abstract

The new amide ligands **I**, **II** and **III** are prepared by reacting salicylic acid, cinnamic acid and benzoic acid with α -naphthyl amine respectively. The Copper (II) complexes are also prepared and their nature of combination is studied using IR, UV and conductivity studies. The ligands are irradiated in micro wave oven. The UV absorption at 525, 500 and 503nm confirms the formation of complex A, B and complex C. From the value of molar conductance of the Copper II complexes shows that the complexes are non-electrolytic in nature. The mode of coordination is **N-Cu—O**, **N-Cu—C**, and **N-Cu** for complex A, complex B, complex C respectively.

Keywords: α -naphthyl amine, salicylic acid, cinnamic acid, benzoic acid, conductivity measurements

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Introduction

The chemistry of transition metal complexes has received considerable attention largely due to their catalytic, bioinorganic and biological activities such as antibacterial, antifungal, antiviral, antimalarial and antitumor¹⁻⁵.

The identification of deprotonated carboxamide-N coordination in a few metalloenzymes has prompted the synthetic chemists to incorporate amide functional group in the ligand design⁶. A large number of examples are available in literature where amide-based ligands have been explored for their co-ordination chemistry⁷.

Some of these ligands have been highly successful in stabilisation of metal ion in their high oxidation state⁸. This fact is attributed to the strong donation ability of deprotonated amide group^{9,10,11,12} the resulting complexes are of considerable interest as biological models for metalloproteins^{13,14} and functional catalysis¹⁵.

Copper participate in many biological reactions such as reversible binding of dioxygen eg:-haemocyanin(Cu), activation of dioxygen eg:-dopamine hydroxylase(Cu), also utilized in the synthesis of the hormone Epinephrine, electron transfer eg:-Plastocyanins(Cu), dismutation of superoxide by Cu redox active metal¹⁶ etc.

Experimental work**Materials and Reagents**

Thin Layer Chromatography (TLC) was performed using glass plates coated with silica gel. Petroleum ether and ethyl acetate was used as eluant. Spots were visualized with iodine. Purification of crude sample was carried out using chromatographic column packed with silica gel. IR spectra were recorded in NICOLET IR 200-FT-IR spectrometer using KBr disc and the absorption frequencies quoted in reciprocal centimeters. UV spectra were recorded in UV-VIS spectrophotometer 3000⁺, LAB INDIA. Elemental analysis was carried out with Perkin Elmer 2400 series for C,H, O and N, the solvents and reagents used for synthesis were of reagent grade and purified by standard methods.

Procedure

Preparation of ligand –I

Equal moles of α -naphthyl amine and Salicylic acid was dissolved in 20 mL of ethanol and stirred continuously for 5 minutes. The reaction mixture was irradiated for 30 seconds in microwave oven. Completion of the reaction was monitored by TLC. The product was filtered, washed thoroughly with water and then dried in vacuum. The compound was recrystallized from ethanol.

Preparation of ligand –II

Equal moles of α -naphthyl amine and Cinnamic acid was dissolved in 20 mL of ethanol and stirred continuously for 5 minutes. The reaction mixture was irradiated for 30 seconds in microwave oven. Completion of the reaction was monitored by TLC. The product was filtered, washed thoroughly with water and then dried in vacuum. The compound was recrystallized from ethanol.

Preparation of ligand –III

Equal moles of α -naphthyl amine and Benzoic acid was dissolved in 20 mL of ethanol and stirred continuously for 5 minutes. The reaction mixture was irradiated for 2 minutes in microwave oven. Completion of the reaction was monitored by TLC. The product was filtered, washed thoroughly with water and then dried in vacuum. The compound was recrystallized from ethanol.

Table 1 Physical Data and Conductivity measurement of ligands and complexes*

Compound	Ligand-I	Ligand-II	Ligand-III	Complex-A	Complex-B	Complex-C
M.F	C ₁₇ H ₁₃ NO ₂	C ₁₉ H ₁₅ NO	C ₁₇ H ₁₃ NO	C ₁₇ H ₁₂ NO ₂ (PPh ₃)CuCl	C ₁₉ H ₁₅ NO CuCl ₂	C ₁₇ H ₁₃ NO(PPh ₃) CuCl ₂
M.wt (g/mol)	263	273	247	556	408	577
m.p^oc	158	156	132	370	370	337
Colour	Dark red	Dark violet	Dark brown	Dark red	Violet	Brown
Yields (%)	80	80	85	80	80	80
Conductivity ohm⁻¹ m².mol⁻¹	-	-	-	7.5	9.6	14.0

Preparation of New Copper (II) Complex A:

0.5g (0.004mol) of dichlorobis(triphenyl phosphine) copper (II) dissolved in 20mL of ethanol and 1g (0.004mol) of ligand I was added to it. The reaction mixture was refluxed for 30minutes and completion of the reaction was monitored by TLC. Dark crystals obtained were separated, washed with ethanol and dried under vacuum.

Preparation of New Copper (II) Complex B:

0.5g (0.004mol) of dichlorobis(triphenyl phosphine) copper (II) dissolved in 20mL of ethanol and 1g (0.004mol) of ligand II was added to it. The reaction mixture was refluxed for 30minutes and completion of the reaction was monitored by TLC. Dark crystals obtained were separated, washed with ethanol and dried under vacuum.

Preparation of New Copper (II) Complex C:

1g (0.004mol) of ligand III and 0.5g (0.004mol) of dichlorobis(triphenyl phosphine) copper (II) was dissolved in 20mL of ethanol and the uniform solution was refluxed for 1 hour and completion of the reaction was monitored by TLC. Dark crystals obtained were separated. Then washed with ethanol and dried under vacuum.

Results and Discussion

The **ligand I** was synthesized by reacting salicylic acid and α -naphthylamine. Equal moles of salicylic acid and α -naphthylamine were irradiated under microwave for 30 seconds. The progress of the reaction was monitored by TLC periodically. After the completion of the reaction, the reaction mixture was poured into water, filtered and dried. Recrystallisation of the crude from ethanol gave brown colored crystals.

After obtaining the **Ligand I**, the copper complex was prepared by reacting the **Ligand I** with $\text{CuCl}_2(\text{PPh}_3)_2$. Accordingly, an ethanolic solution of $\text{CuCl}_2(\text{PPh}_3)_2$ (0.004 mol), and **Ligand I** (0.004 mol) was refluxed for 30 minutes. After the completion of the reaction, the reaction mixture was diluted with ethanol and kept overnight. The crystals obtained were washed with petroleum ether and recrystallised from ethanol.

The **ligand II** was synthesized by reacting cinnamic acid and α -naphthylamine. Equal moles of cinnamic acid and α -naphthylamine were irradiated under microwave for 30 seconds. The progress of the reaction was monitored by TLC periodically. After the completion of the reaction, the reaction mixture was poured into water, filtered and dried. Recrystallisation of the crude from ethanol gave brown coloured crystals.

After obtaining the **Ligand II**, the copper complex was prepared by reacting the Ligand II with $\text{CuCl}_2(\text{PPh}_3)_2$. Accordingly, an ethanolic solution of $\text{CuCl}_2(\text{PPh}_3)_2$ (0.004 mol), and Ligand II (0.004 mol) was refluxed for 30 minutes. After the completion of the reaction, the reaction mixture was diluted with ethanol and kept overnight. The crystals obtained were washed with petroleum ether and recrystallised from ethanol.

The amide was prepared by reacting α -naphthylamine with benzoic acid. Accordingly, an ethanolic solution of α -naphthyl amine and benzoic acid were irradiated under microwave for 2 minutes. The residue obtained was poured into water, filtered, dried and recrystallised from ethyl acetate.

Accordingly, an ethanolic solution of $\text{CuCl}_2(\text{PPh}_3)_2$ (0.004 mol) and **Ligand III** (0.004 mol) were mixed together and refluxed for 1 hour. The content was diluted with ethanol and was allowed to stand overnight. The crystals were formed and washed with petroleum ether and recrystallised from ethanol. The characterization of ligand and complexes were given below

- Infrared Spectra

A detailed interpretation of the IR spectra of ligand and effect of binding with Cu on the vibrations frequencies of the free ligand discussed. The IR spectra of the free ligand and its metal chelates were carried out in the 4000-400cm⁻¹ range.

The IR (cm⁻¹) (v_{max}) spectrum for **ligand-I** showed a band at 1676 cm⁻¹ which indicated the presence of 'C=O' group and the spectrum showed bands at 3381 and 3600 cm⁻¹ assigned for (O-H) & (N-H).

The IR (cm⁻¹) (v_{max}) spectrum for **complex-A** showed a band at 1657cm⁻¹ which indicated the presence of 'C=O' group and the spectrum showed bands at 3233 cm⁻¹ for (N-H) and the O-H band was disappeared.

The IR(cm⁻¹) (v_{max}) spectrum for **ligand-II** showed a bands at 1682 & 1328 cm⁻¹ which indicated the presence of 'C=O' & C=C group and the spectrum showed bands at 3014 cm⁻¹ assigned for (N-H).

The IR(cm⁻¹) (v_{max}) spectrum for **complex-B** showed a bands at 1671 & 1323 cm⁻¹ which indicated the presence of 'C=O' & C=C group and the spectrum showed bands at 2973 cm⁻¹ assigned for (N-H).

The IR(cm⁻¹) (v_{max}) spectrum for **ligand-III** showed a band at 1655 cm⁻¹ which indicated the presence of 'C=O' group and the spectrum showed bands at 3222 cm⁻¹ assigned for (N-H).

The IR(cm⁻¹) (v_{max}) spectrum for complex-C showed a band at 1681 cm⁻¹ which indicated the presence of 'C=O' group and the spectrum showed vibrational bands at 3018 cm⁻¹ assigned for (N-H). The Shift of IR from 3222cm⁻¹ (NH) of ligand-III to 3018cm⁻¹ (NH) of the **complex C** showed the occurrence of coordination.

- Electronic Spectra

The electronic spectra for amides and their Copper (II) complexes were recorded in ethanol solvent, the electronic data of the ligand exhibit in UV-region.

The UV Spectrum of the **Ligand I** showed absorption bands at 265,295 & 308nm for (n- π*) & (π- π*) transitions.

The UV Spectrum of the **Complex-A** showed absorption bands at 295,305nm & 525nm for (n- π*) & (π- π*) transitions. The UV absorption at 525nm confirmed the formation of complex-A.

The UV Spectrum of the **Ligand II** showed absorption bands at 266, 291 & 367nm for (n- π*) & (π- π*) transitions.

The UV Spectrum of the **Complex-B** showed absorption bands at 264, 285 & 500nm for (n- π*) & (π- π*) transitions. uv absorption at 500nm confirmed the formation of **Complex-B**.

The UV spectrum of the **ligand- III** shows absorption bands at 239nm and 367nm for (n- π*) & (π - π*) transitions. UV spectral data of the **Complex-C** shows absorption bands at 296, 469nm for charge transfer and 503nm d- d for the absorption of copper complex.

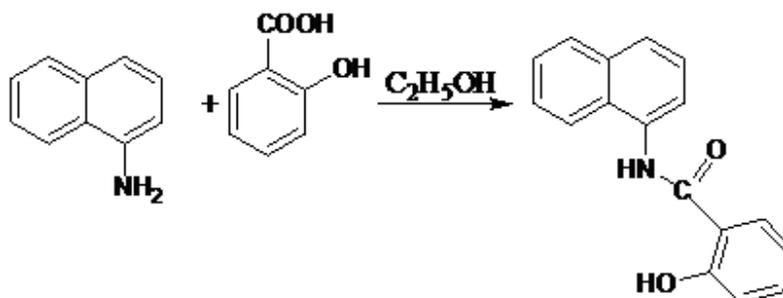
- Molar Conductance Measurements :-

The molar conductance of this complex-A in water was 7.50 ohm⁻¹cm²mol⁻¹ at room temperature showed that the **complex-A** was non-electrolytic in nature.

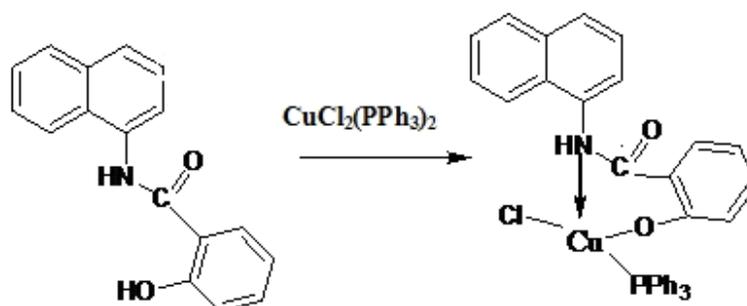
The molar conductance of this complex-B in water was $9.6 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ at room temperature showed that the **complex-B** was non-electrolytic in nature.

The molar conductance of this complex-C in water was $14 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ at room temperature showed that the **complex-C** was non-electrolytic in nature.

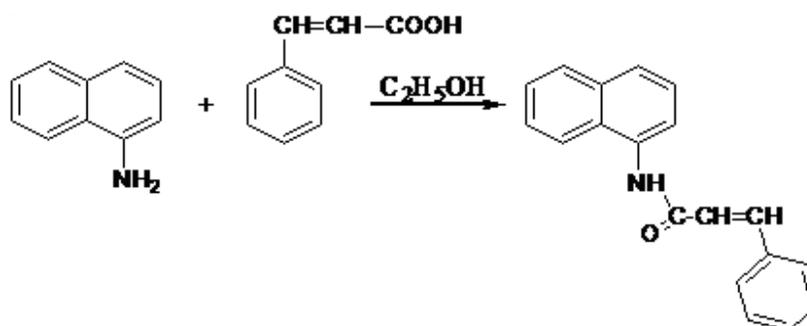
- Plausible mode of coordination of the Metal Complexes :-



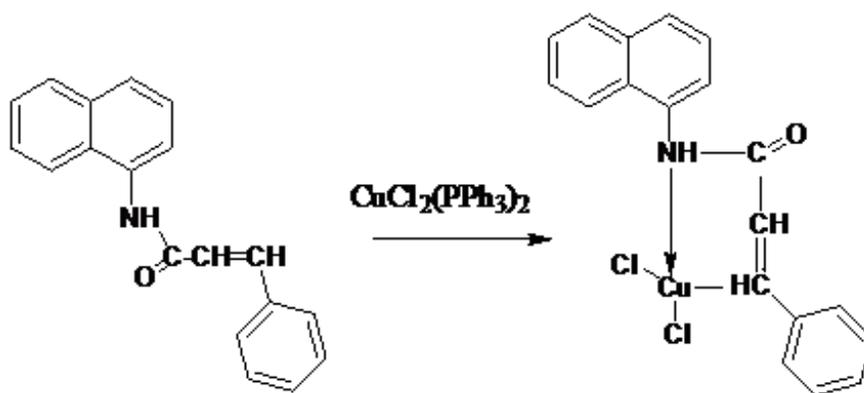
Scheme 1



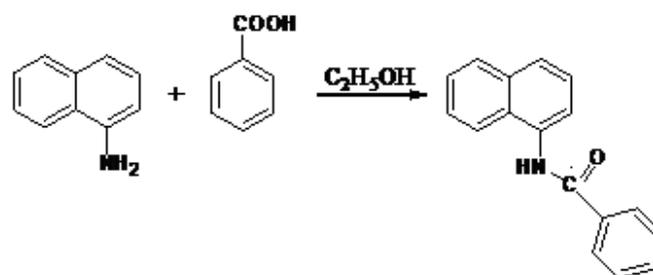
Scheme 2 Complex-A



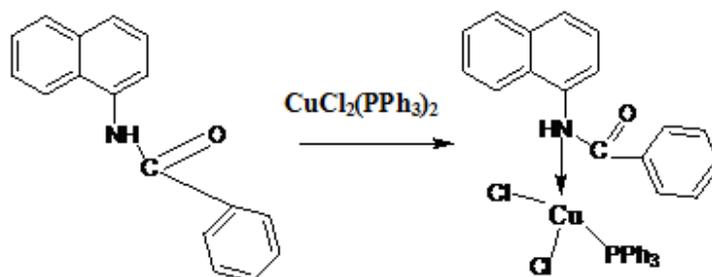
Scheme 3



Scheme 4 Complex-B



Scheme 5



Scheme 6 Complex-C

Conclusion

The Cu (II) complexes of ligand I, II, III were prepared and their nature of coordination were studied with the help of IR and UV and conductometric studies. From the spectral and analytical data it was found that in salicylic acid complexes the mode of co-ordination is N Cu—O and it forms six membered rings and in cinnamic acid complex the mode of co-ordination is N Cu—C, it forms five membered rings and benzoic acid mode of co-ordination is one N Cu and it did not form a ring. Hence from these results it might be concluded that the complex formed from salicylic acid amide was stable than that of cinnamic acid amide and benzoic acid amide.

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