

Synthesis and Characterization of Mixed Ligands Complexes of Copper(II) Ion with Nitrilotriacetic Acid and Amino Acids

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The mixed ligand complexes of copper (II) ion with nitrilotriacetic acid and amino acids (alanine, glycine, lysine and histidine) were synthesized and characterized by IR and UV-vis spectroscopy. The IR spectra of complexes display the typical absorption bands of nitrilotriacetic acid and amino acid ligands. Electronic spectra data for the complexes were in accordance with distorted octahedral environment around the central Cu(II) ion. The amino acids groups act as bidentate chelating ligand.

Key Words: Mixed ligand complexes, Cu(II), Nitrilotriacetic acid, Amino acid.

INTRODUCTION

Copper is an essential trace element required by all living organisms^{1,2}. It plays a key role as integral component of many enzymes³. While trace amounts of copper are required for normal metabolic processes, it can be extremely toxic in excess⁴. Copper exists only in bound forms in the body both in metalloproteins and low molecular weight complexes to avoid its inherent toxicity. Sarkar and Kruck⁵ detected and isolated copper(II)-L-amino acid complexes from the normal human blood serum using thin-layer chromatograph. Proteins constitute one of the most common classes of substances present in biological systems. Their chemical properties are of fundamental importance to understand cell mechanisms as membrane transport complexity of protein action in biological systems, the interaction of forming block between the set of amino acids and the species. Amino acids have two principal potentially active sites in the formation of peptide bonds the acid carboxyl group and the basic amino group. However natural amino acids can also include other functional groups in the chain during the peptide bond formation with sites for chemical activity in the peptide chains⁶.

When cations are incorporated in proteins these molecules manifest catalytic activity over countless reaction involving biomolecules, such as enzymes, which action depends on metal complexation. This feature calls attention to the importance in following the interaction between cations with amino acids^{7,8}. Preparation of some of the Cu(II) complexes with amino acids also investigated^{9,10}.

The aim of this work is the preparation, chemical characterization of the mixed ligand complexes of Cu(II) ion with nitrilotriacetic acid and amino acids (alanine, glycine, lysine and histidine).

EXPERIMENTAL

A Shimadzu (model 160 A) UV-visible spectrophotometer (Shimadzu, Kyoto, Japan) was used to measure the absorbance at 400-1000 nm. Recording range is 0-2. All of the spectra were normalized for a 1 cm path length. Spectrophotometric titrations were carried out directly in quartz cuvette. The IR spectra of complexes and ligands were acquired from KBr pellets at room temperature using a Shimadzu 470 IR in the range of 4000-400 cm^{-1} . pH of solutions adjustment with a Horiba pH meter model M-13.

Histidine, glycine, alanine, lysine and dopamine hydrochloride were purchased from Merck biochemical grade reagents and used without any purification. All reagents used were of analytical reagent grade and the water was always double distilled.

Synthesis of $\text{Na}[\text{Cu}(\text{nta})(\text{H}_2\text{O})_3]$ (1): Nitrilotriacetic acid (nta, 1 mmol, 0.19 g) as ligand A until was dissolved in 2 mL of H_2O by adding NaOH to all acids was dissolved. Copper chloride (1 mmol, 0.135 g) was dissolved in minimum amount of H_2O and added. After 1 h this resulted in a blue precipitate, which removed by gravity filtration. A dilute solution of the compound in water was crystallized by slow diffusion of ethanol, which produced blue crystals of $\text{Na}[\text{Cu}(\text{nta})(\text{H}_2\text{O})_3]$ (yield 44 %).

Synthesis of $\text{Na}_2[\text{Cu}(\text{nta})(\text{gly})(\text{H}_2\text{O})]$ (2): Nitrilotriacetic acid (1 mmol 0.192 mg) as ligand A was dissolved in 2 mL of H_2O by adding NaOH until all of acid was dissolved. Copper chloride (1 mmol, 0.135 g) was dissolved in minimum of amount of H_2O (A solution). Glycine (1 mmol, 0.075 mg) was dissolved in 2 mL of H_2O and slowly added to the A solution and the pH of solution was adjusted to 7 with NaOH. The mixture was placed on an ice bath. After 6 weeks blue-coloured crystals were obtained (yield 25 %).

Synthesis of $\text{Na}_2[\text{Cu}(\text{nta})(\text{ala})(\text{H}_2\text{O})]$, $\text{Na}_2[\text{Cu}(\text{nta})(\text{his})(\text{H}_2\text{O})]$ and $\text{Na}_2[\text{Cu}(\text{nta})(\text{lys})(\text{H}_2\text{O})]$ (3-5): The complexes were prepared in the same way as above, but instead of glycine, alanine and histidine was used. For alanine the crystals colourless cubes after 3 weeks were appeared (yield 29 %) and for histidine mixed ligand complex purple coloured cubes and needle crystals were observed after 4 weeks (yield 22 %).

RESULTS AND DISCUSSION

IR Spectra: The free nitrilotriacetic acid, the bands $\nu(\text{COO}^-)$ of carboxylic group are observed in the region 1720 cm^{-1} . In complex **1**, the bands of COO^- in the region 1660-1590 cm^{-1} observed; a lowering of the frequency of this band suggests the coordination of the carboxylic oxygen to the metal ion¹¹. The IR spectra of

complex **1**, the $\nu(\text{OH})$ stretching vibrations of coordinated water are located in the region $3510\text{--}3395\text{ cm}^{-1}$. In complex **2**, the band due to $\nu(\text{COO}^-)$ of carboxylic group is observed in the region 1618 cm^{-1} and bands of $3514\text{--}3395\text{ cm}^{-1}$ disappeared and a band in the region 3170 cm^{-1} observed. The band positions of $\nu(\text{NH}_2)$, $\nu(\text{COO}^-)$ and comparison with similar compounds¹¹ was shown that the amino acid coordinated *via* nitrogen and oxygen atoms of amino acid coordinated to copper ion.

For complexes **2-5**, (Cu-N) and (Cu-O) bands are manifested by the appearance of 2 bands in the ranges $540\text{--}518$ and $576\text{--}546\text{ cm}^{-1}$, respectively¹². This is further evidence for coordination of the metal ions through nitrogen and oxygen atoms of the amino acid.

The IR bands between 1740 and 1700 cm^{-1} for a typical undissociated carboxylic acid group, indicating the obvious shift to lower frequency caused by coordination to metal. The IR spectra of this complex a band at 3500 cm^{-1} and a band 1624 cm^{-1} were appeared, a very broad band at $3390\text{--}3195\text{--}3070\text{ cm}^{-1}$. These observations, that showed two coordination mode of Cu-Nta-amino were happened.

UV-vis spectra: The UV-vis spectrum of an aqueous solution $2 \times 10^{-3}\text{ mol L}^{-1}$ of each complex was recorded. The complex **1** had octahedral structure and one set *d-d* band at maximum absorbance at 815 nm (1230 cm^{-1}) with a shoulder that due to Jahn-Teller effect and can be attributed to (${}^2\text{Eg} \rightarrow {}^2\text{T}2\text{g}$) transition. The complex **2** absorption spectra of ternary complex of Cu-Nta the maximum wavelength is shifted to 845 nm , respectively and had deformed octahedral and has one *d-d* band at 845 nm , that confirm the coordination of nta as tridentate ligand and three water moles are present in the coordination sphere. The complex **3** is also octahedral and glycine acts as bidentate ligand and two of molecules of aqua substituted with nitrogen and oxygen atom of gly and maximum wavelength shift to the 680 nm (Fig. 1). It is due the chelating effect and formation of 5-membered ring.

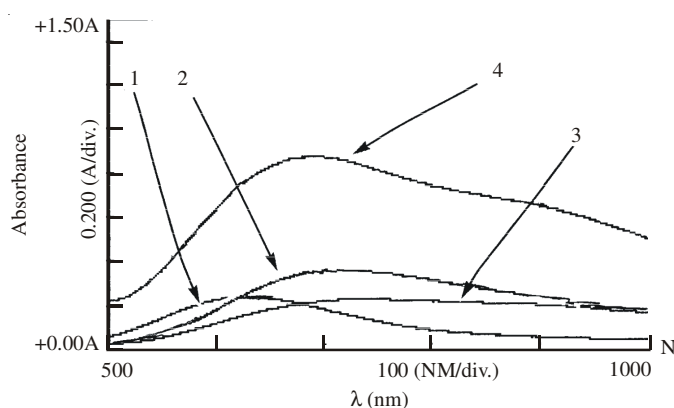


Fig. 1. The visible spectra of mixed ligand complexes of Cu^{2+} with nta and α -amino acids. (1) $\text{Na}_2[\text{Cu}(\text{nta})(\text{ala})(\text{H}_2\text{O})]$, (2) $\text{Na}_2[\text{Cu}(\text{nta})(\text{lys})(\text{H}_2\text{O})]$, (3) $\text{Na}_2[\text{Cu}(\text{nta})(\text{gly})(\text{H}_2\text{O})]$ and (4) $\text{Na}_2[\text{Cu}(\text{nta})(\text{his})(\text{H}_2\text{O})]$

For other mixed ligand complexes with copper ion, Nta and ala, lysine and histidine, similar results were observed. The absorption spectrum of mixed ligand complex of Cu-Nta-ala maximum wavelength is shifted to 632 nm. The shift of maximum wavelength shows that the coordination mode or coordinated ligand was changed.

In the mixed ligand complexes effect of ratio of copper ion and ligands were investigated. Fig. 2 is recorded absorption spectra of ternary system Cu-Nta-gly with ratios 1:1:1, 1:1:2 and 1:1:4 and similar results for maximum wavelength were observed. It means that with ratio 1:1:1 amino acid also acts a bidentate ligand and effect of second ligand concentration is negligible and couldn't causing changes in maximum wavelength and coordination mode of ratios of 1:1:2 and 1:1:4 also were similar.

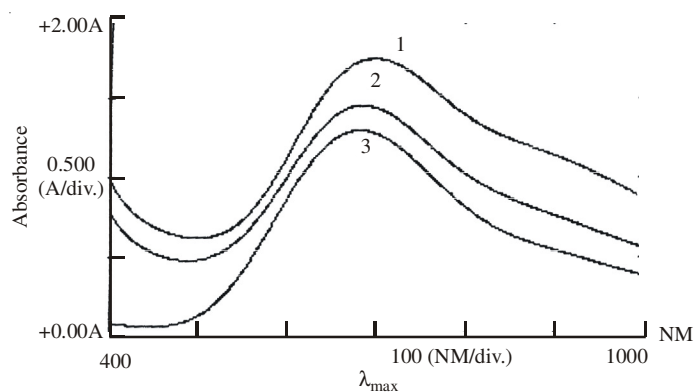


Fig. 2. Visible spectra of mixed ligand complexes of Cu^{2+} with nta and α -glycine Cu:nta:gly at pH 7: (1) 1:1:1 (2) 1:1:2 (3) 1:1:4

Effect of pH: Effect of pH on the reaction was studied at different pH values range 3-12. The absorption spectra of complex Cu-nta-gly with 1:1:1 ratio show that, when the pH was 3 and 5 or acid medium bands are appeared in high wavelength and similar, while the pH is natural media (pH = 7) and to alkaline medium 8, 9 and 12, bands shift into shorter wavelength. With the increase of pH value, the gradual shift into shorter wavelength region is attributed to the deprotonation of amino acid of glycine. These results clearly point to a stable complex formed in neutral to alkaline solution, but when protonated immediately form the aqua complex and glycine coordinated by oxygen atom, which by addition of base, glycine coordinated by both oxygen and nitrogen atoms. The rapid change of spectrum with the addition of HCl in solution can be attributed to protonation of amine group of amino acid (Fig. 3).

The molecular structure of mixed ligand complexes in present complex was proposed as Fig. 4.

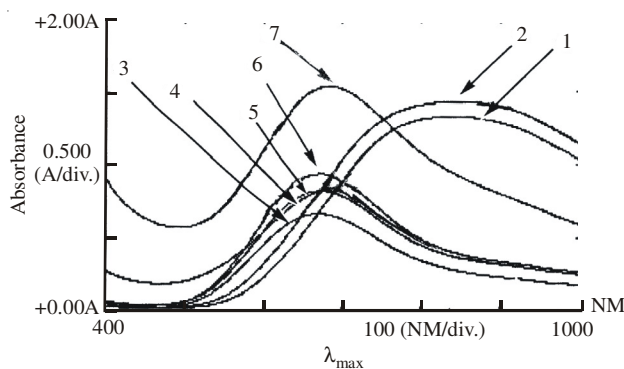


Fig. 3. Absorption spectrum of mixed ligand octahedral complexes of Cu^{2+} with nta and glycine with ratio 1:1:1 at different pHs (1) pH = 3 (2) pH = 5 (3) pH = 7 (4) pH = 8 (5) pH = 9 (6) pH = 10 (7) pH = 12

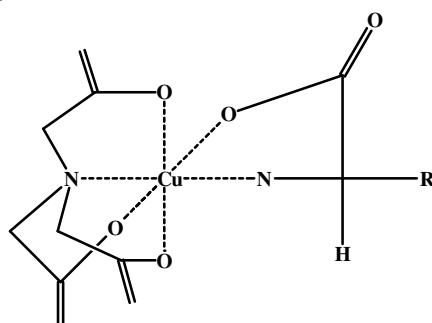


Fig. 4. The proposed molecular structure of $[\text{Cu}(\text{nta})(\text{amio acid})]^{2-}$

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