



NOTE

Synthesis and Characterization of Novel Mixed Ligand Complexes of Cu(II)-Imidazol-Amino Acids

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Some mixed ligand complexes with formula $[\text{Cu}(\text{imi})(\text{amino acid})_2(\text{H}_2\text{O})]$ (amino acid = argenine, glycine, methionine and histidine and imi = imidazol) were prepared. The structures of copper(II) complexes have been characterized on the basis of elemental analysis, conductivity measurements, UV-vis and IR spectroscopies. Electronic spectral data for the complexes were in accordance with distorted octahedral environment around the central Cu(II) ion. The amino acids act as bidentate chelating ligand.

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

Proteins constitute one the most common classes of substances present in biological systems. Their chemical properties are of fundamental importance to understand cell mechanisms as membrane transport, secretion or digestion. Amino acids have two principal potentially active sites in the formation of complexes, 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 chains¹. Imidazole as a ligand plays an important role in biological systems, since the imidazole moiety of the histidyl residue in a large number of metalloproteins form all or part of the binding site of many transition metal ions²⁻⁴. The imidazolate anion is known to act as a bridging ligand in certain metalloenzymes, for example, in bovine superoxide dismutase⁵ bridge formation takes place between Cu^{2+} and Zn^{2+} (Cu-B-Zn). Only a few studies have been reported on the aqueous coordination chemistry of imidazolate bridged complexes^{6,7}. Recently some solution equilibrium studies of imidazolate bridged complexes with Cu^{2+} , Ni^{2+} and Zn^{2+} were done⁸⁻¹⁰. The study is now extended by taking potentially tridentate ligands, *viz.*, L-cysteine, L-threonine, salicylglycinate and salicylvalinate, three metal ions (Cu^{2+} , Ni^{2+} and Zn^{2+}) and imidazole. The aqueous coordination chemistry of simple imidazolate bridged metal complexes is explored using pH-potentiometric and UV/vis spectroscopic techniques. Preparation of Cu(II) complexes with amino acids also investigated¹¹⁻¹³.

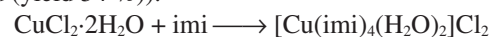
We report herein the preparation, chemical characterization of the mononuclear mixed ligand complex, $[\text{Cu}(\text{imi})(\text{amino}$

$\text{acid})_2(\text{H}_2\text{O})]$ (amino acid = argenine, glycine, histidine and methionine, imi = imidazol).

All experiments were carried out in open air. Amino acids (glycine, argenine, methionine and histidine), imidazol and copper(II) chloride, were purchased from Merck. All chemicals were of high purity and were used as purchased, without any further purification. Nano pure-quality water and the ethanol of Merck were used throughout this work.

The infrared spectra were recorded on a 470 Shimadzu infrared spectrophotometer as KBr pellet. The electronic absorption spectra measurements were carried out on UV-160A Shimadzu spectrophotometer. The elemental analysis performed by an elemental Costech-ECS-4010 apparatus. The Horiba-conductivity meter Es14 was used for electro conductivity of complexes.

Preparation of complex $[\text{Cu}(\text{imi})_4(\text{H}_2\text{O})_2]\text{Cl}_2$: 1 mmol of CuCl_2 (0.134 g) was dissolved in 5 mL of water. Then solution containing 1 mmol (0.068 g) of imidazol in 2 mL ethanol was added. (After one day the blue precipitate was formed (yield 54 %)).



Preparation of complexes $[\text{Cu}(\text{amino acid})_2(\text{H}_2\text{O})_2]$: For preparation of $[\text{Cu}(\text{amino acid})_2(\text{H}_2\text{O})_2]$, (amino acids argenine, glycine, methionine and histidine) 1 mmol (0.134 g) of CuCl_2 in 2 mL H_2O dissolved. Then 1 mmol of amino acids (glycine, argenine, methionine and histidine) in 2 mL H_2O was added. The reaction mixture continuous stirred for 1 h. The resulting solution was filtered off and washed to remove impurities and allowed to stand at room temperature. After 5 days blue to green precipitate was formed.

TABLE-1
 INFRARED BANDS (cm⁻¹) FOR BINARY (a) AND TERNARY (b) Cu(II) COMPLEXES

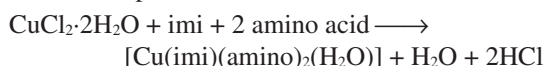
TABLE-1							
INFRARED BANDS (cm ⁻¹) FOR BINARY (a) AND TERNARY (b) Cu(II) COMPLEXES							
(a)							
[Cu(amino) ₂ (H ₂ O) ₂]	v(O-H)	v _{as} (COO)	v _s (COO)				
1-Arginine	3410	1624	1453				
2-Glycine	3330	1604	1389				
3-Met	3510	1621-1597	–				
4-Histidine	3315	1921	1474				
(b)							
[Cu(amino) ₂ (imi)(H ₂ O)]	v(O-H)	v _{as} (COO)	v _s (COO)	v(C-O-C)	v(C=N)	v(Cu-N)	v(Cu-O)
1-Arginine	3230	1634.1667	1393	1299	1487	478.44	768 562
2-Glycine	3300	1635.1672	1415	1282	1489	408	803 540
3-Lysine	3500	1633.1670	1415	1280	1487	408	804 539
4-Histidine	3430	1634.1679	1416	1276	1404	407	804 542

 TABLE-2
 ELEMENTAL ANALYSIS AND COLOUR OF COMPLEXES

Complex	Colour	C (%)		H (%)		N (%)	
		Exp.	Calcd.	Exp.	Calcd.	Exp.	Calcd.
[Cu(Gly) ₂ (H ₂ O) ₂]	Blue	19.32	19.59	3.96	4.08	11.83	11.42
[Cu(me) ₂ (H ₂ O) ₂]	Blue	20.31	20.22	7.30	6.54	6.89	7.05
[Cu(Arg) ₂ (H ₂ O) ₂]	Blue-green	25.90	26.50	5.40	5.80	20.20	20.60
[Cu(His) ₂ (H ₂ O) ₂]	Blue-green	34.80	35.50	5.00	4.40	19.80	20.70
[Cu(imi)(H ₂ O)(gly) ₂]	Blue	20.31	20.22	6.70	6.54	7.12	7.05
[Cu(imi)(H ₂ O)(me) ₂]	Blue	34.30	35.20	5.18	5.19	12.26	12.60
[Cu(imi)(H ₂ O)(arg) ₂]	Blue	35.30	36.81	6.70	6.83	27.20	28.40
[Cu((imi)(H ₂ O)(his) ₂)]	Blue	38.20	39.40	4.00	4.10	24.50	24.60

Preparation of complexes [Cu(imi)(amino acid)₂(H₂O)₂]:

The mixed ligand amino acid-imidazol complexes of Cu(II) were prepared by reaction solutions of complexes. Then suitable amount 1mmol of amino acids (**1-4**) dissolved in water and added (amino acid 1 = arginine, 2 = glycine, 3 = methionine and 4 = histidine). The resulting mixture was filtered off, washed with a mixture of EtOH and H₂O (1:1). The product was dried in room temperature.



All complexes are air stably and these compounds are soluble in water at room temperature.

The IR spectra of the complexes (Table-1) show the characteristic bands of imidazol and amino acid moieties, strong and broad bands in the 3400-3230 cm⁻¹ range are attributed to the v(OH) and v(NH) stretching vibrations, respectively.

For the binary imidazol complex the bands 3000-2800 cm⁻¹ region attributed to imidazol ligand. In the ternary complexes these peaks are weaker and replaced to higher wave number. The peaks at 1050 and 1480 cm⁻¹ attributed to C-H and C=N imidazol ring.

The electronic absorption spectra of the complexes **1-4** were taken in water in the range from 200-1000 nm. Complex (**1**) shows one broad asymmetric band at λ_{max} 630-830 nm with a high energy shoulder. Complex (**2**) shows the broad asymmetric bound at λ_{max} ca. 715 nm. Complex (**3**) shows the weak and broad asymmetric bound at λ_{max} ca. 750 nm and complex (**4**) shows the broad asymmetric bound at λ_{max} ca. 620 nm. The spectra absorption at 650-730 nm can be attributed to the electronic transitions ²E_g → ²T_{2g} of copper(II) ion in a distorted octahedral symmetry environment. The spectra show more intense bands centered at 200-220 and 220-340 nm, which may be attributed π → π* and n → π* transition

within the ligands and ligand to metal charge transfer (LMCT), respectively.

The elemental analysis data (carbon, nitrogen and hydrogen) of complexes are listed in Table-2.

The conductivity measurements of the binary and ternary mixed ligand complexes **1, 2, 3** and **4** were taken in water. The binary complexes of [Cu(imi)₄(H₂O)₂]Cl₂ shows 1:2 electrolyte and complexes [Cu(amino)₂(H₂O)₂] show non electrolyte nature. The molar conductance values of ternary mixed ligand complexes of [Cu(imi)(H₂O)(amino)₂] show non electrolyte nature of the complexes.

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