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NOTE

Synthesis and Characterization of Mixed Ligand Complexes of Cu(II)-Oxalate-Amino Acids (Aspartic acid and Cysteine)

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The mixed ligand complexes of Cu(II) with oxalate as primary ligand and amino acids (aspartic acid and cysteine) as secondary ligands have been synthesized. The structures of complexes have been characterized on the basis of elemental analysis, conductivity measurements, UV-visible and IR spectroscopy. Electronic spectral data for the complexes were in accordance with an octahedral environment around the central Cu(II) ion. The oxalate group acts as bidentate chelating ligand.

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

Coordination chemistry of transition metals has been interest for several years. Copper(II) amino acid complexes in recent years have been receiving much attention[1]. The complexes of copper are particular interest due to their biological and antitumor properties[2-5]. Copper(II) can inactivate the HIV protease[6]. The ternary complexes of copper(II) plays an important role in biological processes. 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 are the building units of all proteins and enzymes[7]. 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 chains[8]. Preparation and characterization of Cu(II) complexes with amino acids also investigated[9-11].

The objective of this work involved the preparation and characterization of ternary complexes of copper(II) with oxalate as primary ligand and amino acids (aspartic acid, cysteine,) as secondary ligand.

All the chemicals were of high purity and were used as purchased, without any further purification. Copper(II) nitrate, oxalic acid, L-aspartic acid, cysteine, methanol were used throughout this work. All experiments were carried out in open air. Nano pure-quality water and the ethanol of Merck were used. All experimental were carried out in open air.

The infrared spectra were recorded on a 470 Shimadzu infrared spectrophotometer as KBr pellet (in the spectra region 4000-400 cm^{-1}). The electronic absorption spectra measurements were carried out on UV-160 A 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.

Synthesis of complexes $K_2[Cu(OX)_2(H_2O)_2]$: Water solutions of oxalate complexes of Cu were prepared. For preparation of $K_2[Cu(ox)_2(H_2O)_2]$, 1 mmol of $CuCl_2$ (0.134 g) was dissolved in 5 mL of water. Then solution containing 1 mmol (0.184 g) of $K_2C_2O_4{\cdot}2H_2O$ in 2 mL H_2O was added. The blue precipitate was formed after 1 h.

Preparation of complexes [Cu (amino acid)$_2$(H_2O)$_2$]: For preparation of [Cu (amino acid)$_2$ (H_2O)$_2$], 1 mmol (0.134 g) of $CuCl_2{\cdot}2H_2O$ in 2 mL H_2O dissolved. Then 1 mmol of amino acids (1-aspartic acid, 2-cysteine) in 2 mL H_2O was added. The reaction mixture continuous stirred for 1 h. The resulting solution was filtered off to removed imparities and the allowed to stand at room temperature.

Preparation of complexes K_3[Cu (OX)$_2$(amino acid)]: The mixed ligand amino acid- oxalate complexes of Cu(II) were prepared by reaction solutions of oxalate complexes. The suitable amount (1 mmol) of amino acids (1-6) dissolved in water and added (amino acid 1-aspartic acid, 2-cysteine). The resulting mixture was filtered off, washed with a mixture of EtOH and H_2O (1:1). The product was dried in room temperature.

TABLE-1
ELEMENTAL ANALYSIS CARBON, HYDROGEN, NITROGEN AND COLOUR OF COMPLEXES

Complex	Yield (%)	Molar conductance ($\Omega cm^2 mol^{-1}$)	Colour	Analysis calcd. (exp) %			
				C	H	N	S
$K_4[Cu(C_2O_4)_3]$	48.5	550	Blue	11.63 (13.2)	-	-	-
$[Cu(Asp)_2(H_2O)_4]$	48.1	75	Blue	18.9 (21.7)	3.9 (4.3)	11.04 (8.1)	-
$[Cu(Cys)_2(H_2O)_4]$	44.1	65	Green	19.8 (22.9)	4.6 (3.9)	11.58 (9.2)	17.65 (19.6)
$K_2[Cu(Asp)_2(H_2O)_2(Ox)]$	49.1	245	Blue	18.9 (23.9)	3.4 (2.9)	8.8 (5.2)	-
K_2 [Cu(Cys)$_2$ (H_2O)$_2$ (Ox)]	44.1	248	White	28.9 (25.08)	4.8 (5.1)	16.26 (12.7)	14.8 (18.9)

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

The structure of the complexes was determined by elemental analysis, electronic spectra and molar conductance. The conductivity measurements of the binary and ternary mixed ligand complexes 1 were taken in water. The observed molar conductance values of the mixed ligand complexes indicate their non electrolytic nature.

The important IR spectral bands for the ligands and their copper complexes are given in Table-2. The IR frequencies for ligands are in good agreement with those reported in the literature[12,13].

TABLE-2
INFRARED BANDS (cm^{-1}) FOR PREPARED COMPLEXES

No	Complex	ν(OH)	ν(C=O)	ν(C-O)	ν(M-O)	ν(M-N)
1	$K_4[Cu(C_2O_4)_3]$		1630	1360	822	
2	$[Cu(Asp)_2(H_2O)_4]$	3475	1620	1300	831	593
3	$[Cu(Cys)_2(H_2O)_2]$	3405	1618	1380	772	537
4	K_2 [Cu(Asp)$_2$ (Ox)]	3410	1640	1317	819	505
5	K_2 [Cu(Cys)$_2$ (Ox)]	3510	1585	1334	842	538

The mixed ligand complexes exhibit strong characteristic vibrations for the carbonyl groups of the oxalate ligand. The electronic absorption spectra of the complexes were taken in water in the range from 200 to 800 nm.

Complex (**1**) shows one broad asymmetric band at λ_{max} 520 nm with a high energy shoulder. Complex (**2**) shows the broad asymmetric bound at λ_{max} 610 nm. Complex (**3**) shows the week and broad asymmetric bound at λ_{max} 670 nm and complex (**4**) shows the broad asymmetric bound at λ_{max} 640 nm. Complex (**5**) shows the broad asymmetric bound at λ_{max} 650 nm. The spectra absorption at 520 to 610 nm can be attributed to the electronic transitions of copper (II) ion in a distorted octahedral symmetry environment. The spectra show more intense bands centered at 210-225 nm and 230-330 nm, which may be attributed $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition within the ligands and ligand to metal charge transfer (LMCT) respectively.

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