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Synthesis and Characterization of Novel Anionic Mixed ligand fluoro Copper (II) Complex incorporating Citric as Coligand

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ABSTRACT

The mixed ligand complexes of copper (II) display interesting properties. Mixedligand anionic complex of the type $(\text{NH}_4)_2[\text{Cu}_2(\text{L})(\text{H}_2\text{O})_2\text{F}_2]$ (L= citric acid) has been synthesized by treating hydrated copper(II) oxide $\text{CuO} \cdot n\text{H}_2\text{O}$ with citric acid solution in the presence of bifluoride, HF_2^- , in aqueous solution. The pH of the reaction solution, metal: ligand ratio and the order of addition of the ligands are crucial to the synthesis. The synthesized mixedligand fluoro complex has been characterized by elemental analysis, magnetic susceptibility measurement, FT-IR and ESR studies. The complex has been conjecture to possess a tetra coordinate geometry around the copper (II) centre.

Keywords: mixed ligand, aqueous medium.

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INTRODUCTION

The continued interest in mixedligand copper(II) complex originates from their relevance to the activity of superoxide dismutase, their anti microbial, catalytic, electronic, anti cancer and potent applications in nano science [1-9]. Mixedligand amino acid complexes have drawn lot of current attention due to their relevance in enzyme inhibition [10].

Crown ether complex of copper (II) with Schiff bases derived from benzo-15-Crown-5 are used to develop biomimetic models of metalloenzymes and to prepare supramolecules, self assembling systems and anticancer drugs [11].

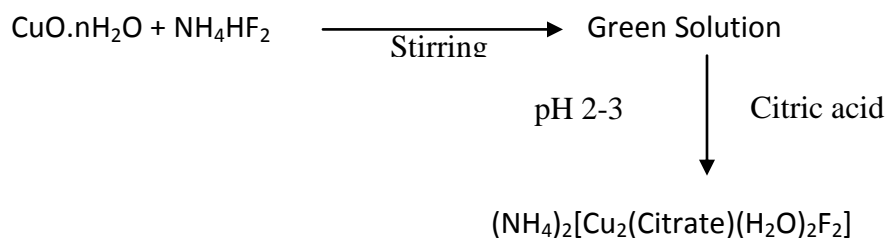
Mono and dinuclear complexes containing carboxylate and imidazolate as ligand have been shown to have a variety of pharmacological effects such as superoxide dismutase and catacholase activity [12,13].The anions Cl^- , Br^- , NO_3^- , SCN^- have been extensively used as ancillary ligands but fluoride as coligand is scarce. Aqueous medium synthesis of such copper (II) complexes is quite complicated. The nature of complex species formed is often dependent on slight variation in reaction condition such as concentration of reactants, temperature, pH and order of addition of reagents. In the present paper, we report the synthesis and spectroscopic, magnetic and some physicochemical properties of anionic mixedfluoro citrate complex of copper (II).

MATERIALS AND METHODS

All the chemicals used were of analytical grade. The ligands and the metal salts were procured from Sisco Research Laboratories Pvt. Ltd. (Mumbai). All the solutions and reagents were freshly prepared before use. The pH values of the reaction solutions were recorded by using Systronics digital pH meter 335. The FT-IR spectra were recorded on Bruker IFS 66v spectrophotometer using KBr pellets. The X-band ESR spectra were recorded on polycrystalline sample at room temperature using DPPH as g-marker. The magnetic susceptibility of the synthesized complex was recorded using Gouy method. Microanalyses on C, H and N were performed using Heraeus Carb Erba-1108 elemental analyzer. The crystal textures were recorded using Polarizing Microscope (Nikon Optiphot 2 pol).

Synthesis of the complex

To freshly prepared slurry of hydrated copper (II) oxide, $\text{CuO}\cdot n\text{H}_2\text{O}$ (1g, 0.004 mol), an aqueous solution of ammonium bifluoride, NH_4HF_2 , (0.456g, 0.008 mol) and an aqueous solution of citric acid, $\text{C}_6\text{H}_8\text{O}_7$, (0.7685 g., 0.004 mol) were added with constant stirring using a magnetic stirrer. A clear green solution resulted and the pH of the reaction mixture at this stage was 2-3. This solution on warming over a water bath for half an hour yielded a green micro crystalline product. The precipitated complex was filtered, washed with ethanol and dried in vacuo. The yield was recorded (1.4 g, 58%).



RESULTS AND DISCUSSION

The synthesized complex has been found stable in air at room temperature, sparingly soluble in water but insoluble in acetonitrile, DMSO and methanol. The elemental analyses (Table 1) agree with the proposed formulation. The magnetic susceptibility value at room temperature indicates that the complex is binuclear.

Table 1: Characteristic physical and analytical data [found (calcd) %] of the complex $(\text{NH}_4)_2[\text{Cu}_2(\text{L})(\text{H}_2\text{O})_{2\text{F}_2}]$

Colour	pH	Magnetic Moment (μ_{eff})BM	Cu	F	C	H	O
Green	2-3	2.79	29.90 (29.88)	8.95 (8.93)	16.90 (16.94)	3.75 (3.79)	33.85 (33.86)

Magnetic Susceptibility

The magnetic susceptibility measurement led to magnetic moment value (Table 1) that is concordant with multinuclear core for the complex. The moment value for the complex (2.79 BM) is suggesting >1 electron para magnetism. The nature of magnetic interaction present in the complex is, however, not immediately discernible.

Infra-red Spectral Data

The FT-IR spectra of the complex exhibit diagnostic patterns (Table 2). The band at ca. 360 cm^{-1} is assigned to Cu-F stretch [14-15]. A medium intensity band observed at ca. 417 cm^{-1} may be attributed to the Cu-O stretch [16-17]. The strong band at ca. 1400 cm^{-1} is typical of deformation mode ($\delta_{\text{H-N-H}}$) of NH_4^+ ion and corresponding N-H stretching vibration near 3359 cm^{-1} confirms the presence of NH_4^+ as counter ion. A positive chemical test further supports the assignment [18]. The coordination of water molecules in the complex may be evidenced from the appearance of broad band at ca. 3450 cm^{-1} and relatively weak bands at ca. 795 cm^{-1} and 598 cm^{-1} due to stretching ($\nu_{\text{O-H}}$), rocking ($\rho_{\text{H-O-H}}$) and wagging ($\rho_{\text{H-O-H}}$) vibrational modes respectively [14-15].

The coordination of carboxylate group to the metal centre is attributed to the presence of asymmetric (ν_a) and symmetric stretch (ν_s) for COO^- group at ca.1569 and 1436 cm^{-1} respectively.

Table 2: Structurally significant IR frequencies (cm^{-1}) of the complex

Complex	IR cm^{-1}	assignments
$(\text{NH}_4)_2[\text{Cu}_2(\text{citrate})(\text{H}_2\text{O})_2\text{F}_2]$	360	$\nu_{\text{Cu-F}}$
	417	$\nu_{\text{Cu-O}}$
	598	$\rho_{\text{H-O-H}}$
	795	$\rho_{\text{H-O-H}}$
	1400	$\delta_{\text{H-N-H}}$
	1436	$\nu_s(\text{COO}^-)$
	1569	$\nu_a(\text{COO}^-)$
	2928	$\nu_{\text{C-H}}$
	3359	$\nu_{\text{N-H}}$
	3450	$\nu_{\text{O-H}}$

ESR Spectral Data

The X-band ESR spectra were recorded on a polycrystalline solids at 300K. The complex exhibited isotropic ESR signal, i.e., having only one intense broad signal with no hyperfine structure. This may be due to the dipolar exchange and unresolved hyperfine interaction [17]. The g_{iso} suggests the presence of grossly misaligned tetragonal axes (which is also supported by the theoretical treatment under MM2 calculations as depicted in the energy optimized structure of the complex in Fig.1).

Photomicrograph of the complex were indicated the micro-appearance of the crystals of the complexes. The crystals seemed isotropic under POM with crossed polarisers which indicated **cubic** crystal structure.

The evidences obtained from IR, ESR, magnetic moment etc. studies suggest a tetracoordinate geometry around the copper (II) centre as supported by MM2 energy optimized calculations. The proposed MM2 energy optimized tentative structure of the compound is presented in Fig.1.

Fig.1. Proposed structure of the complex, $(\text{NH}_4)_2[\text{Cu}_2(\text{citrate})(\text{H}_2\text{O})_2\text{F}_2]$

CONCLUSION

The mixedligand complexes of copper (II) with organic ligands enjoy global interest in scientific community due to their potential pharmacological activities. In this work, we have successfully synthesized the spiro type mixedfluoro complex of copper (II) using citrate ligand. The synthesis leading to the specific type of mixedligand complex has been shown to be dependent on metal: ligand stoichiometry. The simple aqueous medium based strategy for synthesis of the compound can serve as paradigm for the synthesis of yet newer array of mixedligand complexes. The coordination of water group provides interesting structural motif of relevance to bioinorganic chemistry.

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