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A Review of XANES, EXAFS, UV, and IR spectroscopy methods used to investigate Cu (II) mixed ligand complexes

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Introduction

A few copper complexes with pyrazole and glycine as one of the ligands are discussed in this review work, along with their X-ray absorption near-edge structure, extended X-ray absorption fine structure, UV studies, and IR studies-

X-ray absorption spectroscopy-A homogeneous sample of thickness x is passed through by a monochromatic beam of X-rays with energy E that is attenuated. This attenuation is comparable to the Lambert-Beer law and can be explained as follows: It is defined as $I_t = I_0 e^{-\lambda \mu x}$, where I0 and It are the X-ray intensities that were incident and transmitted, respectively, and μ is the linear absorption coefficient that indicates how strongly X-rays are absorbed in relation to the X-ray energy E. Typically, when energy increases, smoothness diminishes, making X-rays more piercing. An absorption edge results from the absorption dramatically increasing at specific energies. X-ray absorption spectroscopy is sometimes abbreviated to either XAS or XAFS. In the hard X-ray absorption region, the absorption due to valence electrons is small, while that due to core electrons is predominant. The core absorption spectra exhibit prominent structures with sharp peaks near the core absorption edges, called XANES. On the high-energy side of XANES, these structures decrease in intensity with the weak oscillatory structure called EXAFS. The data of the copper complexes have been obtained by different techniques and analysed by different methods according to the results, which we have to find out. Similar to how the data from the complexes was processed using the EXAFS and XANES data analysis programmes, Athena was used to determine the experimental measurements, such as the energies of the K-absorption edge, chemical shifts, edge widths, effective nuclear charge, covalency, and shifts of the principal absorption maximum in the complexes [1].

UV spectroscopy is one of the oldest instrumental methods of analysis. UV spectroscopy can be used to characterize a wide range of materials. Based on the degree of absorption or transmission of a different wavelength of beam light and the diverse responses of samples, UV spectroscopy provides information. The general law known as Beer's law can be used to quantitatively describe how radiation is absorbed by materials. It is easy to operate and handle the UV spectrometer. It can be applied to both qualitative and quantitative analyses. Wavelengths between 200 and 700 nm are commonly used to analyse metal and metal oxide nanoparticles. The UV spectrum can also be used to better understand the complex mechanism of complexation between templates, monomers, and cross-linkers during polymerization [2].

IR Spectroscopy-The study of how matter interacts with light radiation as waves pass through a medium (matter) is known as infrared spectroscopy. The electromagnetic nature of the waves interacts with the polarity of the chemical bonds in the molecules. The infrared interaction is passive, and the molecule does not produce an IR spectrum if it lacks polarity (a dipole moment). For the purpose of identifying and characterising molecules, infrared spectroscopy is employed in chemistry and industry. IR is used to characterise compounds because it is the "fingerprint" of every molecule. Since infrared spectroscopy is a non-destructive technique, it can be used to investigate the secondary structure of more complex systems, including biological molecules like proteins, DNA, and membranes.Accurate measurements can also be taken of samples in solutions. The spectra of different compounds can be compared to a database of hundreds of reference spectra. Here are a few examples of particular IR spectroscopy applications: The degree of polymerization in the production of polymers has been successfully measured using IR spectroscopy. Since the IR spectrum is a substance's "fingerprint," IR spectroscopy is important for detecting, characterising, and verifying compounds' identities. As a result, IR serves a forensic function, and IR spectroscopy is used to examine materials including paint, alcohol, narcotics, fibres, and blood. The reader will find a lot of examples of these applications in the various parts provided in the book. [3]

Discussion -For the purpose of detecting Cu (II) in water, Bhagat and colleagues employed the glycine-mediated simple colorimetric technique. Visual detection and UV light absorption properties have been used to confirm the Cu (II) concentrations (0.1–5 mM) dependant colour intensity. The information from UV spectroscopy is also used to calculate the Cu (II)-glycine complex's formation constant [4].

The mixed ligand complexes of the copper (II) ion with the amino acids alaine, glycine, lysine, and histidine have been examined by S. Hashemian. In order to synthesise and characterise the

complexes, he used IR and UV spectroscopy. The IR spectra of complexes show the usual absorption bands of amino acid ligands and nitrilotriacetic acid ligands. The deformed octahedral environment around the core Cu(II) ion was consistent with the electronic spectra data for the complexes. The groups of amino acids function as bidentate chelating ligands[5].

J. Zhang and co workers have been studies the four mixed ligand copper complexes, viz., $[Cu_2(glyha)(bpy)_2(H_2O)]\cdot 2ClO_4\cdot H_2O$, $[Cu_2(glyha)(phen)_2]\cdot 2ClO_4$, $[\{Cu_2(alaha)(phen)_2\}\{Cu_2(alaha)(phen)_2(NO_3)\}]\cdot 3NO_3$ ($glyha^{2-}$ = dianion glycinehydroxamic acid, $alaha^{2-}$ = dianion alaninehydroxamic acid, bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline). The interactions of these complexes with calf thymus DNA (CT-DNA) were studied through UV spectroscopy, fluorescence spectroscopy, and circular dichroism. The results revealed that complexes 1–4 could interact with CT-DNA through intercalation [6].

A New mixed ligand complexes of Co(II) and Cu(II) with thiosemicarbazones or semicarbazones and the amino acid glycine (A1H) have been described by A. Choudharya and colleagues. By reacting metal dichloride in a 1:1:1 molar ratio with ligands IPMCHTSC, TBHSC, or TBHTSC and A1H in refluxing ethanol, the complexes were created. The newly created complexes (1–12) have been identified using elemental analyses, molar conductance, electronic, IR, and FAB mass spectroscopy, and thermogravimetric examination. For all of these complexes, a square pyramidal shape was suggested based on this spectral data. In comparison to the uncomplexed ligands, the results of these experiments indicate that metal (II) complexes are more effective against one or more species of bacteria and fungi [7].

According to A. Waleed and colleagues, novel metal ion complexes of chromium (III), iron (III), cobalt (II), nickel (II), copper (II), and cadmium (II) have been explored. They were made using mixed Schiff base ligands (HLs 1 and 2) for the Schiff bases. In the HL-2 complex, glycine serves as a ligand. Utilising spectroscopic methods including FT-IR and UV spectra, the metal complexes were identified. All of the ligand and their metal complex analyses were in excellent agreement with the theoretical values, indicating the purity of the Schiff base ligands and their metal complexes. The molecular structures for all of the metal complexes were predicted to be octahedral based on the aforementioned information [8].

The two mixed ligand complexes [Cu(BzOH)(Gly)]ClO4 and [Cu(BzOH)(Glu)]ClO4 have been explored by M. M. Ibrahim and colleagues. BzOH stands for 1-benzimidazolylethanol, Gly for glycine,

and Glu for L-glutamic acid. Elemental analysis, IR, Raman, UV-vis, and ESR spectroscopy were used to characterise them after they were synthesised and to describe their structures and physical characteristics. Square-planar CuN2O2 coordination geometries are suggested by spectral characteristics for both complexes. To correlate the structural characteristics of the complexes with their catecholase and catalase-like activities, spectroscopic and electrochemical experiments were carried out [9].

The simplest amino acid, glycine (Gly), does not appear to react simply with the copper metal ion (Cu2+) in aqueous solutions at 25 °C, according to Y. Z. Hamadda and colleagues who used potentiometric titrations, UV-Vis, IR, and speciation diagrams. Cu2+ discharged a net of two protons (2H+) into the solution, according to the potentiometric observations. One proton (H+) was released into the solution by free Gly from the lone ammonium group. As opposed to free Gly, however, when glycine hydrochloride (Gly.HCl) was utilised, both the carboxylate and the ammonium groups released their protons. Any molar ratio of Cu2+ to Gly.HCl resulted in the release of at least four protons (4H+) into the solution, with one H+ from each [10].

E. Aljuhani and co-workers have been studied pyrazole derivatives with copper (ii) complexes. New pyrazole derivatives were prepared and used to synthesize new bioactive agents from Cu (II) complexes that have OSN donors. Analytical and spectral (IR, UV, MS, NMR, ESR, and XRD) instruments characterized these complexes as well as their corresponding ligands. The geometry of isolated complexes was commonly proposed based on electronic transitions and ESR spectral parameters via computational approaches; these structures were optimized using standard programs under the required basis set. The interaction features summarized from docking processes, reveal effective inhibition validity for new Cu(II) complexes versus breast cancer cells. This according to scoring energy values and the stability of docking complexes in true interaction path (bond length 3.5 Å) particularly with Cu(II)-L 3 and Cu(II)-L 4 complexes. This reflects the possibility of successful behavior during practical application through in- vitro assay that intended in this study. Finally, the degree of toxicity of such new compounds to the breast cancer cell line was determined by in-vitro screening [11].

By adjusting the Cu(II):Glycine molar ratio while comparing the XANES spectra of the standard reference copper and starting solution of CuCl2, Klaiphet and coworkers have examined the Cu K-edged XANES spectra of copper (II) chloride aqueous solution mixed with glycine aqueous solution. By recording X-ray absorption near-edge structure (XANES) spectra in the area of the copper K-edge for various Cu(II):glycine molar ratios and for varied pH values, these solutions' structural alterations are examined. Comparing the spectra acquired for low and high concentrations of CuCl2 in the mixed

solutions reveals somewhat different XANES characteristics. Low CuCl2 concentrations in mixed solutions without pH adjustment result in distinct XANES profiles from those at a pH adjusted to 5.0. This emphasises the significance of keeping these factors under control[12].

The X-ray absorption fine structure (XAFS) of copper (II) mixed ligand complexes using tetramethylethylenediamine (tmen) as one of the ligands has been explored by S. Sharma and colleagues. Cu(tmen)(gly)ClO4, Cu(tmen)(bipy)(ClO4)2, and Cu(tmen)(phen)(ClO4)2 are examples of the ligands. It has been noted that each complex's K-edge has been discovered to divide into two edges, K and K′. The effective nuclear charge (ENC) and copper oxidation state in the complexes have been determined using the chemical shift. Using Levy's, Lytle's, and Lytle, Sayers, and Stern's (LSS) approaches, the EXAFS data has been examined to determine the bond lengths in the complexes. The value of the first shell phase uncorrected bond length is given by the first peak in the Fourier transform of the spectra [13].

The structures of the mono-, bis-, and tris(glycinato) copper(II) complexes in aqueous solution have been determined using X-ray absorption spectroscopy, according to P. D'Angelo and colleagues. It has been discovered to have a deformed octahedral geometry, with two bidentate glycine ligands coordinating to the Cu2+ ion in the equatorial plane and two more water molecules occupying the axial positions at 2.40 ± 0.06 Å. According to this observation, the Cu(II) and water interaction at the axial site is weaker as the axial bonds lengthen during the development of the Cu-glycine complexes[14].

Bis(pyrazol-1-yl)acetic acid (HC(pz)2COOH) and bis(3,5-dimethyl-pyrazol-1-yl)acetic acid (HC(pzMe2)2COOH) are two copper complexes that have been explored by M. Pellei and colleagues. These complexes were changed into the methyl ester derivatives (LOMe) and (L2OMe), which were then used to make Cu(I) and Cu(II) complexes, respectively. The electronic and molecular structures of the complexes, as well as the local structure around copper ions in a few Cu(I) and Cu(II) coordination compounds, were studied using complementary techniques based on synchrotron radiation (XPS, NEXAFS, and XAS[15].

A. Gaur and co-workers have been reported the X-ray absorption fine structure of six Cu(II) complexes, Cu2(Clna)4 2H2O (1), Cu2(ac)4 2H2O (2), Cu2(phac)4 (pyz) (3), Cu2(bpy)2(na)2 H2O (ClO4) (4), Cu2(teen)4(OH)2(ClO4)2 (5) and Cu2(tmen)4(OH)2(ClO4)2 (6) (where ac, phac, pyz, pyz, bpyz, bpyz, bpyz, bpyz, bpyz, bpyz, bpy, na, teen, tmen = acetate, phenylacetate, pyrazole, bipyridine, nicotinic acid, tetraethyethylenediamine, tetramethylethylenediamine, respectively). The square planar and pyramidal coordination geometries for these complexes were intended. Four complexes, 1-4, have

spectra that show the existence of an intense pre-edge characteristic, which suggests square pyramidal coordination. A pronounced shoulder in the rising part of the edge, whose strength diminishes in the presence of axial ligands and shows four coordinations in these complexes, is another significant XANES feature that is found in complexes 5 and 6. Counting and estimating scattering's distance [16].

A. Mishra and colleagues investigated the results of X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) on three copper complexes employing (diethyl 4-amino-1-phenyl-1H-pyrazole-3,5 dicarboxylate) as ligand. Using a rotating anode and a tube voltage and current of 40 kV and 100 mA, the Rigaku RINT-2000 X-ray diffractometer was used to record the X-ray diffraction studies of copper complexes [17].

S. Burlova and co-workers have been reported the syntheses of a series of novel N,O,O and N,O,S donor tridentate Schiff base ligands H_2L^1 and H_2L^2 via the condensation of 1-phenyl-3-methyl-4-formylpyrazol-5-ol(thiol) with 2-hydroxymethylaniline and their Co(II), Ni(II), Cu(II), Fe(III), and Mn(II) complexes. The compounds are characterized by the C, H, N, S, metal elemental analysis, IR spectroscopy; ^{1}H NMR data for ligands, low-temperature magnetic measurements, X-ray absorption Spectroscopy. The crystal structures for Ni(II) and Cu(II) coordination compounds with the compositions NiL21 and Cu2L21 are established by X-ray crystallography [18].

A. Uraev and co-workers have been reported the copper complexes of different composition (CuL2 1 and CuL2OAc) and structure were obtained by coupling the 1-phenyl(isopropyl)-3-methyl-4-(N- substituted)aldimino-5-oxy(thio, seleno)pyrazoles (HL1), and 2-hydroxy(tosylamino)-N-(8-quinolyl)benzaldimine (HL2) with copper(II) acetate. According to X-ray structural data, the CuL2 1 complexes possess the pseudotetrahedral structure, and the CuL2OAc complexes, the square-pyramidal one. The complexes were studied by EXAFS spectroscopy. EXAFS spectral data on the nearest ligand environment show a good correlation with the X-ray structural results [19].

Conclusion

According to the aforementioned work, distinct copper complexes can be examined using UV, IR, XANES, and EXAFS techniques by including pyrazole and glycine as one of the ligands. We have utilised a variety of methodologies in the UV, IR, XANES, and EXAFS techniques to calculate the various complexes necessary characteristics, including chemical shift, ENC, oxidation state, and structural data such as bond length, coordination numbers, nearby atoms, geometric structure, etc. To confirm our findings, we may also compare the XANES and EXAFS results of the complexes with the

UV and IR spectroscopy results of the same complexes. For the investigation of any complex in any form, such as solid, liquid, aqueous solution, amorphous, etc., these methodologies are therefore unique.

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