CHAPTER 3

Synthesis and characterization of copper(II) complexes
3 Synthesis and characterization of copper(II) complexes

3.1 General

This chapter deals with the synthesis and characterization of drug based mixed ligand copper(II) complexes with neutral bidentate N, S –donor ligands.

Among all the noble metals, copper is the only essential one and it takes part in various biological processes, along these lines its homeostasis is entirely managed. Copper(II) complexes have been explored for numerous therapeutic purposes, for example antimalarial, antifungal, antibacterial agents, in the treatment of Alzheimer’s disease, Parkinson’s disease, diabetes, skin wounds, amyotrophic lateral sclerosis, cardiovascular diseases, inflammatory states, and leishmaniasis. In spite of the fact that their mode of action is not yet wholly understood and it requires extra justifications. Nonetheless, one very much upheld hypothesis is based on the intracellular formation of reactive oxygen species (ROS) by means of the thiol-mediated reduction of Cu(II) to Cu(I), and further backing has originated from the latest studies.[1] DNA cleavage has additionally been exposed in a few studies, particularly for polypyridines and polyphenols.[2]

Many fluoroquinolone metal complexes has been synthesized to understand their physicochemical properties and biological activities.[3, 4] During the last four decades, fluoroquinolones have been perceived as an intense gathering of antibiotics, in light of their efficacy, good pharmacokinetic properties and tolerability.[5] Huge number of quinolone molecules are zwitterionic, taking in to account of the occurrence of a carboxylic acid functional group at the third position and a basic piperazinyl ring (or another N-heterocycle) at the seventh position. Weak acidic and weak basic nature of functional groups give rise to good solubility for the quinolones in acidic or basic media. Quinolones form metal complexes owing to their ability to bind metal ions. The quinolones can form metal complexes by acting as bidentate ligand, as unidentate ligand and also as bridging ligand. Oftentimes, they coordinated in a bidentate manner, by means of one of the oxygen atoms of deprotonated carboxylic group and the ring carbonyl oxygen atom. Cu(II)–quinolone complexes are either four or five coordinate. The activity of quinolones as antibacterial drugs is mostly centered around the inhibition of DNA replication by targeting essential type II bacterial topoisomerases viz. DNA gyrase and topoisomerase IV; in this way, interaction of quinolones and also their complexes with DNA is regarded of great importance.

From the literature review, it was concluded that the metal complex of quinolone can interact with DNA by an intercalative binding mode.[6, 7] The consequence of interaction with metal ions on the biological activity of quinolones show that the chelates of quinolones obtained in solid state, an equal or superior
activity was observed compared to that of parent drugs perhaps due to resulting higher liposolubilities which leads to greater intracellular accumulations.

A large number of copper(II) complexes have been synthesized and explored for their biological activities because of its biological relevance.[8, 9] The antifungal and antibacterial properties of many copper(II) complexes have been evaluated against several pathogenic fungi and bacteria.[10, 11] Thus they could be exploited as SOD imitate agents as well as in antimicrobial therapies due to their different paths of cellular intake and different mechanisms of action.

3.2 Materials and instrumentation

All the chemicals used were of analytical grade. Solvents were dried and distilled prior to their use following standard procedure.[12] Copper(II) chloride was purchased from E. Merck (India) Ltd., Mumbai. Gatifloxacin hydrochloride was purchased from Bayer AG (Wuppertal, Germany).

Thermogravimetric analysis were performed with a Q600 SDT Simultaneous DSC-TGA, Waters Ges.m.b.H., Vienna, Austria. Infrared spectra were recorded on an FT-IR (IRAffinity-1) Shimadzu spectrophotometer as KBr pellets in the range 4000 to 350 cm⁻¹. In the range 800 to 200 nm, the absorption spectra of the complexes were recorded on UV-160A UV–vis spectrophotometer, Shimadzu, Japan and 10 mm path length quartz cell. Euro Vector EA3000 elemental analyzer was used to analyze carbon, hydrogen, and nitrogen. The molar-conductance measurements were carried out on Equip-Tronics EQ-660A, conductivity meter (India). Metallic content of the complex was determined by volumetrically, after decomposing it under effect of acid mixture (HClO₄, H₂SO₄ and HNO₃; 1:1.5:2.5) and titrating against EDTA solution.[13] The magnetic moments were measured by Gouy’s method using mercury tetrathiocyanatocobaltate(II) as the calibrant (χ₈ = 16.44×10⁻⁶ cgs units at 20 °C). The diamagnetic correction was made using Pascal’s constant. The X-band electron paramagnetic resonance (EPR) spectra were recorded from powdered samples and from DMSO solution with a Varian E-line Century Series Spectrometer equipped with a dual cavity and operating at X-band (~9.5 GHz) with 100 kHz modulation frequency at room temperature using TCNE (g = 2.0027) as an internal standard. The Varian quartz tubes were used for measuring EPR spectra of polycrystalline samples. Mass spectra were recorded on Shimadzu LC-MS 2010. Photo quantization of the gel after electrophoresis was carried out on AlphaDigiDoc™ RT, Version V.4.0.0 PC–Image software.

3.3 General synthesis of copper(II) complexes

Methanolic solution of CuCl₂·2H₂O (1.5 mmol) was added to a methanolic solution of different pyrimidine derivatives (Lₙ) (1.5 mmol), followed by the addition of a previously prepared methanolic solution of gatifloxacin (1.5 mmol)
in presence of CH₃ONa (1.5 mmol). The pH of the reaction mixture was adjusted to ~6.8 using dilute solution of CH₃ONa. The resulting solution was refluxed for 2 h on a water bath, followed by concentrating to half of its volume. A fine, green amorphous product obtained was washed with chloroform and dried in a vacuum desiccator. Reaction scheme for the synthesis of complexes has been shown in scheme 3-1 and 3-2. The melting points of all complexes were found to be above 300 °C. The newly synthesized complexes are air-stable and insoluble in common solvent while partially soluble in dimethylformamide and completely soluble in dimethylsulfoxide.

Scheme 3-1 General reaction scheme for synthesis of copper(II) complexes with N, S –donor ligand and gatifloxacin
Scheme 3-2 General reaction scheme for synthesis of copper(II) complexes with N, S –donor ligand and gatifloxacin
### 3.4 Physicochemical data of the synthesized complexes

**Table 3-1 Physicochemical parameter data of copper(II) complexes (1–7)**

<table>
<thead>
<tr>
<th>Complex</th>
<th>% Yield</th>
<th>MW (g/mol)</th>
<th>Λ\text{m}a (Ω\text{−1} cm\text{2} mol\text{−1})</th>
<th>λ\text{max} (nm)</th>
<th>mp °C</th>
<th>Element analysis % found (required)</th>
<th>Empirical and Molecular formula of the complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65.45</td>
<td>780.73</td>
<td>5.35</td>
<td>&gt;300</td>
<td>8.37</td>
<td>C_{33}H_{35}ClCuF_{2}N_{6}O_{6}S</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>64.59</td>
<td>780.73</td>
<td>4.25</td>
<td>660</td>
<td>10.81</td>
<td>C_{33}H_{35}ClCuF_{2}N_{6}O_{6}S</td>
<td></td>
</tr>
<tr>
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<td>770</td>
<td>11.40</td>
<td>C_{33}H_{35}ClCuF_{2}N_{6}O_{6}S</td>
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<tr>
<td>4</td>
<td>52.04</td>
<td>841.63</td>
<td>7.38</td>
<td>&gt;300</td>
<td>9.82</td>
<td>C_{33}H_{35}ClCuF_{2}N_{6}O_{6}S</td>
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</tr>
<tr>
<td>5</td>
<td>51.81</td>
<td>797.18</td>
<td>9.01</td>
<td>670</td>
<td>8.12</td>
<td>C_{33}H_{35}ClCuF_{2}N_{6}O_{6}S</td>
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<tr>
<td>6</td>
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<td>C_{33}H_{35}ClCuF_{2}N_{6}O_{6}S</td>
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<td>52.04</td>
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<td>9.01</td>
<td>&gt;300</td>
<td>8.17</td>
<td>C_{33}H_{35}ClCuF_{2}N_{6}O_{6}S</td>
<td></td>
</tr>
</tbody>
</table>

* a Molar conductance measured for 1.0 X 10^{-3} M solution of complex in DMSO, Ω\text{−1} cm\text{2} mol\text{−1}. 

Note: The empirical and molecular formulae of the complexes are given for the solid state. The physicochemical parameters and elemental analysis are provided for both the solution and solid states.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Empirical and Molecular formula of the complex</th>
<th>Elemental analysis % found (required)</th>
<th>mp °C</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Ω $^a$ cm$^{-1}$ mol$^{-1}$</th>
<th>MW (g/mol)</th>
<th>% Yield</th>
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<tr>
<td></td>
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<td>C</td>
<td>H</td>
<td>N</td>
<td>Cu</td>
<td>Solid state</td>
<td>Solution state</td>
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<tr>
<td>8</td>
<td>[Cu(GFL){L$^8$}Cl]·3H$_2$O</td>
<td>48.32 (48.44)</td>
<td>4.23 (4.31)</td>
<td>8.51 (8.56)</td>
<td>7.85 (7.77)</td>
<td>&gt;300</td>
<td>675</td>
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<td>C$<em>{33}$H$</em>{35}$ClCuF$_2$N$_5$O$_7$S</td>
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<tr>
<td>9</td>
<td>[Cu(GFL){L$^9$}Cl]·3H$_2$O</td>
<td>47.58 (47.49)</td>
<td>4.02 (4.23)</td>
<td>8.30 (8.39)</td>
<td>7.59 (7.61)</td>
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<td>687</td>
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<td>7.33 (7.23)</td>
<td>&gt;300</td>
<td>666</td>
</tr>
<tr>
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<tr>
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<td>[Cu(GFL){L$^{11}$}Cl]·3H$_2$O</td>
<td>48.60 (48.44)</td>
<td>4.53 (4.31)</td>
<td>8.40 (8.56)</td>
<td>7.50 (7.77)</td>
<td>&gt;300</td>
<td>673</td>
</tr>
<tr>
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<td>C$<em>{33}$H$</em>{35}$CuF$_2$N$_5$O$_7$S</td>
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<td>[Cu(GFL){L$^{12}$}Cl]·3H$_2$O</td>
<td>47.55 (47.49)</td>
<td>4.30 (4.23)</td>
<td>8.52 (8.39)</td>
<td>7.73 (7.61)</td>
<td>&gt;300</td>
<td>684</td>
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<tr>
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<td>C$<em>{33}$H$</em>{35}$CuFN$_5$O$_7$S</td>
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<tr>
<td>13</td>
<td>[Cu(GFL){L$^{13}$}Cl]·3H$_2$O</td>
<td>45.12 (45.09)</td>
<td>4.02 (4.01)</td>
<td>7.71 (7.97)</td>
<td>7.18 (7.23)</td>
<td>&gt;300</td>
<td>675</td>
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<tr>
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<td>C$<em>{33}$H$</em>{35}$BrCl$_2$CuFN$_5$O$_7$S</td>
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</tr>
<tr>
<td>14</td>
<td>[Cu(GFL){L$^{14}$}Cl]·3H$_2$O</td>
<td>49.32 (49.19)</td>
<td>4.42 (4.61)</td>
<td>8.21 (8.44)</td>
<td>7.58 (7.65)</td>
<td>&gt;300</td>
<td>670</td>
</tr>
<tr>
<td></td>
<td>C$<em>{34}$H$</em>{36}$Cl$_2$CuFN$_5$O$_8$S</td>
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</tr>
</tbody>
</table>

$^a$ Molar conductance measured for 1.0 $\times$ 10$^{-3}$ M solution of complex in DMSO, Ω$^{-1}$ cm$^2$ mol$^{-1}$
Chapter 3

3.5 Electronic spectra of the copper(II) complexes

3.5.1 General

A conspicuous contrast between specific compounds is their colour as they absorb some colors (wavelengths) and reflected or transmit others. The colors we see are the wavelengths that are reflected or transmitted. To comprehend this phenomenon we must make a precise estimations of light absorption at distinctive wavelengths in and close to the visible part of the spectrum. Matter-Electromagnetic radiation interactions occurs in different routes over the spectrum. Therefore, in spite of the fact that these various types of electromagnetic radiation frame a quantitatively constant range of frequencies and wavelengths, the spectrum stays divided for practical reasons related to these qualitative interaction differences. Figure 3-1 demonstrates the various regions of electromagnetic radiation.

![The electromagnetic spectrum](image)

*Figure 3-1 The electromagnetic spectrum*

On passage of continuous radiation through a transparent material, a part of the radiation may be absorbed. If it is so, the transmitted radiation, when passed through a prism, yields a spectrum with gaps in it, called an absorption spectrum. As an aftereffect of energy absorption, atoms or molecules go from a state of low energy (the initial, or ground state) to a state of higher energy (the excited state). Figure 3-2 delineates this excitation process, which is quantized. The electromagnetic radiation that is absorbed has energy precisely equivalent to the energy difference between the excited and ground states.

UV/Visible light absorption prompts the electronic transitions of valance electrons. Valence electrons can for the most part be found in one of three sorts of electron orbital: 1 single or σ bonding orbitals; 2 double or triple bonds (π bonding orbitals); and 3 non-bonding orbitals (lone pair electrons). For numerous molecules, the lowest-energy occupied molecular orbitals are the σ orbitals, which correspond to the most stable electrons. The π orbitals lie at somewhat higher energy levels, and orbitals that hold unshared pairs, the nonbonding (n) orbitals,
lie at even higher energies. The unoccupied, or antibonding orbitals ($\pi^*$ and $\sigma^*$), are the orbitals of highest energy.

Most of the transitions from bonding orbitals are of too high a frequency (too short a wavelength) to measure easily, so most of the absorptions observed involve only $\pi \rightarrow \pi^*$, $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions. Each electronic state is well defined for a particular system.

The Figure 3-2 shows the different transitions between the bonding and anti–bonding electronic states.

![Figure 3-2](image.png)

**Figure 3-2** Possible electronic transitions between bonding and anti–bonding electronic states

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital.

The energy of the UV/Visible radiation is higher than that of the rotational and vibrational energy levels. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each electronic level which leads the broadening of the UV/Visible peak in the spectra.

In general the electronic spectrum of a complex, can be sub classified into three main divisions

1) **Transitions between levels primarily located on the ligands.**

   **$\sigma \rightarrow \sigma^*$ Transitions:** An electron in a bonding $s$ orbital is excited to the corresponding anti bonding orbital. The energy required is large.

   **$n \rightarrow \sigma^*$ Transitions:** Saturated compounds containing atoms with lone pairs (non–bonding electrons) are capable of $n \rightarrow \sigma^*$ transitions. These transitions usually need less energy than $\sigma \rightarrow \sigma^*$ transitions. The number of organic functional groups with $n \rightarrow \sigma^*$ peaks in the UV region is small.
n→π* Transitions: These transitions involve moving an electron from a nonbonding electron pair to an antibonding π* orbital. They tend to have molar absorbptivities less than 2000 and undergo a blue shift with solvent interactions. This is because the lone pair interacts with the solvent, especially a polar one, such that the solvent aligns itself with the ground state. The absorption peaks for these transitions fall in an experimentally convenient region of the spectrum (200–700 nm). These transitions need an unsaturated group in the molecule to provide the π electrons.

π→π* Transitions: These transitions involve moving an electron from a bonding π orbital to an antibonding π* orbital. They tend to have molar absorbptivities on the order of 10,000 and undergo a red shift with solvent interactions. This could either be due to a raising of the ground state energy or lowering of the excited state energy.

2) Transitions between levels primarily located on the metal, d-d transitions.

d–d Transitions: The excitation of an electron of metal from one d–orbital to another d–orbital takes place in d–d transitions. Transition metal complexes with more than one d–electron often show more than one d–d bands which are due to electron–electron repulsion and may have more than one state for a given electronic configuration. This forbidden character is manifests itself in the intensity of the observed d–d transitions. The d–d transitions are very useful to evaluate the geometry of the complexes.

3) Transitions in which there is an electron transferred from the metal to the ligands, or vice versa.

Charge–transfer transitions: In some complexes a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. The source molecule from which the charge is transferred is called the electron donor and the receiving species is called the electron acceptor.

The transition is classified as a ligand-to-metal charge-transfer transition (LMCT transition) if the migration of the electron is from the ligand to the metal, and as a metal-to-ligand charge-transfer transition (MLCT transition) if it occurs in the opposite direction.

(a) LMCT transitions: Ligands possess σ, σ*, π, π*, and nonbonding (n) molecular orbitals. If the ligand molecular orbitals are full, charge transfer may occur from the ligand molecular orbitals to the empty or partially filled metal d-orbitals. The absorptions that arise from this process are called ligand-to-metal
charge-transfer bands (LMCT). LMCT transitions result in intense bands. Forbidden d-d transitions may also take place giving rise to weak absorptions.

(b) MLCT transitions: Charge-transfer transitions from metal to ligand are observed when the metal is in a low oxidation state and the ligands have low-lying acceptor orbitals. The transition occurs at low energy and appears in the visible spectrum if the metal ion is in a low oxidation state, as its d orbitals are then relatively close in energy to the empty ligand orbitals.

3.5.2 Literature survey

Filitsa Dimiza et al.,[14] synthesized copper(II) complexes with naproxen, the non-steroidal anti-inflammatory drugs (NSAIDs), and diclofenac with nitrogen donor heterocyclic ligands (2,2′-bipyridine, 1,10-phenanthroline or pyridine). They recorded UV–vis spectra of the complexes as Nujol mull and in DMSO solution and suggested that the complexes retain their structure in solution giving one low-intensity band in the region 680–715 nm assigned to d–d transitions, typical for square planar Cu(II) complexes, while for [Cu2(nap)(H2O)2] and [Cu2(dicl)4(H2O)2] this band is observed at 720–730 nm. For octahedral local symmetry, this band can be attributed to a 2Eg→2T2g transition. Additionally, an absorption band assigned to charge transfer transition exists at 410–415 nm.

Eleni K. Efthimiadou et al.,[15] synthesized mononuclear copper(II) complexes with quinolones and nitrogen–donor heterocyclic ligands and reported that the complexes exhibits d–d transition band at around 640–650 nm (ε ~ 35–50 M⁻¹cm⁻¹) and an additional weak broad d–d transition band at 820–840 nm (ε ~ 5–10 M⁻¹cm⁻¹) typical for distorted square pyramidal geometry. They also reported a ligand to metal charge transfer band in the region of 400–430 nm with the extinction coefficient in the range of 170–250 M⁻¹cm⁻¹.

Atittaya Meenongwa et al.,[16] studied interaction of two copper(II) complexes, namely [Cu(L1)Cl2]2 (1) and [Cu(L2)Cl2]2 (2), where L1 = 1-amidino-O-methylurea and L2 = N-(benzyl)-amidino-O-methylurea, with DNA. The electronic spectra of 1 and 2 actually display intense absorption bands at λmax = 226 and 209 nm, respectively, which are assigned to π-π* intraligand transitions.

Xin Li et al.,[17] synthesized copper(II) complexes with formulas of [Cu4(bhpox)2(dabt)2](ClO4)2 (1) and [Cu4(bhpox)2(dmbt)2](ClO4)2·2H2O (2), and structurally characterized, by using N-benzoate-N’-[3-(2-hydroxyethylammino)propyl]-oxamide (H3bhpox), as a bridging ligand and terminating 2,2′-diamino-4,4′-bithiazole (dabt) and 2,2′-dimethyl-4,4′-bithiazole (dmbt). They reported inter- or intraligand (π-π*) transition at 221–230 nm and the broad bands at about 620 nm observed at the lower frequency in the spectrum match well with the d–d transition.
George Psomas et al.,[18] synthesized neutral and cationic mononuclear copper(II) complexes with enrofloxacin with nitrogen donor heterocyclic ligand and reported that, all the complexes exhibit a d–d transition band at around 630 nm and an additional relatively weak and broad band at around 820 nm suggesting that distorted square pyramidal geometry. An absorption band at 420–430 nm is present in the spectra of all complexes and can be assigned to the ligand to-metal charge-transfer transition (LMCT) for the quinolone ligand.

Mei-Jin Li et al.,[19] reported the synthesis of the new mononuclear copper(II) complexes, [Cu(L)]^{2+} (1), [Cu(acac)(L)]^{+} (2), and [Cu(acac-Cl)(L)]^{+} (3) (L = 2-(4-pyridine)oxazo[4,5-f]1,10-phenanthroline (4-PDOP); acac = acetylacetone; acac-Cl = 3-chloroacetylacetone). They reported bands between 260–400 nm attributed to π to π* transitions of the aromatic nitrogen donor ligands. The low-energy bands around 450 nm for complex 1 are assigned as the (dπ(Cu))→ligand (π*(N–N)), and the bands around 640–709 nm for complexes 1–3 are all assigned as metal d–d transitions typical of copper(II) complexes.

Subhash Padhye et al.,[20] synthesized [Cu(cfH)(phen)Cl]BF_{4} ⋅ 4H_{2}O complex and carried out electronic spectra and reported that complex exhibits d–d band at 640 nm, and suggesting square pyramidal geometry around central metal atom. The ligand-based transitions are observed in the 220–271, 277–283, and 316–331 nm region.

3.5.3 Result and discussion

Absorption spectrum of the representative complex 1 is shown in Figure 3-3. The spectra of the free ligands showed the two type of transitions appearing around 265 and 360 nm are due to π–π* and n–π* transitions involving molecular orbital of the pyrimidine ring, C=C and C=N chromophore.

The electronic spectra of the complexes are very similar to each other and show a low energy ligand field (LF) band (660 ± 5 nm). The Cl–Cu charge transfer band usually appeared around 400 nm as less intense band, but in our case this peak might be masked due to medium intensity charge transfer band around 360 nm. Due to complexation the bands corresponding to π–π* and n–π* transitions are shifted to higher value at around 280 and 360 nm, respectively. Also a band around 660 nm is obtained, which is attributed to the dd transition of Cu(II) ion. The Cu(II) ion with five coordinating donor sites can lead to formation of two possible geometries viz. square-pyramidal geometry and trigonal bipyramidal geometry. The possibility of trigonal bipyramidal geometry at metal centre was ruled out because peak of λ_{max} greater than 800 nm in the case of synthesized complexes.[21] The spectra suggest that compounds have a square pyramidal geometry of the ligands donor atoms around the Cu(II) center since it shows only a broad band at ~ 660 nm in visible electronic transition spectra.
3.6 Magnetic moments measurement of the copper(II) complexes

3.6.1 General

Magnetic moments are often used in conjunction with electronic spectra to gain information about the oxidation number and stereochemistry of the central metal ion in coordination complexes. The magnetic properties are due entirely to the electrons of the atom, which have a magnetic moment by virtue of their motion orbital and spin. The nucleus also has a small magnetic moment, but it is insignificant compared to that of the electrons, and it does not affect the gross magnetic properties.

Magnetic materials can be classified in terms of the arrangements of magnetic dipoles in the solid. The response of the atom to an applied magnetic field depends on how the magnetic dipoles represented by each atom react to the field. For an atom or ion with only paired electrons, the individual electron contributions to the overall spin magnetic quantum number, \( M_s \), cancel one another, giving a zero net value of the overall spin quantum number; i.e., \( S = 0 \). Such a species is said to be **diamagnetic**. If a diamagnetic material is placed between the poles of a strong magnet it will experience a repulsion for the applied field. The repulsion arises from circulation of the electrons caused by the applied field, resulting in an induced magnetic field in opposition, thus a loss in weight is observed compared to its true weight outside the field. The magnitude of the induced magnetic moment is extremely small, and in a direction opposite to that of the applied field. For the sample contains unpaired electrons, the overall spin quantum number will be greater than zero; i.e., \( S > 0 \). Such a species is said to be **paramagnetic**. 

![Figure 3-3 Absorption spectrum of the complex 1](image)

**Figure 3-3 Absorption spectrum of the complex 1**

[Image: Figure 3-3 Absorption spectrum of the complex 1]
**paramagnetic.** If a paramagnetic species is placed between the poles of a strong magnet it will experience an attraction for the field, due to the alignment of the permanent paramagnetic moment with the applied field and thus a gain in weight is observed compared to its true weight outside the field.

Transition metal ions, by definition, have at least one oxidation state with an incomplete $d$-orbital. Since electrons spin and generate a magnetic field, the magnetic properties of transition metal ions are of great interest. The measurement of the magnetic susceptibility of a transition metal compound allows us to determine the number of unpaired electrons in the compound. This knowledge of the number of unpaired electrons associated with the transition metal in the compound is especially useful in understanding the compound's bonding, magnetic and spectral characteristics, determining the oxidation state, electronic configuration and so on.

Most organic compounds and main group element compounds have all their electrons paired. Such molecules are diamagnetic and have very small magnetic moments. Many transition metal compounds, however, have one or more unpaired electrons, and are termed paramagnetic. The number of unpaired electrons on a given metal ion determines the magnetic moment, affecting it both by virtue of their spin and their orbital motion. The spin is more important, and a close estimate of the magnetic moment can be obtained using the following equation.

$$
\mu_s = g \sqrt{S(S+1)} \mu_B
$$

where, $g$ is the gyro magnetic ratio ($\cong 2$) and $S$ is spin of the unpaired electrons ($\frac{1}{2}$ for each). The unit of the magnetic moment is Bohr Magneton ($\mu_B$). Actual magnetic moments are somewhat larger than the spin-only values, because of the orbital contribution. The value of $\mu_{\text{eff}}$ may vary slightly from one compound to another. Once the effective magnetic moment is determined, it is simple to find the number of unpaired electrons, and from that, the electronic configuration (hybridization) of the metal. This can lead to an understanding of the geometry and bonding in the molecule.

### 3.6.2 Literature survey

Kalagouda B. Gudasi *et al.*, [22] reported the magnetic moment value 1.69 BM for copper(II) complex, which is close to 1.73 BM as expected for discrete magnetically non-coupled spin only value for copper(II) ion.

M. González–Á lvarez *et al.*, [23] reported the magnetic moment value 1.76 $\mu_B$ for copper(II) complex of sulfathiazole and benzimidazole, which consistent with the presence of the unpaired electron in monomeric copper(II) complexes.
A. Haleel et al.[24] reported the effective magnetic moment value 1.93 BM, for copper(II) complexes which is slightly higher than the spin only values (1.73 μeff) expected for a d⁹ system with one unpaired electron.

M. P. Lopez-Gresa et al.[25] synthesized copper(II) complex with ciprofloxacin and carried out magnetic susceptibility measurements using Hg[Co(SCN)₄] as a standard and reported that, the complex shows magnetic moment value 1.70 μB, which is close to that of spin–only magnetic moment.

P. Ruiz et al.,[26] studied the magnetic moment measurement of synthesized ternary complexes of copper(II) with 1,10–phenanthroline and norfloxacin and reported that the magnetic moments of complexes lie in the range 1.74–1.91 μB.

3.6.3 Result and discussion

Information regarding the number of unpaired electrons and the oxidation state of element hence, the information about the geometry of the complexes can be obtained from the magnetic moments value. The magnetic moments of the complexes in the range 1.75 – 1.8 B.M. (Table 3–3), which is very close to the spin-only value (1.73 B.M.), indicating the paramagnetic behavior of them and have one unpaired electron confirming copper +2 in d⁹ configuration (t²g⁶e²g³).

<table>
<thead>
<tr>
<th>Compound</th>
<th>μeff BM</th>
<th>Compound</th>
<th>μeff BM</th>
</tr>
</thead>
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3.7 LC–MS spectra of the copper(II) complexes

3.7.1 General

The partition force of cutting edge chromatography consolidated with the selectivity and low detection limits of advanced mass spectrometers empowers us to examine exceptionally complex specimens with a high level of certainty, high sensitivity and selectivity. Liquid chromatography–mass spectrometry (LC–MS, or alternatively HPLC–MS) is a method that mixes the physical separation capacities of liquid chromatography (or HPLC) with the mass analysis capabilities of mass spectrometry. As the name recommend the instrumentation involves a high performance liquid chromatography (HPLC) appended, through a suitable
interface, to a mass spectrometer (MS). The essential point of preference HPLC/MS has over GC/MS is that it is equipped for analyzing a much more extensive scope of components. Compounds that are thermally labile, display high polarity or have a high atomic mass may all be analyzed utilizing HPLC/MS, even proteins may be routinely investigated.

Mass spectrometry is an indispensable analytical tool in chemistry, biochemistry, pharmacy, medicine, and many related fields of science. Whatever the analytical interest may be: mass spectrometry aims to identify a compound from the molecular or atomic mass(es) of its constituents. The information delivered by mass alone can be sufficient for the identification of elements and the determination of the molecular formula of an analyte.

The basic principle of mass spectrometry (MS) is to engender ions from either inorganic or organic compounds by any appropriate technique, to distinct these ions by their mass-to-charge ratio (m/z) and to identify them qualitatively and quantitatively by their corresponding m/z and abundance.

In its simplest form, the mass spectrometer has five components (Figure 3-4).

![Figure 3-4 The components of a mass spectrometer](image)

**Sample inlet:** It brings the sample from the laboratory environment (1 atm) to the lower pressure of the mass spectrometer.

**Ion source:** Here the sample molecules are transformed into gas phase ions. The analyte may be ionized thermally, by electric fields or by impacting energetic electrons, ions or photons.

**Mass analyzer:** the region of the mass spectrometer where the ions are separated according to their mass-to-charge (m/z) ratios by applying the magnetic field in a direction perpendicular to the direction of motion of ions.
3.7.2 Literature review

Mark B. Bushuev et al.,[27] synthesized copper(II) complexes with N, N-donor ligands and characterized by electrospray ionization mass spectrometry, to confirm the metal-to-ligand molar ratio and hence the participating species.

Angira Koch et al.,[28] synthesized the mixed ligand copper(II) complexes from benzoic acid and bipyrimidine ligand and characterized using the single crystal analysis and mass spectrometry to demonstrates formation of the heterodinuclear complex ion rather than a mixture of mononuclear or corresponding homobinuclear copper(II) complexes.

Ramazan Gup et al.,[29] synthesized the copper complexes of Schiff base-hydrazone ligands and characterized by microcopy and spectral studies. They confirmed the structure from the presence of molecular ion peak in the mass spectra.

3.7.3 LC–MS spectrum of complex 1

The mass spectrum and proposed mass fragmentation pattern for complex 1 is shown in Figure 3-5 and Figure 3-6 respectively.

Molecular ion peak [M]+ at 744.33 m/z and [M+2] at 746.05 m/z in the LC–MS spectrum of complex 1 confirms the structure of complex 1. Peak at 709.76 m/z is due to the loss of one chlorine atom from the complex. Due to the loss of pyrimidine heterocyclic ligand a peak at 473.95 is appeared which on further loss of chlorine atom generates the molecular ion giving peak at 437.93 m/z. The peak at 375.16 m/z corresponds to gatifloxacin moiety. The peak at 370.31 m/z is due to pyrimidine heterocyclic ligand attached to copper(II) including coordinated chlorine atom. After a gatifloxacin loss the a fragment with the loss of chlorine is recorded at 334.86 m/z which upon loss of copper atom give a peak at 271.06 m/z.
Figure 3-5 LC–MS spectrum of complex 1

Figure 3-6 Probable mass fragmentation pattern of complex 1
3.7.4 LC–MS spectrum of complex 8

Figure 3-7 represents the LC–MS spectrum of complex 8. Mass spectrum of the complex 8 show molecular ion [M+] at 764.00 m/z and [M+2] at 766.27 m/z and [M+4] at 768.05 m/z. Peak at 727.09 m/z is due to the loss of chlorine atom from the molecular ion. The peak at 472.05 m/z and 474 m/z corresponds to gatifloxacin attached to copper(II) including coordinated chlorine atom while the removal of the chlorine atom from this ion give the peak at 437.08 m/z. Peaks at 389.90 m/z and 391.21 m/z are due to ligand attached with copper and one chlorine atom, which on removal of chlorine atom gives the peak at 352.94 m/z. The peak at 290.01 m/z is due to the neutral bidentate ligand. The proposed mass fragmentation pattern for complex 1 is shown in Figure 3-8.

![Figure 3-7 LC–MS spectrum of complex 8](image-url)
3.8 Thermogravimetric analysis of the copper(II) complexes

3.8.1 General

Thermogravimetric analysis (TGA) measures the amount of weight change of a material, either as a function of increasing temperature, or isothermally as a function of time. The measurement is normally carried out in air or in controlled atmosphere, such as helium or argon. Sometimes, the measurement is performed in a lean oxygen atmosphere (1 to 5% O$_2$ in N$_2$) to slow down oxidation.

A TGA consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment (Figure 3-9). The furnace should have a zone of uniform temperature. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust.

**Figure 3-8** Probable mass fragmentation pattern of complex 8

![Mass fragmentation pattern of complex 8](image)
Applications of Thermogravimetry

- Determination of alteration in temperature and weight of decomposition reactions frequently lets quantitative composition analysis which can be utilized to estimate presence of the amount of lattice water coordinated water.

- Analysis of reactions with air, oxygen, or other reactive gases is possible.

- Evaporation rates of liquid mixtures can be measured.

- Curie temperatures of magnetic transitions can be determined by quantifying the temperature at which the force exerted by a nearby magnet vanishes on heating or reappears on cooling.

- Helps to recognize plastics and organic materials by measuring the temperature of bond scissions in inert atmospheres or of oxidation in air or oxygen.

- Measurement of the heaviness of fiberglass and inorganic fill materials in primers, plastics, paints, laminates and composite materials by burning off the polymer resin. The fill material, for instance carbon black, TiO$_2$, CaCO$_3$, MgCO$_3$, Al$_2$O$_3$, Al(OH)$_3$, Mg(OH)$_2$, talc, Kaolin clay, or silica, can then be identified by XPS and/or microscopy.

- Can measure the fill materials added to some foods, such as silica gels and titanium dioxide.

- The purity of a mineral, inorganic compound, or organic material can be determined.
• Distinguishes different mineral compositions from broad mineral types, such as borax, boric acid, and silica gels.

3.8.2 Literature survey

Sartaj Tabassum et al.,[30] studied a copper(II) Schiff-base complex using thermal analysis in a N₂ atmosphere and reported the weight loss in the temperature range 80–240 °C that corresponds to the loss of coordinate or crystalline water molecules.

Tarek A. Mohamed et al.,[31] synthesized Co(II), Ni(II), Cu(II) and Pd(II) complexes of 4-amino-5-pyrimidinecarbonitrile and carried out thermogravimetric analysis. The weight loss within the temperature range of 342–989 °C corresponds to the loss of organic moiety leaving Cu metallic residue.

L. Perello et al.,[32] synthesized copper(II) and cobalt(II) complexes with two quinolone family members, ciprofloxacin and enoxacin, and they carried out thermogravimetric analysis to find water content in the synthesized complexes.

Iztok Turel et al.,[33] synthesized metal quinolone complexes and characterized by crystal structure determination and carried out thermogravimetric analysis to ascertain water molecule in the synthesized metal complexes.

3.8.3 Thermogravimetric analysis of complex 1

The TGA (Figure 3-10) shows the three steps of decomposition.[34] The complex 1 shows a weight loss in the range 50–110 °C, indicating the presence of two lattice water molecules. In the second, step weight loss during 190–250 °C corresponding to one coordinated chlorine atom. A loss in weight found between 250 and 860 °C corresponds to decomposition of ligand. Metal oxide left behind at the end of TG curve (>860 °C) is used to calculate the metal content and found in close proximity to the expected one.

3.8.4 Thermogravimetric analysis of complex 8

From the thermogram (Figure 3-11) the complex 8 showed a weight loss in the range 50–130 °C, indicating the presence of three lattice water molecules. In the second step, weight loss during 185–260 °C corresponding to one coordinated chlorine atom. A loss in weight found between 260 and 830 °C corresponds to decomposition of ligand. Metal oxide left behind at the end of TG curve (>830 °C) was used to calculate the metal content and was found in close proximity to the expected one.
Figure 3-10 The thermogram of complex 1

Figure 3-11 The thermogram of complex 8
3.9 Infrared spectroscopy of the copper(II) complexes

3.9.1 General

Infrared spectroscopy is a helpful device to study molecular structural, identification, and quantitative examinations of materials. Abundant organic and inorganic substances absorb infrared radiation. The wavelength region of IR is not entirely defined but the wavelength regions generally accepted for near-infrared, mid-infrared, and far-infrared radiation are as per the following: 700 nm to 2.5 μm for near-infrared, 2.5–25 μm for mid-infrared, and 25 μm to 1 mm for far-infrared. The absorbance is taken as the ordinate axis of an infrared spectrum. The wavenumber (ν̅), the number of light waves per unit length (usually 1 cm) and corresponds to the reciprocal of the wavelength, is used as the abscissa axis of an infrared spectrum is always expressed in units of cm⁻¹. The relation between wavenumber and energy (E) is given by

\[ E = h\nu \]

where \( h \) is the Planck constant and \( c \) the speed of light. This proportionality between \( E \) and \( \nu \) is the reason why the wavenumber is now used as the abscissa axis of an infrared spectrum. Thus in terms of wavenumber above mentioned IR region can be written as 14,000–4000 cm⁻¹ for near-infrared, 4000–400 cm⁻¹ for mid-infrared, and 400–10 cm⁻¹ for far-infrared. Infrared absorptions arise from the transitions between the energy levels of molecular vibrations. In liquids and solids, free rotation of molecules does not occur, so that infrared spectra observed from liquids and solids are “pure” vibrational spectra. If the dipole moment of a molecule changes with a molecular vibration, infrared radiation with the frequency equal to the frequency of the molecular vibration is absorbed by the molecule.

There are two types of molecular vibrations, stretching and bending. Each atom has three degrees of freedom, corresponding to motions along any of the three Cartesian coordinates (X–, Y–, Z-axis). A polyatomic molecule of \( n \) numbers of atoms has 3n numbers of total degrees of freedom. However, 3 degrees of freedom are required to describe translational motion, the motion of the entire molecule through space. Additionally, 3 degrees of freedom correspond to rotation of the entire molecule. Therefore, the remaining 3n–6 degrees of freedom are truly, fundamental vibrations. Linear molecules possess 3n–5 fundamental vibrational modes because for linear molecule only 2 degrees of freedom are sufficient to describe rotation.

The simplest modes, of vibrational motion in a molecule are the stretching and bending modes. The terms scissoring, rocking, wagging, and twisting are commonly used in the literature to describe the origins of infrared bands. In general, asymmetric stretching vibrations occur at higher frequencies than
symmetric stretching vibrations; also, stretching vibrations occur at higher frequencies than bending vibrations. Simple stretching vibrations appeared in the region 1600–3500 cm\(^{-1}\), called “functional group region”. Complex vibrations appeared in the region 600–1400 cm\(^{-1}\), called “fingerprint region”. The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms.

The vibrations arise by excitation from the ground state to the lowest-energy excited state are called fundamental absorptions. IR spectrum results from a presence of weak overtone (integral multiples of the fundamental absorption frequencies), combination (two vibrational frequencies in a molecule couple to give a vibration of a new frequency within the molecule i.e. sum of the two interacting bands), and difference bands (results from the difference of the two interacting bands) of all possible stretching and/or bending vibrations of the individual bonds and the whole molecule. When a fundamental vibration couples with an overtone or combination band, the coupled vibration is called Fermi resonance. Thus total numbers of observed absorption bands are generally different from the total number of fundamental vibrations. The intensities of overtone and combination bands are less than those of the fundamental bands. The combination and blending of all the factors thus create a unique IR spectrum for each compound.

However, the individual vibrational motion is usually accompanied by other rotational motions. Infrared inactive rotational frequencies of the whole molecule often couple with the stretching and bending vibrations in the molecule to give additional fine structure to these absorptions which may lead to a considerable amount of band broadening.

IR is used to obtain the information about the structure of a compound and as an analytical tool to assess the purity of a compound. It is used to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification.

### 3.9.2 Literature survey

Eleni K. Efthimiadou et al.\(^{[35]}\) reported the bands for quinolone complexes in the range of 1600–1615 cm\(^{-1}\) and 1385–1400 cm\(^{-1}\) which assigned as asymmetric, \(\nu(\text{COO})_{\text{as}}\), and symmetric, \(\nu(\text{COO})_s\), stretching vibrations, respectively.
**Saha et al.,** [20] assigned that ciprofloxacin compounds exhibit two strong bands in the region 1571–1577 cm$^{-1}$ and 1306–1339 cm$^{-1}$ respectively, due to asymmetric and symmetric carboxylate $\nu$(COO) stretching vibration.

Sönmez, Mehmet et al.[36] and Chohan, Zahid H. et al.,[37] assigned the characteristic band of $\nu$(C=O) cyclic and acetyl groups appears at $\sim$1680 and $\sim$1660 cm$^{-1}$, which was shifted towards lower frequency in the complexes. The frequency of separation $\Delta \nu = \nu$(COO$_{as}$) – $\nu$(COO)$_{s}$ for complexes is $\sim$220 cm$^{-1}$, suggesting unidentate nature for the carboxylato group.

### 3.9.3 Infrared spectra of copper(II) complexes (1–7)

In the absence of crystallographic data, IR spectroscopy is regarded as helpful tool for the conformation of ligands coordinating to the metal ion, which can be investigated from the difference in the frequency observed in ligands and their complexes due to specific groups. The IR spectra of complex 1 and the data of all the complexes are represented in Table 3-3 and Figure 3-12 respectively. On comparing the IR-spectra of the free ligand with the IR spectra of their complex the following can be pointed out:

- The broad band around 3300 cm$^{-1}$ is assigned to the physically adsorbed water molecules in the complexes may be linked by hydrogen bonding.
- The peaks around 3100 cm$^{-1}$ is assigned to the $\nu$(C-H)ar. stretching bands of the ligands present in the complexes.
- In IR spectrum of GFLH, bands observed at 3423 cm$^{-1}$, 1724 cm$^{-1}$ and 1635 cm$^{-1}$ are attributed to the stretching vibration of $\nu$(OH), $\nu$(COO) and $\nu$(C=O)p respectively.[38] On coordination with a metal ion, the band of carboxylic group of GFLH is replaced by two strong bands in the range 1563–1581 cm$^{-1}$ [$\nu_{asym}$(C=O)] and 1364–1377 cm$^{-1}$ [$\nu_{sym}$(C=O)]. The unidentate coordination mode of carboxylate group is characterized by $\Delta \nu$ value falling in the range 170–250 cm$^{-1}$ [$\Delta \nu = \nu_{asym}$(C=O)$_c$ – $\nu_{sym}$(C=O)$_c$].[39]
- The IR spectrum of complexes displayed absorption band around 1540-1560 cm$^{-1}$ which can be assigned to C=N stretching frequency of coordinated ligand, whereas for free ligands this band are observed around 1570-1575 cm$^{-1}$. This shifting to lower frequencies of C=N of complexes as compared to free ligand, indicates donation of the lone pair of electrons on pyrimidine nitrogen to copper center.
- Peak in range 1618–1627 cm$^{-1}$ found in case of complexes are for pyridone oxygen $\nu$(C=O) atom, which appeared at 1635 cm$^{-1}$ in gatifloxacin. This shift in band towards lower energy suggests coordination via pyridone oxygen atom.[40] These data are further supported by the weak bands observed at 575–540 cm$^{-1}$, assigned to $\nu$(Cu–O).[41] vibrations.
- All complexes exhibit a broad band between 3470 and 3147 cm$^{-1}$ with a well-defined maxima around 3440 cm$^{-1}$, which corresponds to the vibrations $\nu$(O–
H) as well as to N–H vibration of the piperazinyl moiety and −NH₂ of pyrimidine moiety.[40]

- The medium intensity bands at 525–490, and 425–370 cm⁻¹ are assigned to the Cu–N[41] and Cu–S[42] vibrations, respectively. The absence of such medium intensity bands around in the free ligands indicate the coordination of ligands takes place through N and S atoms of the ligands.

**Figure 3-12** IR spectra of complex 1

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<th>Complexes</th>
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<th>ν(COO)₁₅₅₁</th>
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<th>ν(M–O)₄₁₀</th>
<th>ν(M–N)</th>
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3.9.4 Infrared spectra of copper(II) complexes (8–14)

In IR spectra of GFLH bands observed at 3423 cm\(^{-1}\), 1724 cm\(^{-1}\) and 1635 cm\(^{-1}\) are attributed to the stretching vibration of \(\nu(\text{OH})\), \(\nu(\text{COO})\) and \(\nu(\text{C}=\text{O})\) respectively.\[38\] On coordination with metal ion, the band of carboxylic group of GFLH is replaced by two strong bands in the range 1563–1581 cm\(^{-1}\) \([\nu_{\text{asym}}(\text{C}=\text{O})]\) and 1364–1377 cm\(^{-1}\) \([\nu_{\text{sym}}(\text{C}=\text{O})]\). The unidentate coordination mode of carboxylato ligand is characterized by \(\Delta \nu\) value falling in the range 170–250 cm\(^{-1}\) \([\Delta \nu = \nu_{\text{asym}}(\text{C}=\text{O})_c - \nu_{\text{sym}}(\text{C}=\text{O})_c]\).\[39, 40\] Peak in range 1618–1627 cm\(^{-1}\) found in case of complexes are for pyridine oxygen \(\nu(\text{C}=\text{O})\) atom which appeared at 1635 cm\(^{-1}\) in gatifloxacin this shift in band towards lower energy suggests coordination via pyridone oxygen atom.\[40\] These data are further supported by the weak bands observed at 575–540, 525–490, and 425–370 cm\(^{-1}\), which are assigned to \(\nu(\text{M–O})\), \(\nu(\text{M–N})\),\[41, 43\] and \(\nu(\text{M–S})\)\[42, 44\] vibrations, respectively. All complexes exhibit a broad band between 3470 and 3147 cm\(^{-1}\) with a well-defined maxima around 3440 cm\(^{-1}\), which corresponds to the vibrations \(\nu(\text{O–H})\) as well as to N–H vibration of the piperazinyl moiety.\[40\] The prominent IR spectral data are shown in Table 3-4 and spectra of the representative complex 8 is shown in Figure 3-13.

**Table 3-5 Characteristic IR bands of copper(II) complexes 8–14**

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<tr>
<th>Complexes</th>
<th>(\nu(\text{C}=\text{O}))</th>
<th>(\nu(\text{COO})_{\text{pyridone}})</th>
<th>(\nu(\text{COO})_{\text{as}})</th>
<th>(\Delta \nu)</th>
<th>(\nu(\text{M–O})_{\text{Carbo}})</th>
<th>(\nu(\text{M–N}))</th>
<th>(\nu(\text{M–S}))</th>
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### Conclusion

The coordination mode of ligands and the geometry of complexes are well established from elemental analysis, molar conductivity, IR, $^1$H NMR, mass, electronic spectral and thermal studies. The ligands coordinates in a bidentate fashion with sulphur and adjacent pyrimidine nitrogen donors with square pyramidal geometry.
References