Spectroscopic Studies of Some Transition Metal Copper and Iron Complexes

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Abstract. The present paper deals with the spectroscopic studies of transition metal complexes of copper and iron. Metal complexes are characterized by XRD, FTIR, Mössbauer and VSM (Vibrating sample magnetometer) measurements. The XRD analysis reveals the crystalline nature of both compounds. Mössbauer study interprets paramagnetic nature of iron complex at room temperature. VSM measurements also reveal the paramagnetic nature of iron complex at higher temperature range, while it follows magnetic phase transition from paramagnetic to antiferromagnetic nature at low temperature.

1. Introduction
The metal complexes of Schiff bases have been playing an important role in the development of science and technology. These have been widely studied for industrial, antifungal and biological applications[1,2]. It is found that the complexation of iron, copper, cobalt and other metals with Schiff bases has enhanced their activity[3,4]. These complexes show their antifungal potential against Alternaria alternata, Fusarium oxysporum and Myrothecium roridum by inhibiting spore germination[5]. In this communication, the ligand 2-[N- (2-hydroxy phenyl)ethanimidoyl] phenol has been synthesized and its complexation with iron metal salts has been reported. Mentioned properties of metal complexes are due to varied geometrical arrangements of ligands around the metal ion. Due to biological and industrial applications associated with the Schiff base complexes, these have been chosen for spectroscopic investigations. Therefore, the resulting complexes were studied by XRD, FTIR, Mössbauer and VSM (Vibrating sample magnetometer) measurements in order to elucidate their structures, geometry and magnetic nature.

2. Experimental
2.1. Synthesis of Complexes.
Ligand 2- [N- (2-hydroxy phenyl)ethanimidoyl]phenol was synthesized by condensing ortho hydroxy acetophenone ortho-aminophenol in equimolar proportion. Now one third mole of anhydrous FeCl₃ was added to this ligand in ethanol and the mixture was refluxed for 4-6 hours on water bath to get (2N2HPEPhenol) Fe complex. Copper complex is prepared by using same method as iron complex. In case of copper complex one half mole of copper chloride was added to ligand instead of FeCl₃. After refluxing we get (2N2HPEPhenol) Cu complex.
2.2. Experimental Analysis by Different Methods

All the spectroscopic investigations have been performed in powdered form of the samples. XRD patterns were recorded by a RigakuRINT-2000 diffractometer equipped with a rotating anode with a tube voltage of 40 kV and current of 100 mA. Cu target was used as a source of X-rays having wavelength 1.54 Å. FTIR spectra of the ligand and their complexes were recorded in the range 4000 to 400 cm⁻¹ on a Perkin-Elmer 16 FPC FT-IR using KBr pellet technique. Mössbauer measurements of iron complexes were carried out using standard PC- based spectrometer equipped with Weissel velocity drive operating in the constant acceleration mode. The data was fitted with the NORMOS-SITE program and the obtained parameters are with respect to natural iron. Measurements of DC magnetization have been recorded on commercial 14 T vibrating sample magnetometer from quantum design.

3. Result and Discussion

3.1. X-ray Diffraction:

The XRD pattern of the complexes shows sharp intense peaks throughout the spectrum. It is indicating crystalline nature of the samples. The particle size has been calculated using Scherrer’s formula given by t=0.9λ /B cos θ[6], where t is the particle size (same unit as λ), B is half width (in radians) of diffraction line, θ is the Bragg angle and λ is the wavelength. The particle size of Cu(II) and Fe(III) complexes was found to be 57.85nm and 81.07nm respectively. The XRD pattern of complexes are shown in Figure 1.

3.2. Fourier Transform Infrared Spectroscopy:

Important IR bands of the Schiff base ligands and complexes support their structure. A broad and weak band occurring around 3059-3080 cm⁻¹ may be attributed to the phenolic group due to intra molecular hydrogen bond between phenolic hydrogen and azomethinic nitrogen. This band disappeared in the IR spectra of complexes indicating the deprotonation of phenolic group suggesting that -OH group of the ligand has been utilized in the formation of metal-oxygen bond[7].

Figure1. XRD Pattern of Cu(II) and Fe(III) Complexes
3.3. Mössbauer Spectral Studies:

The Mössbauer effect provides a powerful probe to chemical state and the environment of iron atoms. The Mössbauer spectrum for Fe(III) complex at room temperature is shown in Figure 2. The least square fitting and lorenzian line shape were used for the spectral plots which indicate the presence of quadrupole splitting doublets. This is consistent with the presence of an identical oxidation state of the Fe$^{3+}$ nuclei in the crystal lattice of the present complexes. The spectra of quadrupole splitting at room temperature suggest that the presence of electric field gradient at the metal ion is due to the presence of ligand around the ion. This may be due to the distorted octahedral geometry[8]. The spectra did not show any magnetic splitting on applying external magnetic field which is indicative of absence of effective internal magnetic field at the Mössbauer nuclei in each case and the state remains doubly degenerate, showing the Kramer’s degeneracy[9]. Mössbauer parameters are reported in Table 1.

3.4. Magnetic studies on VSM

The DC magnetization of Fe(III) complex was measured from 10K to 300K. Figure 3 shows the graph between inverse of magnetic moment and temperature, follows Curie Weiss law[10] $\chi = C/T + \theta$, where $\theta$ is Curie Weiss temperature and $C$ is Curie’s constant.

Table 1. Mössbauer parameters of iron complex

| Compound               | Isomer shift (mm/sec) | Quadrupole splitting (mm/sec) | Linewidth (mm/sec) | % Area | Oxidation state |
|------------------------|-----------------------|--------------------------------|--------------------|--------|-----------------|
| (2N2HPEPhenol)         | 0.368±0.005           | 0.563±0.008                    | 0.331±0.039        | 100%   | Fe$^{3+}$        |
| Fe(III) complex        |                       |                                |                    |        |                 |

Figure 2. Mössbauer Spectra of Iron Complex
The Curie Weiss Temperature is found to be negative in reported complex indicating anti ferromagnetic interaction at low temperature. Hence the interaction between Fe(III) ion in the iron complex is antiferromagnetic coupling[11]. Thus iron complex follow magnetic phase transition from paramagnetic to antiferromagnetic nature at low temperature.

4. Conclusion
X-ray diffraction studies of complexes indicate crystalline nature of the samples. FTIR Spectra confirms the structure of the synthesized ligands and their complexes. Mössbauer studies show paramagnetic nature of Fe(III) complex. It also shows oxidation state of iron to be Fe$^{3+}$. VSM supports Mössbauer studies at room temperature. At low temperature VSM shows magnetic phase transition.

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