

Charge-transport and Magneto-dielectric Study in Chelated Metal Complex for Multiferroic Applications

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Abstract— Charge transport and the coupling between the electronic and magnetic properties in charge transfer chelated metal organic frameworks is one of the unexplored area of research. During the last decade several interesting properties like superconductivity, charge transport; ferroelectric properties have been investigated in detail except the magneto-transport and magneto-dielectric effects which have potential applications in multiferroic devices. Magneto-transport properties in materials are usually studied through dc charge transport under magnetic field. In the present work, we have found good magneto-dielectric effects with well magnetization behavior in $[\text{Ni}_2(\text{II})-(5-(4\text{-PhMe})-1,3,4\text{-oxadiazole-}\text{H}^+-2\text{-thiolate})_5](\text{OAc})_4$ metal complex via ac charge transport mechanism. The intermetallic coupling in binuclear systems operated through the σ and π orbital pathways of the bridging ligand results the magnetic super-exchange coupling. A magnetoresistance effect with 60% change and a significant magneto-dielectric response are observed at room temperature. We believe this finding makes the charge transfer complexes a potential material for multiferroic devices.

Keywords- *Magneto-transport, Magneto-dielectric, Charge transfer.*

I. INTRODUCTION

Charge transfer (C-T) chelated metal complexes have been investigated extensively during the last two decades owing to its' interesting physical properties like unique charge transport, superconductivity, superior magnetic and ferroelectric properties. [1,2] In spite of possessing good magnetic and ferroelectric properties, surprisingly, the multiferroic behavior in these complexes, which is currently the most active area of research, has not yet been resolved. Charge transfer metal complex shows emission of colors as a consequence of light absorption due to transfer of an electron from an orbital of the ligand to the metal, or vice versa. Such processes are termed as LMCT or MLCT, depending upon the direction of charge transfer either from ligand to metal or metal to ligand, respectively. Charge transfer phenomenon generated between organic donor-acceptor species gives mainly the conducting property to the system with weak magnetism at very lower temperature, in which $p\pi$ electrons take part in the charge transport. Transfer of an electron from 'p' to 'd' or 'd' to 'p' orbitals in inorganic-organic framework ($d\pi-p\pi$), in which d-electron spins of metal act as an additional

degree of freedom to such π -electron systems, produces unconventional feature like superior magnetic property (ferro-, antiferro-, ac susceptibility, etc.) along with the conducting properties. Many efforts have been given so far for introducing molecular magnetism in charge transfer complexes, where inorganic-organic donor-acceptor species take part in both electrical conduction as well as magnetism, simultaneously. Besides metallic conductivity and superconductivity, a major attention is paid to investigate interesting magnetic properties particularly ac susceptibility, magnetic hysteresis etc. in these chelated metal complexes. In the present work, we have accounted the magnetic interaction between the two metal centers and frequency dependent magneto-dielectric effect in the binuclear $[\text{Ni}_2(\text{II})-(5-(4\text{-PhMe})-1,3,4\text{-oxadiazole-}\text{H}^+-2\text{-thiolate})_5](\text{OAc})_4$ system. [3]

II. EXPERIMENTAL SECTION

Synthesis

To synthesize the binuclear Ni(II) complex, 0.498 g of nickel acetate tetrahydrate (in excess) is taken in a 250 mL beaker containing 30 mL of chloroform and stirred for half an hour with a magnetic stirrer. 0.192 g (1mM) of 5-(4-Methylphenyl)-1,3,4-oxadiazole-2-thiol is added to it in steps under continuous stirring. After few minutes the solution becomes bluish and finally turns intense green to give $[\text{Ni}_2(\text{II})-(5-(4\text{-PhMe})-1,3,4\text{-oxadiazole-}\text{H}^+-2\text{-thiolate})_5](\text{OAc})_4$. After one hour stirring the excess metal precursor is filtered out and the green solution left undisturbed for one day. Polycrystalline blue compound is collected for several characterizations viz. UV-Vis, PXRD, FTIR, etc.

Characterization

The molecular properties are characterized by spectroscopic method with Cary 5000 UV-Vis NIR Spectrophotometer measured in the range of 200–1100 nm and Fourier Transform Infrared Spectrometer using KBr pellets (NICOLET MAGNA IR 750 System). XRD pattern is investigated using powdered sample with an X-ray diffractometer (RICH SEIFERT-XRD 3000P, wavelength 1.54 Å). We have used SQUID magnetometer (Quantum Design MPMS) to investigate the magnetic properties (M-H measurements). Magneto-transport measurements have been carried out with the Agilent LCR meter (Model: E4980A)

using an electromagnet (supplied by M/S control systems and devices; Mumbai, India).

III. RESULTS AND DISCUSSION

UV-Visible Spectra. Diffuse reflectance UV-Vis spectra have been carried out to investigate the stereochemistry of the metal complex as shown in Figure 1a. Combining the absorption spectra with molecular orbital (MO) theory, it is concluded that the bivalent metal-ligand chelated system exists in trigonal bipyramidal configuration. [4] The bands appeared at 405 and 653 nm are referred to the

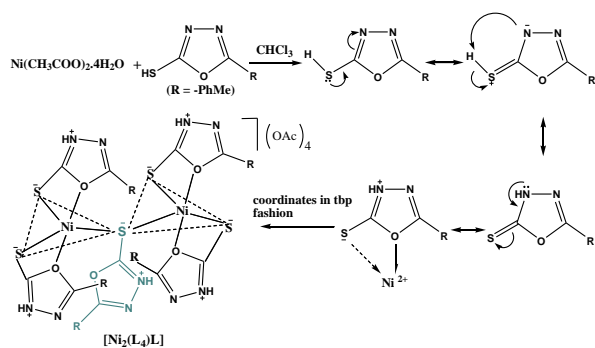
electronic transitions from ${}^3A_2 \longrightarrow {}^3T_1({}^3F)$,

${}^3A_2 \longrightarrow {}^3T_1({}^3P)$ respectively. The low energy band appears

at 965 nm due to ${}^3A_2 \longrightarrow {}^3T_2$ transition.

FT-IR Spectra. Fourier transform infrared spectra (FTIR) are studied to understand the mode of attachment of the functional groups to the metal center and the change of bond pattern into the ligand via resonance. Figure 1b shows the Fourier transform infrared spectra for the complex. The ν_{CO} frequency of the acetate ion present in the second sphere of coordination comes at the 1620 cm^{-1} . The shifting of hydrogen (1,4) from -SH to imine group via resonance is accomplished from the presence of quaternary amine (-NH⁺) group frequency at 1450 cm^{-1} (s, sh) in the metal complex spectra. [5] The peak at 3431 cm^{-1} (w) becomes broader due to the formation of this amine (-NH) group.

Scheme 1. Reaction mechanism proposed for the formation of chelated complex.



Powder XRD. We have performed powder diffraction technique to investigate the crystal structure. Figure 1c shows the XRD pattern of the present complex measured over the range of 2θ values lying between 10° to 80° which indicates the polycrystalline nature of the sample.

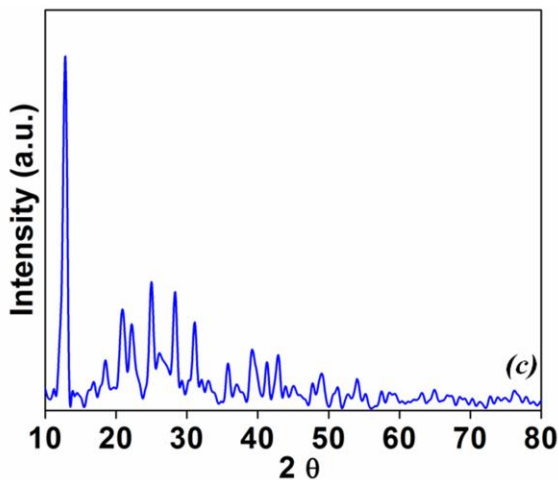
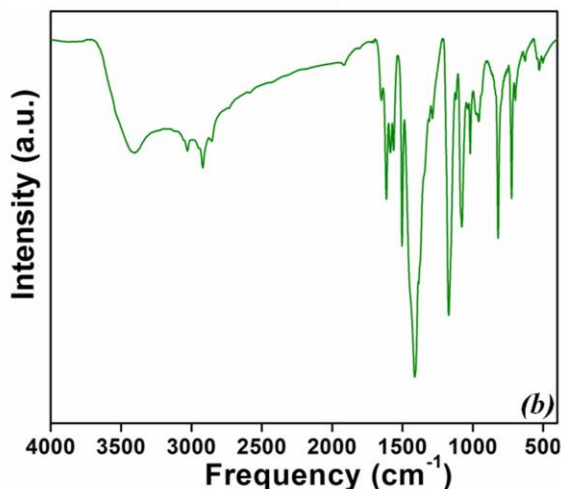
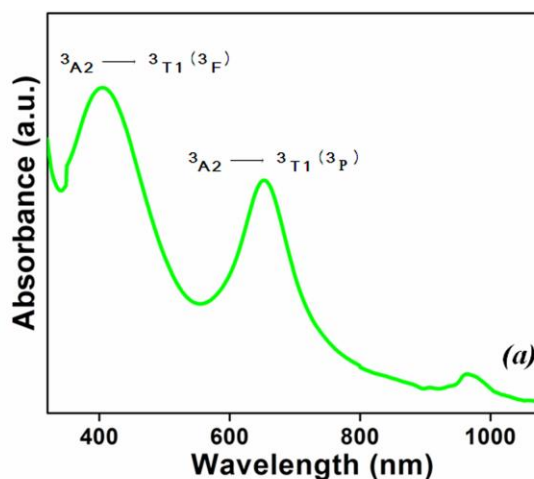


Figure 1. (a) UV-Vis absorbance spectra of the metal complex. (b) FT-IR spectra of the metal complex. (c) Powder X-ray diffraction profile of the synthesized chelated complex.

Magnetic Study. The magnetizations vs. field data are measured at temperatures 2, 5, 50, 100, 200 and 300K respectively. Figure 2 shows the magnetization behavior in an

applied magnetic field up to 50 kOe at 2 and 5 K. The ferromagnetic coupling was confirmed by magnetization measurements performed at 2 K up to an external field of 5 T showing the typical behavior of a soft ferromagnet because coercivity was not observed.

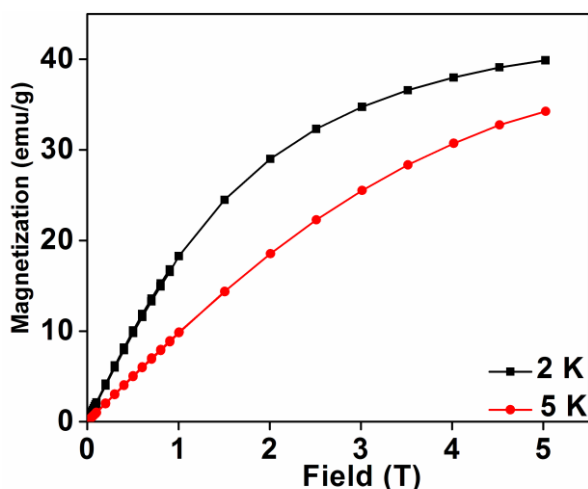


Figure 2. Magnetization-Field hysteresis curves at different temperatures.

Magneto-dielectric Study. To investigate the magneto-dielectric effect in this chelated complex we have measured the modulus spectra at magnetic fields varying from

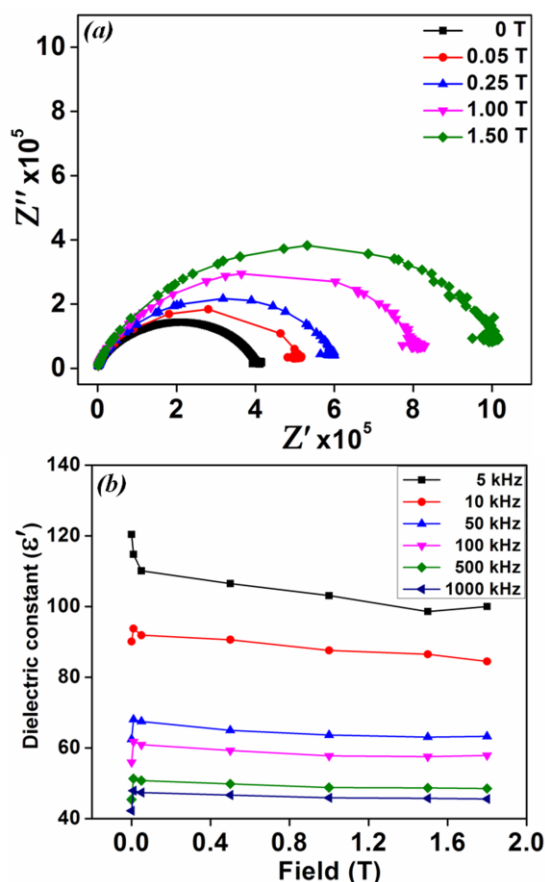


Figure 3. (a) Cole-Cole diagram containing the real and imaginary parts of the complex impedance. (b) Variation of dielectric permittivity as a function of frequency at different fields.

0T–1.8T and frequency range from 20Hz to 2MHz. The dc resistance values at different fields are shown in the Cole-Cole diagram (Figure 3a). A positive magnetoresistance change of 60% is observed up to 2 Tesla magnetic fields. [3]

Figure 3b shows the variation of dielectric permittivity with frequency. Significant changes in dielectric function are observed with increase in magnetic field upto 1.8T. Percentage change in dielectric permittivity values at different frequencies are summarized in Table 1.

Freq.(kHz)	10	50	100	500	1000
Permitt.	84→93	63→68	57→61	48→51	45→47
% Change	10	7	7	6	4

Conclusions

In summary, magneto-transport and magneto-dielectric properties are investigated in $[\text{Ni}_2(\text{II})-(5-(4\text{-PhMe})-1,3,4\text{-oxadiazole-}H^+-2\text{-thiolate})_5](\text{OAc})_4$ chelated complex which shows a magnetoresistance change of 60% and a significant magneto-dielectric response at room temperature as a result of coupling between dielectric function and magnetic field. We believe this finding makes the charge transfer chelated complexes a potential material for multiferroic devices.

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