



Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 3(1), 2007 [19-24]

Electrical And Optical Properties Of Mononuclear Manganese(III) Heterochelates Involving Tetradentate Schiff Base



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Received: 25th January, 2007Accepted: 31st January, 2007

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ABSTRACT

The heat capacity, electrical conductivity and optical properties of mononuclear manganese(III) heterochelates with tetradentate schiff base were investigated. The specific heat capacities of $[\text{Mn(III)(L}^1\text{)}(\text{acac})]$ and $[\text{Mn(III)(L}^1\text{)}(\text{sal})]$ complexes were found as 0.883-2.345 J/g.deg. and 0.994-2.300 J/g.deg. in the temperature range 0-90°C, respectively. The temperature dependence of electrical conductivity, σ , shows a typical semiconducting behavior. Optical absorption studies in the wavelength of range 190-1100 nm at room temperature showed that the allowed direct optical band gap E_{gd} of $[\text{Mn(III)(L}^1\text{)}(\text{acac})]$ and $[\text{Mn(III)(L}^1\text{)}(\text{sal})]$ complexes were 1.96 and 2.00 eV, respectively. © 2007

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KEYWORDS

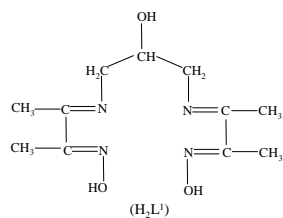
Manganese(III);
Tetradentate schiff base;
Specific heat capacity;
Band gap.

INTRODUCTION

The coordination chemistry of manganese in its higher oxidation states with different Schiff base ligands is of much importance due to its involvement in a number of biological systems^[1,2], as (i) Oxygen evolving complexes (OEC) in Photosystem-II^[3] (ii) Superoxide dismutase^[4] and (iii) Azide insensitive catalase^[5]. The bioactivity of such schiff base manganese complexes have also been examined in a

large number of disease models including Alzheimer's disease^[6], excitotoxic neuronal injury^[7], Parkinson's disease^[8] and multiple sclerosis^[9]. Kochi, Jacobsen and Katasuki(KJK) discovered an experimentally versatile and highly enantioselective route for the epoxidation of olefins by manganese(III) complexes^[11-12]. Manganese compounds have also a wide variety of application in the electrode materials^[13] and in recent advances of nanotechnology^[14-15]. Thus, it is obvious that the importance of manganese com-

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pounds in its different oxidation states is many faceted.

To date, there is limited work reported on electrical, and optical properties of manganese complexes of Schiff base ligands, while studies related to synthetic, structural and biochemical aspects of manganese complexes have been extensively available. Recently, there is an increasing interest in such studies for exploring some unsolved exciting features of such complexes^[16-17]. The present paper reports the results of such investigations with the mononuclear manganese(III)heterochelates of the type [Mn(III)(L¹)(L-L)] where L¹ is the dianion of the Schiff base N,N'-(2-hydroxy)propylenebis{(2-imino-3-oximino)butane} and L-L is the mono anion of acetylacetonate and salicylaldehyde. The structural formulation of the Schiff base ligand is shown below.

EXPERIMENTAL

Synthesis of the ligand

The ligand was synthesized by our previously published methods^[18-19] involving the condensation of 1,3-diaminopropane-2-ol with diacetylmonoxime.

Synthesis of the manganese(III) heterochelates with tetradentate schiff base

The brown [Mn(III)(L¹)(acac)] and [Mn(III)(L¹)(sal)] were synthesized by our recently published methods^[20]. The compounds were characterized with the help of elemental analyses, molar conductances, magnetic susceptibility, molecular weights and spectroscopic(UV-Vis, IR) data and the proposed structure is shown in figure 1. Where manganese(III) ion attains pseudooctahedral geometry. The ligand H₂L¹ functions as a dibasic N₄ donor fashion.

Measurements

The specific heat measurements sample size and

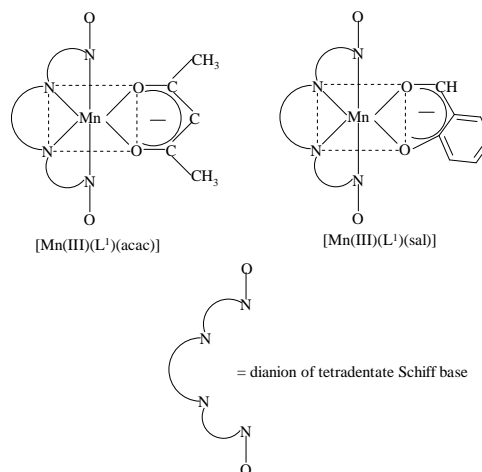


Figure 1 : Proposed structure for heterochelates [Mn(III)(L¹)(acac)] and [Mn(III)(L¹)(sal)]

heating rate are important factors. The sample sizes and heating rates can be taken between 5-100mg and 5–20°C/min. This may be necessary to reduce the heating rate when using larger samples to minimise temperature gradients within the sample. In this study, the specific heat capacities (C_p) of [Mn(III)(L¹)(acac)] and [Mn(III)(L¹)(sal)] were taken between 0-100°C heat range with the heating rate of 20°C/min, in air atmosphere, by DSC

The samples for the electrical measurements were prepared from the complexes in the form of tablets of thickness ~0.1 cm at a pressure of approximately 1x10⁸ Pascal. These tablets were placed between two copper electrodes with silver paste and contacts were tested to be ohmic. The electrical conductivities of the prepared complexes were investigated using a two-probe method, and the current was measured with a high impedance electrometer (Keithley 6514), by applying a dc voltage using a programmable voltage source(Keithely 230).

Optical absorption spectra were taken as a function of wavelength from 190-1100 nm using a double beam spectrophotometer(Perkin Elmer Lambda 2S Double Beam).

RESULTS AND DISCUSSION

Heat capacity

Typical DSC curves for specific heat capacity measurements of [Mn(III)(L¹)(acac)] and [Mn(III)(L¹)(sal)]

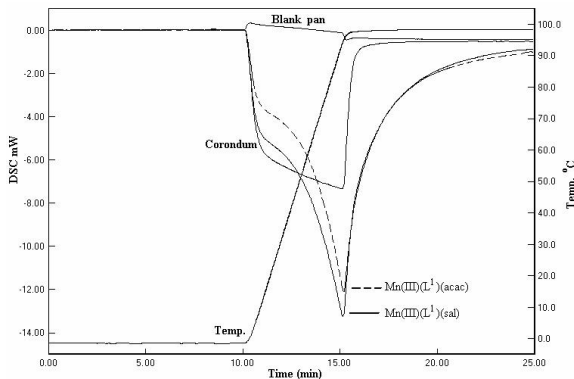


Figure 2: DSC heat flow curves for the blank pan baseline, the corundum standard, $[\text{Mn(III)(L}^1\text{)(acac)}]$ and $[\text{Mn(III)(L}^1\text{)(sal)}]$ samples

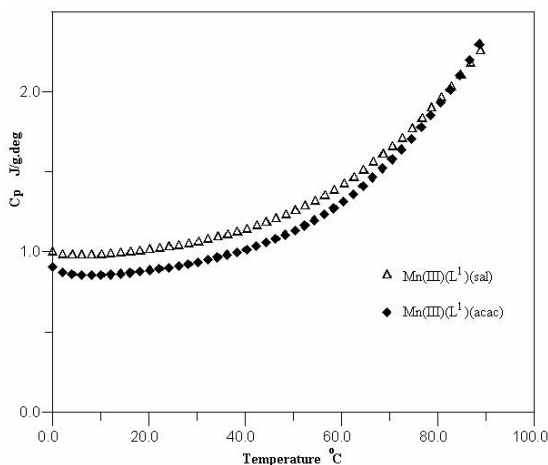


Figure 3: The variation of specific heat capacity C_p with temperature for $[\text{Mn(III)(L}^1\text{)(acac)}]$ and $[\text{Mn(III)(L}^1\text{)(sal)}]$ complexes

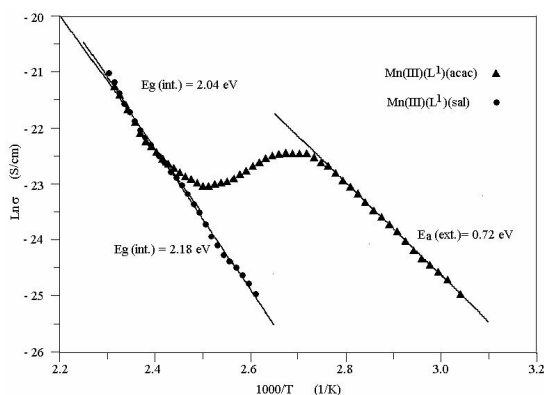


Figure 4: Temperature dependence of the electrical conductivity of $[\text{Mn(III)(L}^1\text{)(acac)}]$ and $[\text{Mn(III)(L}^1\text{)(sal)}]$ samples

(sal)] complexes are given in figure 2 Where curves of empty plate, reference sample, $[\text{Mn(III)(L}^1\text{)(acac)}]$ and $[\text{Mn(III)(L}^1\text{)(sal)}]$ complexes are drawn. The curves were taken from heating rate of $20^\circ\text{C}/\text{min}$ between $0\text{--}100^\circ\text{C}$. The specific heat capacities were found by PKI Muse Standart Analysis Program. The C_p -temperature curves are given in figure 3. The specific heat capacities of $[\text{Mn(III)(L}^1\text{)(acac)}]$ and $[\text{Mn(III)(L}^1\text{)(sal)}]$ complexes were found as $0.883\text{--}2.345$ J/g.deg. and $0.994\text{--}2.300$ J/g.deg. in the temperature range $0\text{--}90^\circ\text{C}$, respectively. The specific heat capacity of $[\text{Mn(III)(L}^1\text{)(acac)}]$ up to $0\text{--}80^\circ\text{C}$ was smaller than the specific heat capacity of $[\text{Mn(III)(L}^1\text{)(sal)}]$. The heat capacity values of both samples were similar above 80°C temperatures.

Electrical conductivity

The electrical conductivity variations with temperature of the samples, shaped as a pellet, were measured and the $\ln \sigma\text{--}1000/T$ graphs were given in figure 4. It can be observed that $[\text{Mn(III)(L}^1\text{)(acac)}]$ complex shows three distinct regions depending on the increase of temperature. At low temperatures the free carriers are trapped on the impurity centers and thus the resistivity increases with temperature. This behavior is sometimes termed the “freezing out” of free carriers onto impurity centers and the corresponding region is called as extrinsic region. The conductivity reached a maximum with the increasing temperature and carrier concentration became independent of temperature in saturation region where the temperature is too low for intrinsic behavior, but high enough that the donors to be freed from impurity concentration. The decrease of conductivity with increasing temperature in the saturation region may be explained by reduction in carrier mobility, which rises with temperature. Intrinsic conductivity occurs at high temperatures, as shown in intrinsic region for $[\text{Mn(III)(L}^1\text{)(acac)}]$ complex (Figure 1). The extrinsic and saturation conductivity occur at low temperatures, while the intrinsic conductivity occurs at high temperatures. Extrinsic and intrinsic regions have a positive temperature coefficient of electrical conductivity.

In spite of showing insulating properties at low temperatures, the $[\text{Mn(III)(L}^1\text{)(sal)}]$ complex showed

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a conduction property at about 380K and intrinsic region formed in this sample only at high temperatures (380-480K). After 410 K both samples showed similar behaviour.

The increasing of conduction with temperature is a semiconductor behaviour. The Arrhenius equation for extrinsic region of p- type semiconductors is

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (1)$$

where, σ_0 is the pre-exponential factor, E_a is the activation energy for this thermally activated process and k is the Boltzmann's constant. In intrinsic region the activation energy can be defined as $E_a = E_g/2$. By using this equation the activation energy or energy gap value can be calculated [21, 22]. The calculated activation energies for [Mn(III)(L¹)(acac)] complex were found to be low (0.72 eV) in the lower temperature range(330-360 K) but considerably high (1.02 eV) in the high-temperature range(410-430K). The energy band gap $E_g(\text{int.})$ for [Mn(III)(L¹)(acac)] and [Mn(III)(L¹)(sal)] complexes were found as 2.04 and 2.18 eV, respectively. The difference between the conductivity curves of [Mn(III)(L¹)(acac)] and [Mn(III)(L¹)(sal)] complexes is supposed to be resulted from the difference in the second ligand (i.e. acac or sal)(Figure 1) in the heterochelates.

On comparing our manganese(III) complexes, with other manganese(III) complexes of similar ligands, the x-ray crystal structures of which are known[23], we could conclude that in our manganese(III) complex systems in the solid-state may show the presence of different weak interactions (H-bonding, C-H... π , π - π interactions etc.) may be present. Such interactions are responsible for

2-D and 3-D supramolecular architecture of these complexes in the solid-state. The semiconducting properties of the present manganese(III) complexes may be explained due to the presence of such supramolecular assembly.

Optical properties

Energy gaps greater than 1.5 or 2.0 eV would certainly necessitate temperatures too high to permit practical determination of energy gap in this manner. For such materials, energy gaps must be determined from different measurements such as optical absorption[24].

The nature of the optical transition involved in the complexes can be determined based on the dependence of absorption coefficient(α) on photon energy ($h\nu$). For transition, α is given by [25,26],

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2)$$

where, E_g is the energy gap between the bottom of the conduction band and the top of the valence band at the same value of wave number(k). The energy gap for allowed direct(E_{gd}) and indirect(E_{gi}) transitions, can be determined by relating;

$$\alpha h\nu = A_a(h\nu - E_{gd})^{1/2} \quad (3)$$

$$\alpha h\nu = A_i(h\nu - E_{gi})^2 \quad (4)$$

Where, α is the absorption coefficient, $h\nu$ is the photon energy, and A_a and A_i are the characteristic parameters for respective transitions, independent on ν . On the basis of Eqs.(3) and(4), E_g can be determined, from extrapolation to zero of linear parts of $(\alpha h\nu)^2 = f(h\nu)$ and $(\alpha h\nu)^{1/2} = f(h\nu)$ curves.

Optical absorption spectra of complexes are given in figure 5(a, b) and analysis of absorption data

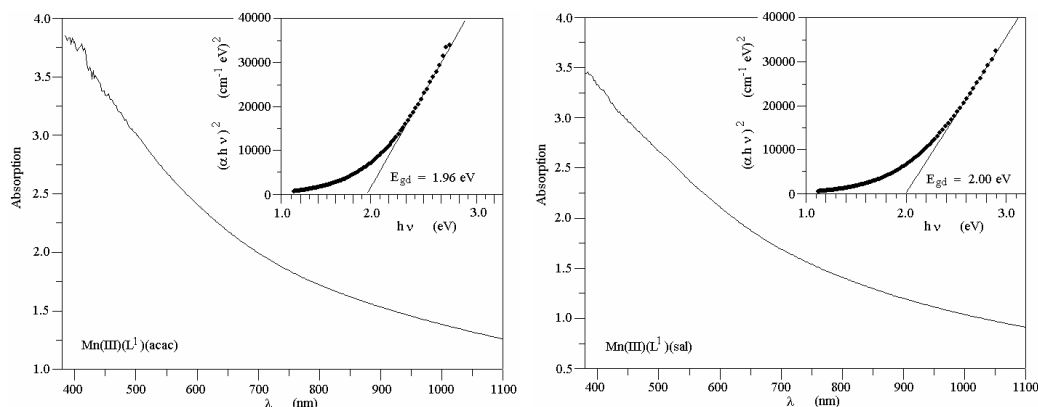


Figure 5: The optical absorption spectra for the complexes; (a) [Mn(III)(L¹)(acac)], (b) [Mn(III)(L¹)(sal)]

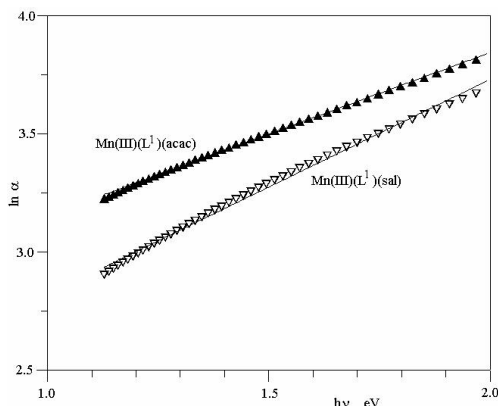


Figure 6 :Plot of $\ln\alpha$ vs. $h\nu$ for $[\text{Mn(III)(L}^1\text{)(acac)}]$ and $[\text{Mn(III)(L}^1\text{)(sal)}]$

was carried out to determine the predominant optical transition. A satisfactory fit was obtained for $(\alpha h\nu)^2$ as a function of $h\nu$, showing the existence of a direct gap. The plots of $(\alpha h\nu)^2$ vs. $h\nu$ of complexes are shown in figure 6. The extrapolation of the graphs to $(\alpha h\nu)^2=0$ yields the optical band gap E_{gd} . The values of the optical band gap E_{gd} were determined from figure 5(a,b) by the least squares fitting of the data. In this study, the optical band gap of $[\text{Mn(III)(L}^1\text{)(acac)}]$ and $[\text{Mn(III)(L}^1\text{)(sal)}]$ is found as E_{gd} 1.96 and 2.00 eV, respectively. Urbach tail width (ϵ) may be estimated from the relation^[26],

$$\alpha = \text{const. exp}(v/\epsilon) \quad (5)$$

By plotting $\ln\alpha$ vs. $h\nu$ (Figure 6). Inverse of the slope of $\ln\alpha$ vs. $h\nu$ gives the value of tail width ϵ . The Urbach tail width of $[\text{Mn(III)(L}^1\text{)(acac)}]$ and $[\text{Mn(III)(L}^1\text{)(sal)}]$ is found as 1.45 and 1.09 eV, respectively.

CONCLUSION

The heat capacity, electrical conductivity and optical properties of the manganese(III) heterochelates with tetradentate schiff base have been investigated. These complexes show typical semiconducting characteristics possibly due to the presence of weak molecular interactions. They act as p-type semiconductors. The electrical studies confirming the differences between the conductivity curves of $[\text{Mn(III)(L}^1\text{)(acac)}]$ and $[\text{Mn(III)(L}^1\text{)(sal)}]$ complexes are supposed to be resulted from the difference in the second ligand in the heterochelates. Optical stud-

ies revealed that the transition is probably the allowed direct one. The values (E_{gd}) estimated for the $[\text{Mn(III)(L}^1\text{)(acac)}]$ and $[\text{Mn(III)(L}^1\text{)(sal)}]$ are 1.96 and 2.00 eV, respectively.

ACKNOWLEDGEMENTS

Investigation of electrical, optical and thermal properties of this study was made at the semiconductor physics research laboratory funded by T.R. Prime Ministry State Planning Organization (Project No: DPT 2003K 120440-1). We are thankful to Kalyani University for some financial help in the form of Teachers' Research Grant.

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