



Hydrazone Schiff Base Functionalize as Dibasic Tridentate (*Ono*) Ligand on Complexation with Mn(III), Fe(III) And Zr(IV) Metal Ions

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Abstract

Three mononuclear Mn(III), Fe(III) and Zr(IV) complexes having formula $[Mn(L)(OAc)(H_2O)]$, $[Fe(L)(Cl)(H_2O)_2]$ and $[Zr(OH)_2(L)(CH_3OH)]$ [$H_2L = 2,4$ -dihydroxyacetophenone-2,4-dichlorobenzoylhydrazone] have been prepared and characterized by using elemental analyses, ultraviolet-visible & infrared spectroscopy, magnetic susceptibility measurements and thermogravimetric analysis. The complexes are nonelectrolytes having a molar ratio $M:L = 1:1$. The ligand shows dibasic tridentate behaviour, bonding through azomethine nitrogen, phenolic oxygen and enolic oxygen atom to the metal ion. The electronic spectral study in solid state as well as magnetic susceptibility measurements indicate an octahedral geometry for Fe(III) and Zr(IV) complexes while square pyramidal geometry for Mn(III) complex. Thermal degradation studies of the complexes show that the final product is the metal oxide

Introduction

Over the past decade, aroylhydrazines and their hydrazone derivatives have been attracting much attention because of their variable bonding when forming the complexes with metal ions. The field of bioinorganic chemistry has increased curiosity in hydrazone complexes since many of these complexes serve as models for biologically important species [1]. These compounds have many applications especially as antimicrobial, antitubercular, anticonvulsant and anti-inflammatory and antiproliferative activities [2-4]. Acyl hydrazone compounds containing CONHN group reduce the toxicity brought to biological organism caused by the NH_2 group of hydrazides structure. Moreover, they also enhance the affinity between receptors because of the participation of both oxygen atom and nitrogen atom in the formation of hydrogen bond in the organism, thus make the hydrazones have the unique biological activity. We were thus motivated to undertake a systematic study of preparation and characterization of transition metal complexes of Mn(III), Fe(III) and Zr(IV) metal ions with 2,4-dihydroxyacetophenone-2,4-dichlorobenzoylhydrazone (H_2L) ligand.

Experimental

Materials and physical measurements

All the solvents, reagents and metal salts used in the present investigation are of reagent grade and were used without further purification. 2,4-dihydroxyacetophenone and 2,4-dichlorobenzoylhydrazide were prepared by known method [5]. Zirconium (IV) acetate and $Mn(OAc)_3 \cdot 2H_2O$ were synthesized by reported



method [6, 7]. Elemental analysis (carbon, hydrogen and nitrogen) was carried at RSIC, C.D.R.I., Lucknow, India. Metal content in each complex was done gravimetrically by decomposing the complexes with conc. HNO_3 and then igniting to metal oxides. The IR spectra were recorded on a Perkin Elmer infrared spectrophotometer in the range $4000\text{-}400\text{ cm}^{-1}$ at CDRI, Lucknow, India. Solid-state electronic spectra of the complexes were recorded on a Cary 2300 spectrophotometer at SAIF, Chennai. $^1\text{H-NMR}$ spectra of ligand was recorded on a Bruker Ac 250 spectrometer at 250 MHz, using TMS as a reference in $\text{DMSO-}d_6$. Thermogravimetric curves of the complexes were recorded in the temperature range $40\text{-}700^\circ\text{C}$ at the heating rate of $10^\circ\text{C}/\text{min}$. The magnetic susceptibilities at room temperature were measured on a Gouy's balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant. Diamagnetic corrections for various atoms and structural units were computed using Pascal's constants. Conductivities of a 10^{-3}M solution of the complexes were measured in DMSO at room temperature using Systronics model 304 conductivity meter.

Synthesis of Schiff base ligand (H₂L)

The Schiff base ligand (H₂L) used in the present work was prepared by following general method (scheme 1). An ethanolic solution (40 ml) of 2,4-dichlorobenzoylhydrazide (50 mmol) was added to an ethanolic solution (30 ml) of 2,4-dihydroxyacetophenone (50 mmol). The resulting reaction mixture was reflux on a water bath for 3-4 h. On cooling to the room temperature colored solid was obtained. The resulting solid mass was filtered, washed several times with ethanol, diethyl ether and subsequently dried over CaCl_2 in a desiccator. The purity of ligand was checked by TLC using silica gel as stationary phase and dimethylformamide as the solvent. Yield: 73%, M.P.: 193°C .

$^1\text{H-NMR}$ data: 13.24 (s, 1H, OH C₂), 11.92 (s, 1H, OH C₄), 9.12 (s, 1H, NH), 6.82-7.95 (m, 6H, Ar-H), 2.31 (s, 3H, CH₃).

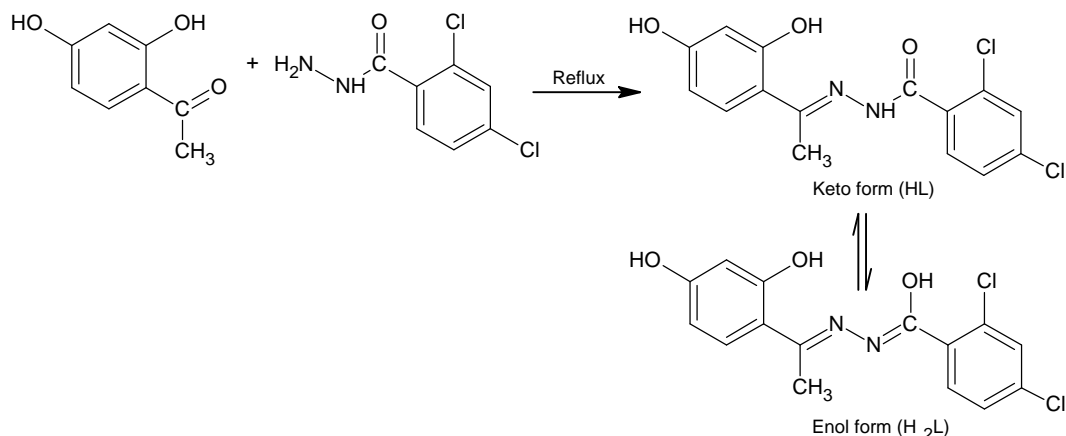
Synthesis of Mn(III) and Fe(III) complexes

An ethanolic solution (20 ml) of the metal salt and Schiff base ligand (H₂L) were mixed in 1:1 molar ratio. The resulting reaction mixture was refluxed for about 3-4 h on water bath. The solid product obtained was filtered, wash thoroughly with ethanol and finally with petroleum ether. All these complexes were dried in vacuum over CaCl_2 .

Synthesis of [Zr(OH)₂(L)(CH₃OH)] complex

Freshly prepared zirconium (IV) acetate (0.001 mol) was allowed to react with the Schiff base (0.001 mol) in methanol (20 ml) under reflux condition for 2 h. The contents were cooled to room temperature. A methanolic solution (10 ml) of sodium methoxide (0.002 mol) was added and the mixture stirred magnetically for 5 min. The mixture was further refluxed for 2 h. The

separated yellow precipitate was filtered, washed with methanol and dried in vacuo at room temperature



Scheme 1.

Table 1: Physical and analytical data of H₂L ligand and its metal complexes

Proposed composition of the complex	Formula weight g mol ⁻¹	Colour	Elemental analysis found (calcd) %				Percent yield	Molar conductance (Ω ⁻¹ cm ² mol ⁻¹)
			C	H	N	M		
H ₂ L	339.17	Mustard	54.31 (53.12)	3.01 (3.57)	8.73 (8.26)	-	73	-
[Mn(L)(OAc)(H ₂ O)]	469.12	Umber	43.98 (43.50)	3.74 (3.21)	5.62 (5.96)	11.02 (11.72)	64	14
[Fe(L)(Cl)(H ₂ O) ₂]	464.48	Black cherry	38.01 (38.79)	3.91 (3.04)	6.52 (6.04)	12.85 (12.02)	62	17
[Zr(OH) ₂ (L)(CH ₃ OH)]	494.43	Hazelnut	38.10 (38.87)	3.04 (3.26)	6.02 (5.67)	18.12 (18.45)	53	16.8

Results and discussion

The resulting compounds are non-hygroscopic and air stable solids. Some physical properties, such as colors, molar conductance and percentage of yields as well as the analytical data of these compounds are given in Table 1. The elemental analyses data are consistent with the proposed molecular formula that showed the ratio of metal:ligand is 1:1 in the complexes.

IR spectroscopy

The IR spectra of the free Schiff base ligand and its metal complexes show several bands in the 400-4000 cm⁻¹ region. The OH stretching frequency of the ligand is observed at 3291 cm⁻¹ due to the intramolecular hydrogen bonding vibration (O–H····N). This band disappeared in the spectra of the complexes, indicate



that phenolic oxygen atom undergo coordination via deprotonation [8]. This is further supported by upward shift of $\nu(\text{C}-\text{O})$ band ($\sim 12 \text{ cm}^{-1}$) in the spectra complexes as compared to free ligand. The free ligand has a characteristic $\text{C}=\text{N}$ bond at 1637 cm^{-1} . For the Schiff base complexes $\text{C}=\text{N}$ was observed in $1629\text{-}1613 \text{ cm}^{-1}$. The $\text{C}=\text{N}$ stretching band of the Schiff base complexes is generally shifted to a lower frequency, indicating a decrease in the $\text{C}=\text{N}$ bond order due to the coordinate bond formation between the metal and the imine nitrogen lone pair [9]. IR spectrum of the free ligand contains a strong $\text{C}=\text{O}$ absorption band at 1672 cm^{-1} and a $\text{N}-\text{H}$ absorption medium band at 3190 cm^{-1} . Both of these bands disappear upon complexation and new $\text{C}-\text{O}$ (enolic) absorption band appears at $1187\text{-}1232 \text{ cm}^{-1}$ for complexes providing strong evidence for ligand coordination to the metal ion in the enol form by losing its $\text{N}-\text{H}$ hydrogen. In Mn(III) complex, the coordinated monodentate CH_3COO^- group appeared at $1539, 1345 \text{ cm}^{-1}$. These two bands are due to $\nu_{\text{asy}}(\text{COO}^-), \nu_{\text{sys}}(\text{COO}^-)$ respectively. The separation of the two bands, $\Delta\nu = (\nu_{\text{asy}} - \nu_{\text{sys}}) = 194 \text{ cm}^{-1}$, is comparable to the values cited for the monodentate character of the acetate group. The strong IR band at 1129 cm^{-1} in Zr(IV) complex is assigned to $\text{Zr}-\text{OH}$ vibration. A new strong band at 1237 cm^{-1} in the spectrum of $[\text{Zr}(\text{OH})_2(\text{L})(\text{CH}_3\text{OH})]$ is assigned to the $\nu(\text{C}-\text{O})$ (enolic). The $\nu(\text{C}-\text{O})$ of CH_3OH occurs at 1048 cm^{-1} and this band undergoes a negative shift in $[\text{Zr}(\text{OH})_2(\text{L})(\text{CH}_3\text{OH})]$ and is observed at $\sim 1023 \text{ cm}^{-1}$ indicating methanol coordination. The absence of a new band in the spectrum of Zr(IV) complex in the range $850\text{-}960 \text{ cm}^{-1}$ due to the $\nu(\text{Zr}=\text{O})$ favors the formulation of the complex as $[\text{Zr}(\text{OH})_2(\text{L})(\text{CH}_3\text{OH})]$ and not as $[\text{ZrO}(\text{L})(\text{H}_2\text{O})(\text{CH}_3\text{OH})]$. The broad band at $3347\text{-}3481, 1692\text{-}1797, 742\text{-}850,$ and at $612\text{-}654 \text{ cm}^{-1}$ in the IR spectra of the complexes are referred to $m(\text{OH}), \delta(\text{H}_2\text{O}), \delta r(\text{H}_2\text{O})$ and $\delta w(\text{H}_2\text{O})$ vibrations for the coordinated water molecule. The IR spectra of metal complexes showed new bands in $467\text{-}486 \text{ cm}^{-1}$ range assigned to $(\text{M}-\text{N})$ and $510\text{-}527 \text{ cm}^{-1}$ range assigned to $(\text{M}-\text{O})$ modes [10]. Therefore, from the IR spectra, it may be concluded that Schiff base behaves as a tridentate ligand with *ONO* donor sites and coordinates to the metal ions via the azomethine nitrogen, phenolic oxygen and enolic oxygen atom.

Electronic spectra and magnetic moment study

The electronic spectrum of the Fe(III) complex shows three bands at $17235, 24760$ and 38361 cm^{-1} , which can be assigned to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G}), {}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$ spin allowed transitions in octahedral geometry [11]. The magnetic moment of 5.89 B.M. at room temperature for this complex lies in the range accepted for octahedral species with five unpaired electrons. The electronic spectrum of Mn(III) complex of exhibit three bands at $12734, 15761$ and 20025 cm^{-1} which have tentatively been assigned to ${}^5\text{B}_1 \rightarrow {}^5\text{B}_2, {}^5\text{B}_1 \rightarrow {}^5\text{A}_1$ and ${}^5\text{B}_1 \rightarrow {}^5\text{E}$, transitions, respectively. The value of magnetic moment is 4.78 B.M. ; which indicates the presence of Mn(III) complex in square pyramidal geometry. As Zr(IV) complex has d^0 electronic configuration do not furnish any $d-d$ transition [12].



Thermogravimetric analysis

The thermal degradation behavior of the H₂L ligand and its Fe(III), Mn(III) and Zr(IV) complexes has been studied by thermogravimetric analysis. TG curve of the ligand show one stage decomposition whereas its complexes show two stages decomposition. The TG curve of [Mn(L)(OAc)(H₂O)] complex is as shown in figure 1. The TG curve of the Fe(III) and Mn(III) complexes shows mass loss in the temperature range 125-195°C corresponds to loss of coordinated water molecules [% mass loss obs/calcd: Fe(III): 6.92/7.75; Mn(III): 3.48/3.83] [13]. The Zr(IV) complex is stable up to 190°C temperature and loss of mass in the temperature 190-225°C indicated the presence of one methanol molecule [% mass loss obs/calcd: Zr(IV):6.12/6.4]. After the loss of water / methanol molecule complexes show mass loss in the temperature range 315-580°C corresponds to the loss of chloride ion / acetate ion along with ligand moiety. The second step is faster as compare to first step and TG curve attains a constant level above 650°C leading to the formation of their respective metal oxide.

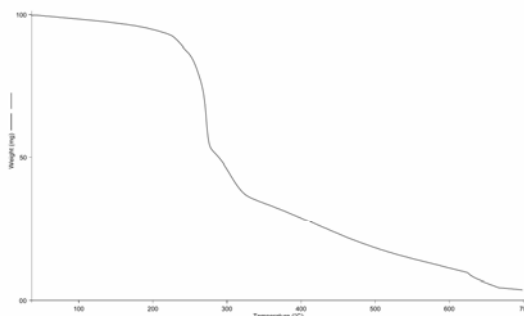


Fig. 1: TG curve of [Mn(L)(OAc)(H₂O)] complex

Conclusions

The synthesized 2,4-dihydroxyacetophenone-2,4-dichlorobenzoylhydrazone (H₂L) Schiff base act as dibasic tridentate ligand. The Fe(III), Mn(III) and Zr(IV) metal ion is coordinated through the azomethine nitrogen, phenolic oxygen and enolic oxygen atoms. The bonding of the ligand to the metal ion was confirmed by the analytical, IR, electronic, magnetic and thermal data. On the basis of spectroscopic data octahedral geometry was assigned to Fe(III) and Zr(IV) complexes whereas square pyramidal geometry for Mn(III) complex.

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