



Synthesis and Characterization of Tridentate *ONO* Schiff Base Complexes of Tri/Tetra-Valent Transition Metals

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ABSTRACT

Mononuclear hydrazone Schiff base complexes $[\text{CrL}(\text{Cl})(\text{H}_2\text{O})_2]$, $[\text{MnL}(\text{OAc})(\text{H}_2\text{O})]$, $[\text{FeL}(\text{Cl})(\text{H}_2\text{O})_2]$ and $[\text{Zr}(\text{OH})_2\text{L}(\text{CH}_3\text{OH})]$, where L is 2,4-dihydroxy-5-nitroacetophenone-2-chlorobenzoylhydrazone (H_2L), has been synthesized and structurally characterized by elemental analysis, reflectance & infrared spectroscopy, magnetic susceptibility measurements and thermogravimetric study. The physico-chemical studies support that ligand act as dibasic tridentate *ONO* donor towards all the metal ion forming octahedral geometrical arrangement around Cr(III), Fe(III) and Zr (IV) ion whereas square pyramidal geometry around Mn(III) ion.

KEYWORDS: *ONO* donor ligand; metal complex; spectroscopic study.

INTRODUCTION

The hydrazone Schiff bases are handy ligands in coordination chemistry, with easy preparation, diversity and structural variation. In recent years, metal complexes of Schiff bases have attracted considerable attention due to their remarkable biological activity, such as antifungal [1, 2], antibacterial [3-5], and antitumor [6, 7]. It has been shown that the Schiff base complexes derived from *o*-hydroxyacetophenone/salicylaldehyde and its derivatives with hydrazide have interesting biological activity. In the present study, ligand, 2,4-dihydroxy-5-nitroacetophenone-2-chlorobenzoylhydrazone (H_2L) and its metal complexes were synthesized using 2,4-dihydroxy-5-nitroacetophenone and 2-chlorobenzoylhydrazide as a starting material. The structures of the complexes were characterized by elemental analysis, FT-IR, and electronic spectra, magnetic susceptibility measurements as well as thermogravimetric analysis.

EXPERIMENTAL

MATERIALS AND PHYSICAL MEASUREMENTS

All the reagent and solvents (ethanol, methanol and diethyl ether) were of reagent grade and used without purification. Chromium chloride pentahydrate and ferric chloride hexahydrate were of S. D's fine chemicals. $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$ was synthesized by reported method [8]. 2,4-dihydroxy-5-nitroacetophenone and 2-chlorobenzoylhydrazide were prepared by general method [9]. Zirconium (IV) acetate was prepared by reported method [10].

Microanalyses of carbon, hydrogen and nitrogen of the compounds were carried at RSIC, CDRI, Lucknow, India. Metal content in each complex was done gravimetrically by decomposing the complexes with conc. HNO_3 and then igniting to metal oxides [11]. 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 carry 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 $\text{DMSO-}d_6$. The magnetic susceptibilities at room temperature were measured on a Gouy 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. Thermogravimetric curves of the compounds were recorded in the temperature range $30\text{-}750^\circ\text{C}$ at the heating rate of $10^\circ\text{C}/\text{min}$.

SYNTHESIS OF SCHIFF BASE LIGAND (H_2L)

The Schiff base ligand (H_2L) used in the present work was prepared by following general method (scheme 1). An ethanolic solution of 2-chlorobenzoylhydrazide (50 mmol) was added to an ethanolic solution of 2,4-dihydroxy-5-nitroacetophenone (50 mmol). The resulting reaction mixture was reflux on a water bath for 4–5 h. On cooling to the room temperature coloured solid was obtained. The resulting solid mass was filtered, washed several times with

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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: 63%, M.P.- 221°C.

$^1\text{H-NMR}$ data: 14.31 (s, 1H, OH C₂), 11.63 (s, 1H, OH C₄), 10.92 (s, 1H, NH), 7.12-8.46 (m, 6H, Ar-H), 2.27 (s, 3H, CH₃).

SYNTHESIS OF Cr(III), Mn(III) AND Fe(III) COMPLEXES

An ethanolic solution (20 mL) of the metal salt and Schiff base ligand (H_2L) were mixed in 1:1 molar ratio. The resulting reaction mixture was refluxed for about 4–5 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 $[\text{Zr}(\text{OH})_2\text{L}(\text{CH}_3\text{OH})]$ COMPLEX

Freshly prepared zirconium (IV) acetate (1 mmol) was allowed to react with the Schiff base (1 mmol) 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 (2 mmol) was added and the mixture stirred magnetically for 5 min. The mixture was further refluxed for 2 h. The separated coloured precipitate was filtered, washed with methanol and dried in vacuo at room temperature.

RESULTS AND DISCUSSION

The data of elemental analysis together with physical properties of ligand and its metal complexes are summarized in Table 1. The elemental analyses suggest 1:1 metal: ligand stoichiometry and were in good agreement with the values calculated from proposed formula. All metal complexes have been obtained as colored solid, stable on prolonged exposure to air and insoluble in most of common organic solvents but soluble in DMF and DMSO.

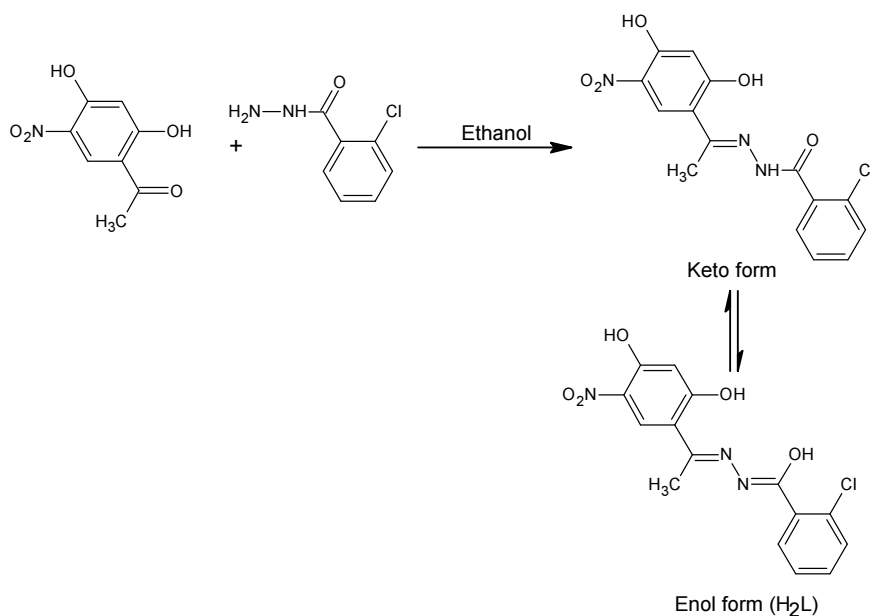
INFRARED SPECTROSCOPY

The O–H stretching frequency of the free ligand is expected in the 3500-3400 cm^{-1} region. However, in the *o*-hydroxy Schiff base this band is generally moved to lower frequency (3242 cm^{-1}) (Table 2) due to the presence of a strong intramolecular hydrogen bonding ($\text{O-H}\cdots\text{N}=\text{C}$) [12]. This band gets disappear on complexation, suggesting that the coordination of phenolic oxygen via deprotonation. Coordination through the phenolic oxygen after deprotonation is revealed by a band due to $\nu(\text{C-O})$ at higher frequencies (1346-1393 cm^{-1}) in all the complexes compared to that of ligand (1337 cm^{-1}) [13]. The ligand show a strong band corresponding to $\nu(\text{C}=\text{N})$ at 1629 cm^{-1} with a remarkable red shift (9-48 cm^{-1}) upon complexation, which indicates participation of azomethine nitrogen in coordination, arising from shift of electron density from nitrogen to metal, lowering the stretching frequency of the corresponding vibration [14]. The bands due to $\nu(\text{C}=\text{O})$ and $\nu(\text{NH})$ were absent in the spectra of complexes, and new C–O band appear at 1193-1238 cm^{-1} . This suggests the occurrence of keto-imine tautomerization of the ligand during the coordination. In case of Zr(IV) complex the band observed at 1130 cm^{-1} corresponds to presence of $\delta(\text{Zr-OH})$. A new strong band at 1230 cm^{-1} in the spectrum of Zr(IV) complex is assigned to the $\nu(\text{C-O})$ (enolic). The $\nu(\text{C-O})$ of CH_3OH occurs at 1029 cm^{-1} and this band undergoes a negative shift in Zr(IV) complex and is observed at 1002 cm^{-1} indicating methanol coordination [15]. Mn(III) complex display two additional bands at 1545, 1349 cm^{-1} are assigned to $\nu_{\text{asy}}(\text{OCO})$ and $\nu_{\text{sym}}(\text{OCO})$ respectively. The separation of these peaks by $\sim 196 \text{ cm}^{-1}$ indicates monodentate nature of acetate group. In the spectra of metal complexes the appearance of wide bands of low intensity in the range 3336-3475 cm^{-1} which may be assigned to stretching vibration of OH group of water molecules. Besides this, complexes show bands 1567-1625 and 854–858 cm^{-1} range assignable to $\delta\gamma(\text{H}_2\text{O})$ and $\delta\omega(\text{H}_2\text{O})$ respectively for coordinated water molecule [16]. Conclusively, the above interpretation is supported by the appearance of the new bands at 493-578 and 450-489 cm^{-1} assigned to (M–O) and (M–N), respectively [17].

ELECTRONIC SPECTRA AND MAGNETIC STUDIES

The electronic spectral data of Fe(III) complex exhibit three bands at 17761, 25706 and 37593 cm^{-1} . The first two bands are assigned to $^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g}(\text{G})$ and $^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g}(\text{G})$ transition and the third band is due to $^6\text{A}_{1g} \rightarrow ^4\text{E}_g(\text{G})$ transitions. The intensity of these bands in complex is consistent with an octahedral structure [18]. The magnetic moment of Fe(III) complex shows 5.92 B.M. that is close to the spin only value expected for five unpaired electrons. The electronic spectrum of the Cr(III) complex displays three bands at 18281, 25510 and 38910 cm^{-1} assign able to $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}(\text{F})$, $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{F})$ and $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{P})$ transitions, respectively, indicating that the complex possesses an octahedral configuration [19]. Cr(III) complex showed the magnetic moment 3.91 B.M., further support the presence of octahedral geometry around the Cr(III) metal ion. The ligand filed parameters of Cr(III)

complex are found, $B = 638 \text{ cm}^{-1}$, $Dq = 1828 \text{ cm}^{-1}$ and $\beta = 0.69$, designate more covalent. Mn(III) complex showing three d-d transition around 13908 , 16468 and 19960 cm^{-1} corresponding to ${}^5B_1 \rightarrow {}^5B_2$, ${}^5B_1 \rightarrow {}^5A_1$ and ${}^5B_1 \rightarrow {}^5E$, transitions, respectively suggesting square pyramidal geometry of the complex. The magnetic moments of Mn(III) complex was found 4.90 B.M. which corresponds to the d^4 system. As Zr(IV) complex has d^0 electronic configuration do not furnish any d-d transition [20].



Scheme 1. Synthetic route for the preparation of H₂L ligand

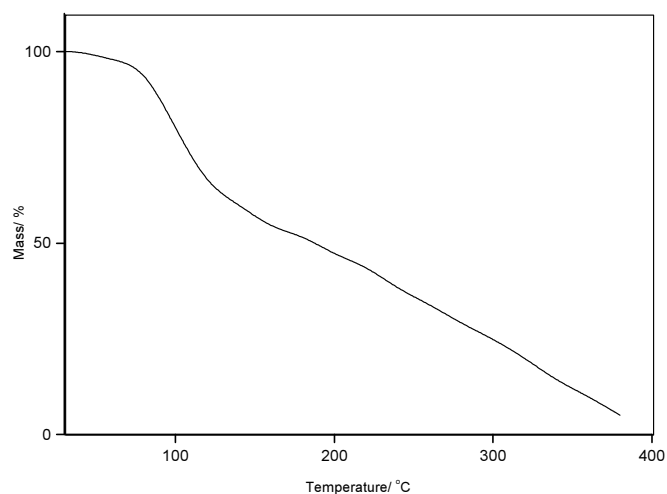


Figure 1; TG curve of H₂L ligand

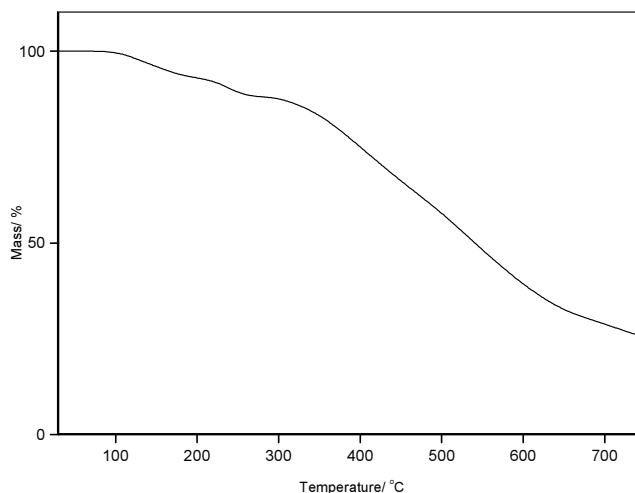


Figure 2; TG curve of $[\text{Zr}(\text{OH})_2\text{L}(\text{CH}_3\text{OH})]$ complex

Table: 1 Analytical and physico-chemical data of H_2L and its metal complexes.

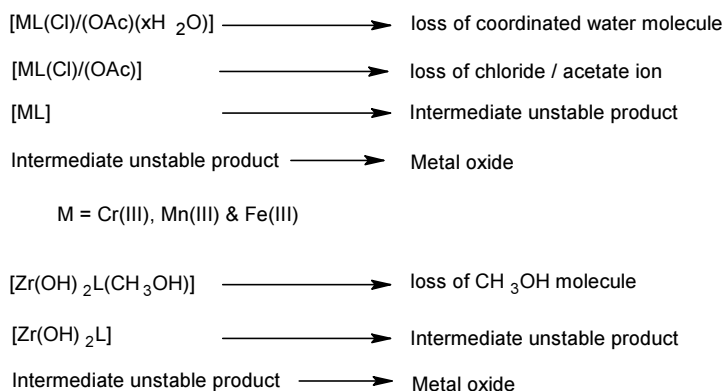
| Compound | Molecular formula | Elemental analysis found (calcd.) (%) | | | | μ_{eff} (BM) |
|--|--|---------------------------------------|-------------|---------------|---------------|-------------------------|
| | | C | H | N | M | |
| H_2L | $\text{C}_{15}\text{H}_{12}\text{ClN}_3\text{O}_5$ | 50.74 (51.51) | 3.04 (3.46) | 12.67 (12.02) | -- | -- |
| $[\text{CrL}(\text{Cl})(\text{H}_2\text{O})_2]$ | $\text{C}_{15}\text{H}_{14}\text{Cl}_2\text{N}_3\text{O}_7\text{Cr}$ | 38.92 (38.24) | 3.13 (2.99) | 8.65 (8.92) | 10.84 (11.04) | 3.91 |
| $[\text{MnL}(\text{OAc})(\text{H}_2\text{O})]$ | $\text{C}_{17}\text{H}_{15}\text{ClN}_3\text{O}_8\text{Mn}$ | 42.47 (42.56) | 3.26 (3.15) | 8.64 (8.76) | 11.37 (11.45) | 4.9 |
| $[\text{FeL}(\text{Cl})(\text{H}_2\text{O})_2]$ | $\text{C}_{15}\text{H}_{14}\text{Cl}_2\text{N}_3\text{O}_7\text{Fe}$ | 38.21 (37.93) | 2.07 (2.97) | 9.02 (8.35) | 12.17 (11.76) | 5.92 |
| $[\text{Zr}(\text{OH})_2\text{L}(\text{CH}_3\text{OH})]$ | $\text{C}_{16}\text{H}_{16}\text{ClN}_3\text{O}_8\text{Zr}$ | 38.73 (38.05) | 3.62 (3.19) | 8.76 (8.32) | 18.83 (18.06) | DM |

Table: 2 Assignments of the IR spectral bands of H_2L and its complexes in cm^{-1}

| Compound | $\nu(\text{OH})_{\text{phenolic}}$ | $\nu(\text{NH})$ | $\nu(\text{C}=\text{O})$ | $\nu(\text{C}=\text{N})$ | $\nu(\text{N}-\text{N})$ | $\nu(\text{C}-\text{O})_{\text{enolic}}$ | $\nu(\text{C}-\text{O})_{\text{phenolic}}$ | $\nu(\text{M}-\text{O})$ | $\nu(\text{M}-\text{N})$ |
|--|------------------------------------|------------------|--------------------------|--------------------------|--------------------------|--|--|--------------------------|--------------------------|
| H_2L | 3242 | 3162s | 1670 | 1629 | 992 | - | 1337 | - | - |
| $[\text{CrL}(\text{Cl})(\text{H}_2\text{O})_2]$ | - | - | - | 1605 | 1010 | 1193 | 1373 | 543 | 486 |
| $[\text{MnL}(\text{OAc})(\text{H}_2\text{O})]$ | - | - | - | 1597 | 1029 | 1238 | 1346 | 501 | 489 |
| $[\text{FeL}(\text{Cl})(\text{H}_2\text{O})_2]$ | - | - | - | 1620 | 1007 | 1236 | 1393 | 493 | 450 |
| $[\text{Zr}(\text{OH})_2\text{L}(\text{CH}_3\text{OH})]$ | - | - | - | 1581 | 1014 | 1230 | 1347 | 578 | 474 |

THERMOGRAVIMETRIC ANALYSIS

During thermal analysis, heating rates were set to $10^\circ\text{C min}^{-1}$ under dynamic air atmosphere and the mass loss was measured in the temperature range 30–750°C. The thermograms of the ligand and its Zr(IV) complex are as shown in figure 1 & 2. Cr(III), Mn(III) and Fe(III) complexes show mass loss in the temperature range 130–195°C correspond to loss of coordinated water molecules [% mass loss obs/calcd: Cr(III): 7.4/7.6; Mn(III): 3.81/3.7; Fe(III): 8.0/7.55] [21]. The Zr(IV) complex is stable up to 195°C temperature and loss of mass in the temperature 195–235°C indicated the presence of one methanol molecule [% mass loss obs/calcd: Zr(IV):6.93/6.32]. After the loss of water/methanol molecules the chloride/acetate ion along with organic part decomposes as further increment of temperature (350–550°C). In this step rapid mass loss is observed in the temperature range 350–550°C, and TG curve attains a constant level above 700°C leading to the formation of their respective metal oxide. The second step of decomposition starts immediately after the first one and losses the organic part of the complexes [22]. In general, the stages of thermal decomposition of the complexes can be written as:



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