



MONONUCLEAR Mn(III), Fe(III) and Zr(IV) Complexes of Hydrazone Ligand Derived from 2,4-Dihydroxy-5-Nitroacetophenone: Synthesis and Characterization

A. Yaul^a, A. Kalsarpe, J. Makode^b, S. Yaul, A. Aswar^{*}

^{*}Department of Chemistry, Sant Gadge Baba Amravati University, Amravati, India

^aDepartment of Chemistry, N. Kale Smruti Model College, Karanja (Gh.), Wardha, India

^bDepartment of Chemistry, Shri Shvaji Science College, Akola, (MS), India.

*Email: aswaranand@gmail.com

Abstract:

Mn(III), Fe(III) and Zr(IV) complexes with a new hydrazone Schiff base ligand derived by the condensation of 2,4-dihydroxy-5-nitroacetophenone and 2,4-dichlorobenzoylhydrazide have been synthesized. The isolated complexes were characterized by elemental analyses, molar conductance, spectral (IR and UV-Vis), magnetic moment measurement and thermal analysis. The IR spectral data suggest that the ligand coordinate in a tridentate manner via the azomethine nitrogen, phenolic and enolic oxygen atoms. The nature of water molecules inside and outside the coordination sphere was determined using thermal data (TGA) and weight loss method. The electronic spectra of the complexes as well as their magnetic moments suggest octahedral geometry for Mn(III) and Zr(IV) complexes whereas square pyramidal geometry for Mn(III) complex.

Introduction:

The synthesis and structural characterization of hydrazones belonging to azomethine class of compounds have much interest due to their ligating behavior. Chemistry of transition metal complexes with such Schiff base ligands is fascinating because these metal ions exhibit different oxidation states [1]. Such complexes with different oxidation states have strong as antitumor [2], antimicrobial [3], antituberculosis [4] and antimalarial agents [5]. They also find the potential applications as catalysts [6]. Therefore, we report here the synthesis and characterization of Mn(III), Fe(III) and Zr(IV) complexes with 2,4-dihydroxy-5-nitroacetophenone-2,

4-dichlorobenzoylhydrazone (H₂L) (Scheme 1.).

Experimental

Materials and physical measurements: All chemicals and solvents in this work were of analytical grade and were used as received. 2,4-dihydroxy-5-nitroacetophenone and 2,4-dichlorobenzoylhydrazide were prepared by known method [7]. Zirconium (IV) acetate and Mn(OAc)₃·2H₂O were synthesized by reported method [8, 9].

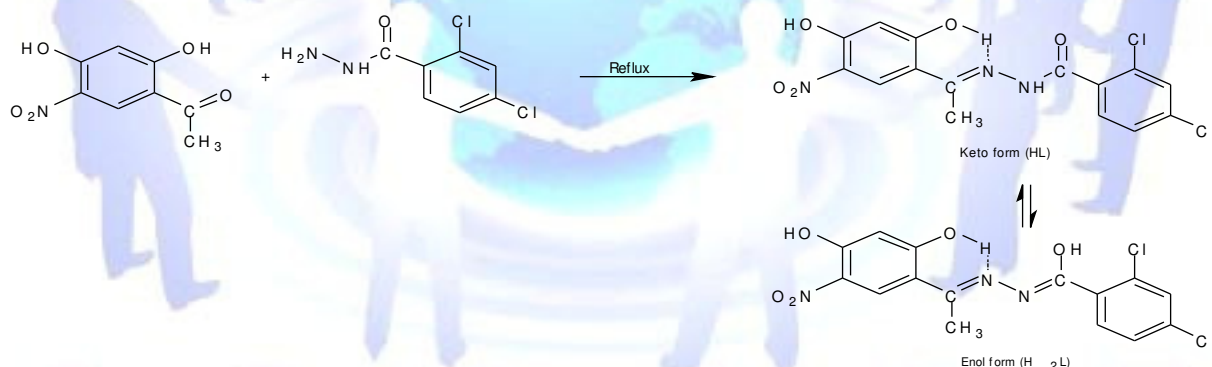
Analyses of C, H and N were determined on a Perkin-Elmer 240 elemental analyzer. Metal content in each complex was done gravimetrically by decomposing the complexes with conc. HNO₃ and then igniting to metal oxides. The IR spectra (4000-400 cm⁻¹) were recorded on a Perkin Elmer spectrophotometer in KBr pellets. Solid-state electronic spectra of the complexes were recorded on a Cary 2300 spectrophotometer. ¹H-NMR spectra of ligand was recorded on a Bruker Ac 250 spectrometer at 250 MHz, using TMS as a reference in DMSO-d₆. Thermogravimetric



curves of the complexes were recorded in the temperature range 40-700°C at the heating rate of 10°C/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 10-3M solution of the complexes were measured in DMSO at room temperature using Systronics model 304 conductivity meters.

Synthesis of Schiff base ligand (H₂L): The Schiff base ligand (H₂L) used in the present work was prepared by following general method. 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: 79%, M.P.: 178°C. ¹H-NMR data: 14.84 (s, 1H, OH C₂), 12.34 (s, 1H, OH C₄), 9.44 (s, 1H, NH), 7.60-8.84 (m, 5H, Ar-H), 2.46 (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.

Table 1. Physical and analytical data of the ligand and its metal complexes

Proposed composition of the complex	Formula weight g mol ⁻¹	Colour	Elemental analysis found (calcd) %			
			C	H	N	M
H ₂ L	384.2	Gold	47.19 (46.90)	3.06 (2.89)	10.10 (10.94)	-
[Mn(L)(OAc)(H ₂ O)]	514.2	Scarlet	39.17 (39.72)	2.86 (2.74)	8.03 (8.16)	10.34 (10.69)



[Fe(L)(Cl)(H ₂ O) ₂]	509.5	Black	36.71 (35.36)	2.83 (2.57)	8.92 (8.25)	11.52 (10.96)
[Zr(OH) ₂ (L)(CH ₃ OH)]	539.4	Crimson	35.12 (35.62)	3.10 (2.80)	7.15 (7.79)	17.67 (16.91)

Results and discussion

The analytical data along with some physical properties of the compounds are summarized in Table 1. The elemental analyses show 1:1 (metal:ligand) stoichiometry for all the complexes. The complexes can be represented by the formulae [Mn(L)(OAc)(H₂O)], [Fe(L)(Cl)(H₂O)₂] and [Zr(OH)₂(L)(CH₃OH)] for Mn(III), Fe(III) and Zr(IV) complexes respectively. The observed molar conductance values indicate their 1:1 nonelectrolytic nature of all the complexes.

IR spectroscopy: The ligand shows a broad band centered at 3439 cm⁻¹ due to presence of phenolic -OH group. The disappearance of ν(OH) band in all the metal complexes indicates the deprotonation of the phenolic -OH group and coordination through a phenolate oxygen atom. This is further supported by the shifting of ν(C-O) towards higher frequency as compared to the free ligand due to the conversion of hydrogen bonded structure into a covalent metal bonded structure [10]. The ν(C=N) band observed at 1613 cm⁻¹ in ligand, also shifted to lower frequency by 07-15 cm⁻¹ in its metal complexes, indicating coordination through >C=N- group [11]. Furthermore, a weak band due to ν(N-N) observed at 982 cm⁻¹ in ligand, shifts to higher frequency by 09-18 cm⁻¹ in its metal complexes indicating the coordination of one of the nitrogen atom of >N-N< group with metal. A shift of ν(C=N) band to a lower frequency is due to the conjugation of the p-orbital on the double bond with the d-orbital on metal ion with reduction of the force constant. IR spectrum of the hydrazone ligand (free ligand H₂L) contains a strong ν(C=O) absorption band at 1654 cm⁻¹ and a ν(N-H) absorption medium band at 3239 cm⁻¹. Both of these bands disappear upon complexation and a new ν(C-O) absorption band appears at 1082-1094 cm⁻¹ for the complexes, providing strong evidence for ligand coordination to the metal ion in the enolic form [12]. In Mn(III) complex, the coordinated monodentate CH₃COO⁻ group appeared at 1543, 1352 cm⁻¹. These two bands are due to ν_{asy}(COO⁻), ν_{sys}(COO⁻) respectively. The separation of the two bands, Δν = (ν_{asy} - ν_{sys}) = 191 cm⁻¹, is comparable to the values cited for the monodentate character of the acetate group [13]. The strong IR band at 1114 cm⁻¹ in Zr(IV) complex is assigned to Zr-OH vibration. A new strong band at 1242 cm⁻¹ in the spectrum of [Zr(OH)₂(L)(CH₃OH)] is assigned to the ν(C-O) (enolic). The ν(C-O) of CH₃OH occurs at 1049 cm⁻¹ and this band undergoes a negative shift in [Zr(OH)₂(L)(CH₃OH)] and is observed at ~1026 cm⁻¹ indicating methanol coordination. The absence of a new band in the spectrum of Zr(IV) complex in the range 850-960 cm⁻¹ due to the ν (Zr=O) favors the formulation of the complex as [Zr(OH)₂(L)(CH₃OH)] and not as [ZrO(L)(H₂O)(CH₃OH)]. The Mn(III) and Fe(III) complexes exhibit a broad band centered at 3467 cm⁻¹ due to the symmetric and asymmetric stretching modes of coordinated H₂O. The H-O-H bending modes occur in the 1587-1574 cm⁻¹ range. Weak bands in the 910-9450, 742-753 and 648-672 cm⁻¹ range represent the wagging, twisting and rocking modes of coordinated water. The IR spectra of complexes show two new bands at 552-510 and 468-445cm⁻¹, assigned to ν (M-O) and ν(M-N), respectively [14].





Diffused reflectance spectra and magnetic moment: The electronic spectrum of the Mn(III) complex gives rise to bands at 12040, 15238 and 19874 cm^{-1} , attributed to ${}^5\text{B}_{1g} \rightarrow {}^5\text{B}_{2g}$, ${}^5\text{B}_{1g} \rightarrow {}^5\text{A}_{1g}$ and ${}^5\text{B}_{1g} \rightarrow {}^5\text{E}_g$, transitions, respectively, in square pyramidal geometry. The magnetic moment value (4.93 B.M.) observed for Mn(III) complex, corresponds to four unpaired electrons and suggests a square pyramidal geometry for the complex [15]. The electronic spectrum of Fe(III) complex display three bands at 16846, 23780 and 17860 cm^{-1} corresponding to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}(\text{G})$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g(\text{G})$ transitions, respectively, characteristic of an octahedral geometry of complexes. The magnetic moment value for this complex was found to be 5.82 B.M. at room temperature which is close to the predicted values for five unpaired electrons in the metal ions [16]. As Zr(IV) complex has d^0 electronic configuration do not furnish any d-d transition.

Thermal analysis: TG study was carried out for the $[\text{Mn}(\text{L})(\text{OAc})(\text{H}_2\text{O})]$, $[\text{Fe}(\text{L})(\text{Cl})(\text{H}_2\text{O})_2]$ and $[\text{Zr}(\text{OH})_2(\text{L})(\text{CH}_3\text{OH})]$ complexes. These complexes decomposed gradually with the formation of the respective metal oxide above 600°C. TGA curves of the complexes, indicates that the complexes are highly stable up to 105°C. Further, these complexes show thermal decomposition in two significant steps. The mass loss of [% mass loss obs/calcd: Mn(III): 3.67/3.50; Fe(III): 3.94/3.53] in the first step is attributed to the loss of coordinated water molecules in the region 105-190°C for Mn(III) and Fe(III) complexes respectively [17]. 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):6.22/5.93]. In the second stage, the decomposition corresponds to a mass loss in the range 235-390°C, showing the combined loss of one chloride ion and the ligand. Further reduction of mass in the higher temperature range is ascribed to the decomposition of remaining part of the ligand and finally the graph become plateau because of the formation of stable respective metal oxide.

Conclusions:

Complexes of Mn(III), Fe(III) and Zr(IV) with 2,4-dihydroxy-5-nitroacetophenone-2,4-dichlorobenzoylhydrazone were obtained and structurally characterized. An octahedral geometry suggested for Fe(III) and Zr(IV) complexes while square pyramidal geometry for Mn(III) complex. Ligand coordinated as dibasic tridentate via the phenolic oxygen, the imine nitrogen and the enolic oxygen atoms.

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