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Synthesis, spectral characterization and thermal studies of Ti (III), Cr (III) and Mn (III) complexes derived from 2-Chlorobenzohydrazone schiff's base

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ABSTRACT

Tridentate Schiff's base ligand, H_2L (1-(1-hydroxynaphthalen-2-yl)ethanone-2-chlorobenzoylhydrazone) and their metal complexes with Ti (III), Cr (III) and Mn (III) ions have been synthesized and characterized by elemental analysis, ^1H NMR, IR, electronic spectroscopy, magnetic susceptibility and molar conductance. From analytical and spectral data, the stiochiometry of complexes has been found to be (1:1) (metal:ligand). The physicochemical data suggest octahedral geometry for Ti (III), Cr (III) complexes and square pyramidal geometry for Mn (III) complex. Thermal stabilities of the complexes have been studied by thermogravimetric analysis.

Keywords: Hydrazone schiff's base, Metal complexes, Spectral studies, Thermal stabilities.

INTRODUCTION

Hydrazones are important class of ligands and played an important role in the development of coordination chemistry as they readily form stable complexes with most transition metals [1, 2]. Hydrazones –NH–N=CRR′ (R and R′ = H, alkyl, aryl) are versatile ligands due to their applications in the field of analytical [3] and medicinal chemistry [4]. Hydrazones are versatile class of ligands which have been studied for a long time as potential multifunctional ligands with various coordination modes [5-7]. Hydrazones are used as plasticizers and stabilizers for polymers polymerization initiators, antioxidants and etc. they act as intermediates in preparative chemistry. They also find applications as indicators and spot test reagents [8].

If hydrazones posseses a phenolic group at ortho position to aldehyde/ ketone part, it involves bonding with metal leads to an ONO coordination mode [9, 10]. The work on ONO hydrazone complexes of divalent metal ions in general has been well reported in a great number of recent literatures [11, 12]. However, studies of hydrazone complexes of ONO ligand of o-hydroxyketones with more valent metal ions are not so numerous.

Thus, the aim of present work is to synthesize and characterize Ti (III), Cr (III) and Mn (III) hydrazone complexes with newly synthesized Schiff base 1-(1-hydroxynaphthalen-2-yl)ethanone-2-chlorobenzoylhydrazone (H_2L^1).

MATERIALS AND METHODS

All the chemicals used were of analytical grade (AR). 2-acetyl-1-naphthol [13] and 2-chloro benzohydrazides [14] are synthesized from literature procedure. Titanium trichloride ($TiCl_3$), Chromium chloride hexahydrate ($CrCl_3 \cdot 6H_2O$) salts were of S.D.fine chemicals. $Mn(OAc)_3 \cdot 2H_2O$ was prepared by oxidation of $Mn(OAc)_2 \cdot 4H_2O$ using Christensen's method [15].

The metal and chloride contents were determined as per Vogel's procedure [16]. The IR spectra of ligand and their complexes were recorded in KBr disc in the range of 4000-350cm^{-1}. The electronic spectra of the ligands and metal complexes were recorded on an Elico SL - 159 double beam UV-Vis spectrophotometer in the range of 200-900 nm in DMF(10^{-3}M) solution. ^1H NMR spectra of ligand was recorded in DMSO-d6 on Bruker 400 MHz spectrophotometer, using TMS as an internal standard. Molecular weight measurements were carried out according to Rast's method [17]. The magnetic susceptibility of the metal complexes was measured at room temperature by Gouy's method using mercury (II) tetra thiocyanatocobalt (II), Hg [Co(SCN)4], as a calibrant. Molar conductivity measurements were recorded on a Elico CM-180 conductivity bridge in DMF (10^{-3} M) solution at room temperature. Thermogravimetric analyses of metal complexes were performed on TG Instrument, model – SDT Q 600 of temperature rang ambident to 800˚C with heating rate of 20˚C/min.

Synthesis of ligands, H_2L

To hot ethanolic solution (15ml) of 2-chlorobenzoylhydrazide (0.01mol), hot ethanolic solution (15ml) of 2-acetyl-1-naphthol (0.01mol) was added with continuous stirring and reaction mixture was heated under reflux on water bath for 3-4 hr. After cooling, the yellow coloured solid obtained was filtered off, washed with ethanol and dried under vaccume of $CaCl_2$. It was finally recrystallized from DMF-ethanol mixture (1:4 v/v).

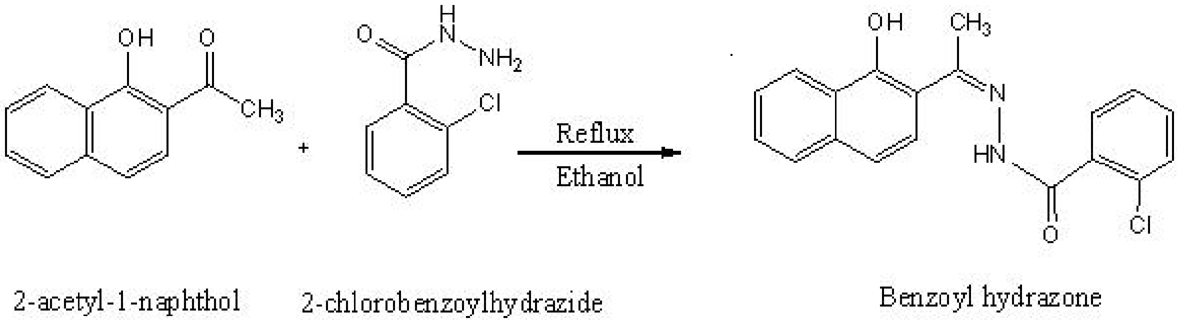


Fig 1: Synthetic route for the preparation of H_2L

(H_2L): % yield = 72%, m.p. = 211˚C, ^1H NMR: δ 14.4 (1H, S, -OH); δ11.6 (1H, S, –NH); δ7.5-δ8.3 (10H, m, Ar-H), δ2.53 (3H, S, $-CH_3$).

General Synthesis of Ti (III), Cr (III) and Mn (III) complexes

To a hot DMF solution (20 ml) of organic ligand (0.01mol), hot ethanolic solutions (20 ml) of the metal salts (0.01mol) are added under continuous stirring. The resulting mixture was refluxed on sand bath for 6-8h. The reaction mixture was digested to half of its volume; solid product was obtained on cooling was washed with ethanol followed by petroleum ether and dried at room temperature (Yield = 65-68%).

RESULTS AND DISCUSSION

The complexes synthesized are coloured, stable towards air and moisture at room tempreture. The complexes are generally insoluble in water, slightly soluble in ethanol and methanol, while completely soluble in DMF and DMSO solvent. The analytical data of the ligands and complexes are given in table 1, which reveals that the complexes are of 1:1 metal to ligand stoichiometry. The molar conductance values of the complexes at 10^{-3}M in DMF fall in the range of 9.2 - 18 $ohm^{-1}cm^2mol^{-1}$ indicating the non electrolytic nature of the complexes [18].

Table –1. Analytical and Physico-Chemical data of the Schiff's base ligand (H_2L^1) and its Metal Complexes

Molecular Formula Ligand/ Complexes	Molecular weight	colour	Elemental Analysis %found (cal.)					μ^{eff} (BM)	Λ^{M*}
			C%	H%	N%	M%	Cl%		
$C_{19}H_{15}ClN_2O_2$ (H_2L)	338.78	Yellow	67.03 (67.36)	4.40 (4.46)	8.18 (8.27)	---	10.38 (10.46)	---	---
$[Ti(L)Cl_2.H_2O]$	474.56	Current	46.00 (46.09)	3.34 (3.40)	5.76 (5.90)	10.00 (10.09)	22.34 (22.41)	1.42	18
$[Cr(L)Cl_2.H_2O]$	478.69	Dark Brown	47.56 (47.67)	3.27 (3.37)	5.49 (5.85)	10.38 (10.86)	22.08 (22.22)	3.56	12.5
$[Mn(L)(OAc).H_2O]$	468.76	Black Berry	53.67 (53.81)	3.54 (3.87)	5.65 (5.98)	11.46 (11.72)	7.34 (7.36)	4.42	9.2

** Molar conductance values in ohm^{-1} cm^2 $mole^{-1}$.*

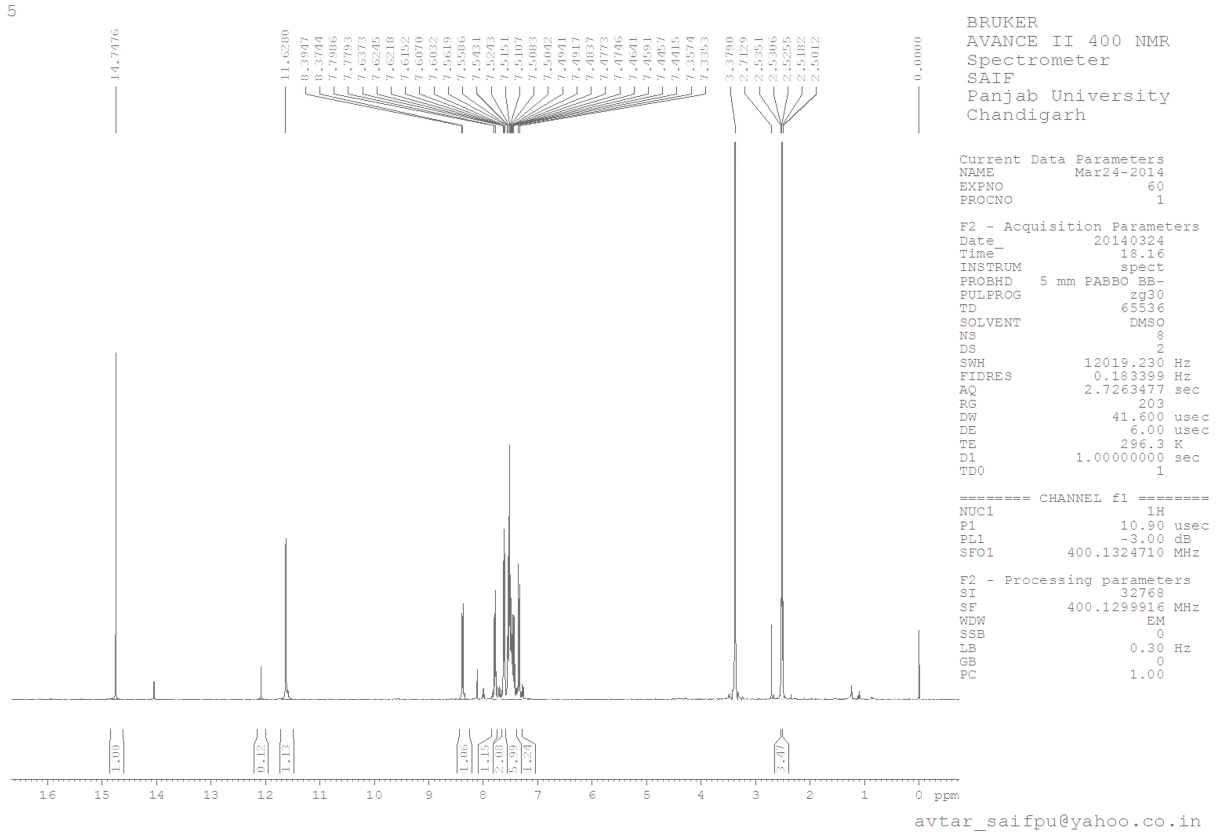


Fig 2: ^{1}HNMR of ligand H_2L

IR Spectral studies

The bonding modes of ligand to metal in complexes are compared with free ligand, by study of IR spectra (Table 2). IR bands for υ (N-H), υ (O-H+N-H), υ (C=O), υ (C=N) and phenolic υ (C-O) are observed at 3190, 2995, 1653, 1587 and 1288 cm^{-1} respectively in free ligand. However, in the o-hydroxy Schiff base this band is generally moved to lower frequency (Table 2) due to the presence of a strong intramolecular hydrogen bonding (O–H…N=C) [19]. In complexes the band due to υ (O-H) of free ligand, disappeared which indicates the coordination of phenolic oxygen to metal ion via deprotonation which was confirmed by upward shift of phenolic υ (C-O) frequency 1321-1382 cm^{-1} compared to ligand with frequency 1288cm^{-1} [20]. Stretching frequency of υ (C=N) in free ligand shift to lower value by 16-20 cm^{-1} in complexes. This indicates coordination of azomethine nitrogen to metal ion in complexes. Presence of υ(C=O) and υ (N-H) vibrations in the spectra of Ti (III) and Cr (III) complexes indicated that hydrazone ligand is in keto form. Which confirmed monobasic tridentate nature of ligand in Ti (III) and Cr (III) complexes. While in case of Mn (III) complex, absence of bands due to υ(C=O) and υ (N-H), indicates dibasic tridentate nature of ligand in Mn (III) complexes. It was further supported by presence of enolic υ (C-O) and υ (-C=N-N=C-) bands in spectra. An additional two absorption bands in Mn (III) complex was appeared at1615cm^{-1} and 1415 cm^{-1} which may be assigned due to ν_{asy} (OCO) and ν_{sy} (OCO) frequency, respectively. This indicates monodentate nature of acetate group [21]. All complexes show bands in region at 3442-3337 cm^{-1}, 1620-1616 cm^{-1} and 794-744 cm^{-1} assignable to υ (OH), δ (H_2O) and ρw (H_2O) modes, respectively. The bands observed in the far-infrared regions at 565-572 and 410-418 cm^{-1} are assignable to the υ (M-O) and υ (M-N) vibrations, respectively [22].

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

Ligand/ Complexes	ν(OH)+ ν(NH) $_{phe}$	ν(NH)	ν(C=O)	ν(C=N)	ν(N−N)	ν(C−O) $_{enol}$	ν(C−O) $_{phe}$	ν(M−O)	ν(M−N)
H_2L	2995	3190	1653	1587	1020	---	1288	---	---
Ti(III)	---	3255	1620	1577	1043	---	1321	565	418
Cr(III)	---	3257	1645	1568	1022	---	1348	572	410
Mn(III)	---	---	1620	1570	1024	1232	1323	569	414

Magnetic Moment and Electronic Spectral studies

The electronic spectra of the Ti (III), Cr (III) and Mn (III) complexes were recorded in freshly prepared DMF solution (10^{-3}M) at room temperature and their magnetic moment values are given in Table-1. Ti (III) complex shows one broad band at 18789 cm^{-1} assigned to $^2T_{2g} \rightarrow {}^2E_g$ transition [23]. The observed value of magnetic moment for Ti (III) complex is 1.42 B.M. which confirms octahedral geometry of complex. The magnetic moment value for Cr (III) was found to be 1.56

B.M. and in electronic spectra of Cr (III) complex, three transitions are observed at 18682, 24874 and 39885 cm^{-1} assignable to $^4T_{2g}$ (F) → $^4T_{2g}$ (F), $^4T_{2g}$ (F) → $^4T_{1g}$ (F) and $^4T_{2g}$ (F) → $^4T_{1g}$ (P) transitions respectively, suggesting octahedral geometry [24]. Weak d-d bands are observed in Mn (III) complex at 13984, 17136 and 20524 cm^{-1} assigned to $^5B_1$→ $^5B_2$, $^5B_1$→ $^5A_1$ and $^5B_1$→ ^5E transitions respectively [25]. The electronic spectra of Mn(III) complex shows band at 28589 cm-1 attributed to the LMCT transition and magnetic moment value is 4.42 B.M. corresponds to square pyramidal geometry of complex.

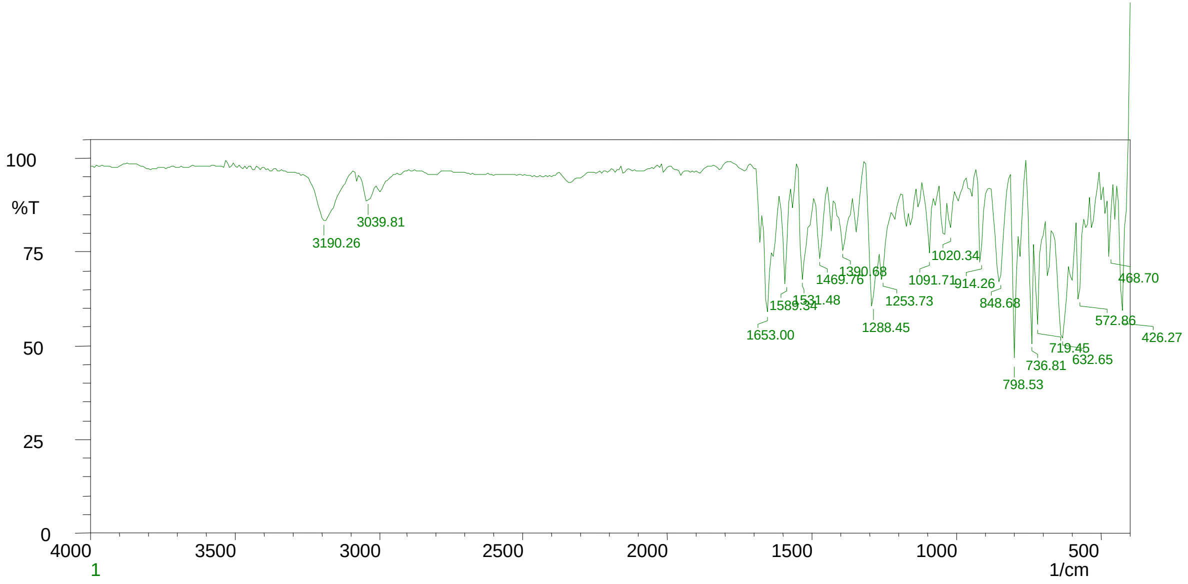


Fig 3: IR spectrum of ligand H_2L

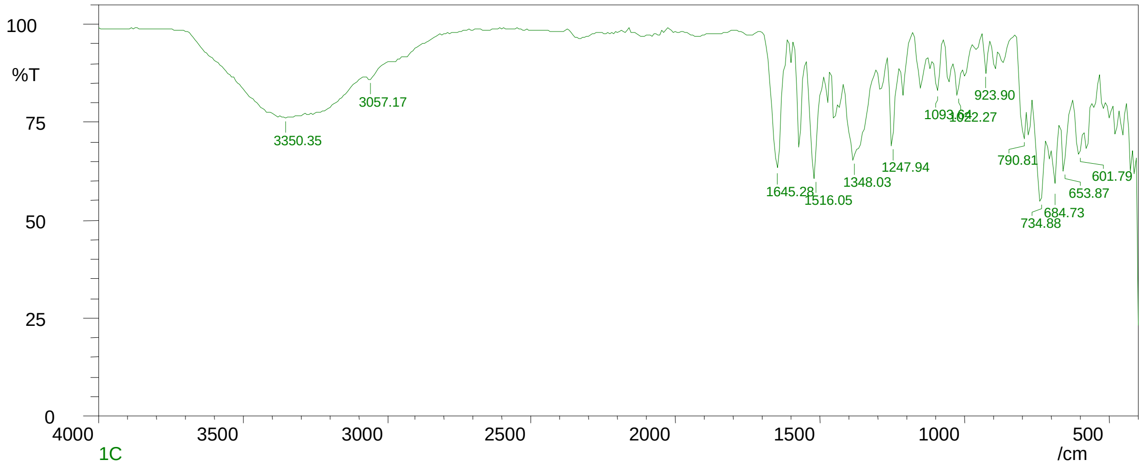
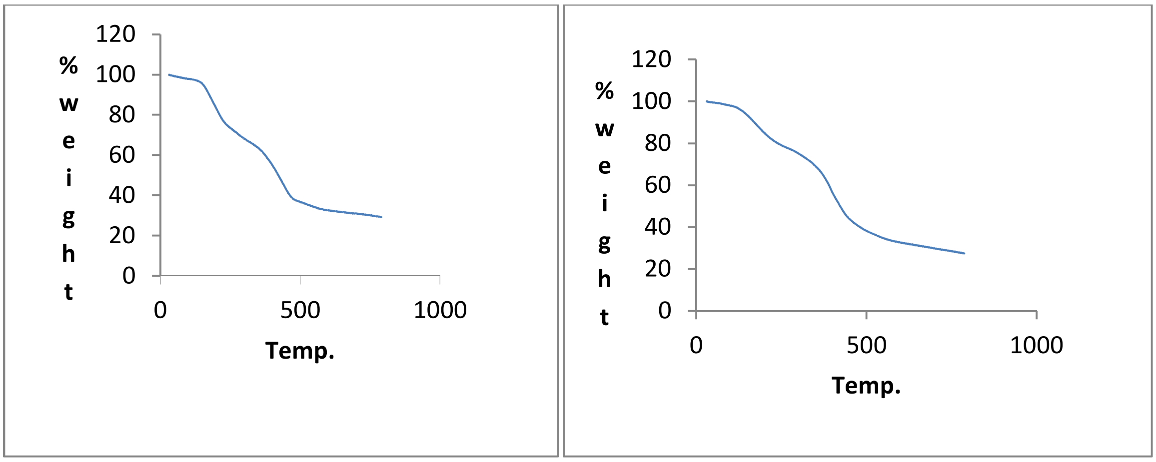


Fig 4: IR spectrum of Cr (III) complex

Thermogravimetric Analysis

Thermal behaviors of metal complexes were investigated by TGA technique. The thermogravimetric analyses for complexes were carried out within temperature ranging from room temperature to 800˚C at heating rate of 20˚C per min. The thermogram of metal complexes indicates that the complexes Ti (III), Cr (III) and Mn (III), shows a three stage decomposition pattern. All polychelates show negligible weight loss up to 90-100°C indicating the absence of any lattice water molecules in these complexes. The weight loss in temperature range 150-203˚C [26] corresponds to loss of one coordinated water molecule for all complexes. The presence of water molecule in all complexes suggested from IR spectra is confirmed by the weight loss observed in first decomposition step of complexes. The gradual weight loss in first step ranging from 200-280˚C corresponds to loss of two coordinated chloride ions in Ti (III) and Cr (III) complexes [27]. The rapid weight loss in the range of 300-550˚C is due to the quantitative elimination of ligand. Thereafter compound showed a gradual decomposition upto 800˚C and onwards leaving behind their respective metal oxide.



[a] **[b]**

Fig 5: TGA curve of (a) Ti (III) and (b) Cr (III) complexes

CONCLUSION

The bonding of ligand to metal was confirmed by the analytical, IR, electronic, magnetic and thermal studies. From the present investigation it has been observed that Schiff base H_2L was monobasic tridentate towards Ti (III), Cr (III) and dibasic tridentate towards Mn (III). Analytical and physicochemical studies reveals that the octahedral geometry was assigned for Ti (III) and Cr (III) complexes while square planer for Mn (III) complex.

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