

# Synthesis, Spectroscopic, Thermal and Electrical Studies of Some Transition Metal Coordination Polymers

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**Abstract:** Coordination polymers of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) coordination polymers of Schiff base ligand (TDINH) derived from Terephthalaldehyde and Isoniazid have been prepared. The ligand is characterized by elemental analyses, IR and electronic spectra, magnetic susceptibility measurements and thermogravimetric analysis. Thermogravimetric analysis decomposition behaviors of all the coordination polymers were studied using thermogravimetric analysis in nitrogen atmosphere. The octahedral geometry have been suggested for Mn(II), Fe(II), Co(II) and Ni(II) coordination polymers, square planar geometry to Cu(II) where as tetrahedral for Zn(II) and Cd(II) coordination polymers. Thermal data have been analyzed for kinetic parameters by both Coat-Redfern and Broido methods. The solid state electrical conductivity of ligand and its coordination polymers has been measured in the temperature range 313-413K and coordination polymers are found to show semiconducting behavior.

**Keywords:** Schiff base, Thermogravimetric and TG/TGA, Electrical Conductivity

## I Introduction

Schiff bases containing an azomethine group ( $-\text{CH}=\text{N}-$ ) are formed by condensation of a primary amine with a carbonyl compound [1]. These bases are ligands, which are active, well designed and stable under a variety of oxidative and reductive conditions [2]. Symmetric and asymmetric transition metal complexes of Schiff bases have been used as catalysts in reactions, such as epoxidation [3], asymmetric synthesis [4], asymmetric sulfoxidation [5], asymmetric silylcyanation [6], and many other applications [7].

The design of new coordination supra molecules and polymers based on the transition metal compounds and multidentate organic ligands has attracted much interest in recent years [8,9]. Coordination polymers are usually known for their thermal stability [10,11] and huge work has been reported [12-15] on the synthesis, characterization and thermal studies of coordination polymers. However, some additional equally good applications have been reported, such as solar energy converters [16] and removal of  $\text{SO}_x$  and  $\text{NO}_x$  from the environment [17]. One major goal in this area is the preparation of new compounds with interesting properties such as functional materials in molecular magnetism [18], catalysis [19], Schiff bases and their complexes have a variety of applications in biological clinical and analytical fields [20]. Recently there has been a considerable interest in the chemistry of hydrazine and hydrazone compounds because of their potential pharmacological applications [21].

## II Experimental

### Material and method

All the chemicals and solvents used were of Analytical Grade (AR) and purchased commercially. All the solvents were purified by standard method and used. The compound Terephthalaldehyde and metal acetate were purchased from E. Merck Ltd. (India), Isoniazid was purchased from Himedia, India and used without further purification.

### Synthesis of bis-ligand

Schiff base ligand has been synthesized by mixing ethanol solution (100 ml) of Isonicotinic acid hydrazide 0.1 mol (12.4g) and ethanol (50ml) solution of Terephthalaldehyde 0.05 mol (6.7g) with continuous stirring in hot condition. The resultant mixture was refluxed on a water bath for about 2 hours and left to cool, where upon crystalline yellow product which had formed was filtered off and washed several times with hot Ethanol to remove unreacted reactant. Product was recrystallized from DMF and dried under reduced pressure over anhydrous  $\text{CaCl}_2$ . The reaction of ligand formation has been shown in following Fig. [1]

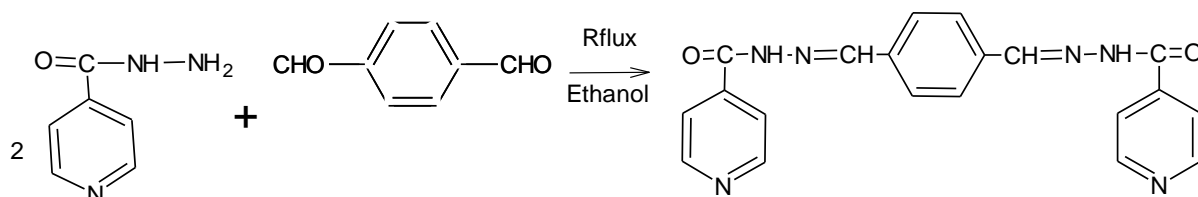


Fig.1 Structure of bis-Ligand

### Synthesis of Transition Metal Coordination Polymers

Coordination polymers of Terephthalaldehyde di-isonicotinoylhydrazone (TDINH) ( $\text{H}_2\text{L}$ ) with Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have been synthesized by dissolving metal acetate in minimum quantity of DMF and were added to a solution of Terephthalaldehyde di-isonicotinoylhydrazone in DMF in 1:1 molar ratio. The reaction mixtures were refluxed in an oil bath at

about 140°C for 7 hours. The products formed were filtered, washed thoroughly first with hot DMF and then with absolute alcohol and dried under vacuum on an anhydrous CaCl<sub>2</sub>. The physicochemical and analytical data of the ligand and its coordination polymers are listed in table 1 and 2.

### Instrumentation

The Infrared spectra were recorded using KBr on a Shimadzu 8201 spectrophotometer in the range 400–4000 cm<sup>-1</sup>. The carbon, hydrogen and nitrogen analyses were carried out on a Carlo Erba 1108 elemental analyzer. <sup>1</sup>H spectra of ligand were recorded on Bruker Advance II, 400MHz and NMR spectrophotometer in DMSO-*d*<sub>6</sub> with TMS as an internal standard. Magnetic measurements were carried out by the Sherwood magnetic susceptibility balance MK-1 at room temperature. The solid-state diffuse reflectance spectra of the complexes were recorded in the 200–1200nm range using MgO as diluent on a Cary 60 UV-Vis spectrophotometer. Thermogravimetric analyses were performed on a Perkin Elmer, Diamond TG thermal analyzer in the temperature range 40–750°C with a heating rate of 10°C min<sup>-1</sup>. Metal contents of the complexes were analyzed gravimetrically after decomposing the organic matter with a mixture of HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> (1:1.5:2.5) and then igniting to metal oxide [25]. The solid state electrical conductivity of the prepared complexes has been measured by using two probe techniques over a temperature range 303–463 K. The samples were in the form of pellet having diameter 13mm and thickness of 2–3 mm at pressure of approximately 1x10<sup>8</sup> Pa. The pellet was placed between two copper electrodes with silver paste on both sides so that there have good ohmic contact between pellet and electrodes. The temperature of sample was measured with the accuracy ±1°C with a calibrated Ni-NiCr thermocouple inserted inside the cell. The activation energies of electrical conductance were calculated using equation,  $\sigma = \sigma^0 \exp(-E_a/KT)$  characterization.

## II Results and discussion

### IR spectrum

IR spectrum of ligand depicts the band around 3250cm<sup>-1</sup> due to –NH– group of secondary amide [22]. However after ligation with ligand ions in coordination polymers this frequency is diapering indicating that the proton on the nitrogen atom is lost upon chelation with metal ions. The ligand also shows the IR absorption bands around 1650 cm<sup>-1</sup> due to >C=O group and 1601 cm<sup>-1</sup> due to –C=N group however the >C=O group bands is lower down 10 cm<sup>-1</sup> in spectra of coordination polymers.

### Magnetic moment and electronic spectra

The information regarding the geometry of the coordination polymers were obtained from their electronic spectral data and magnetic moment values. The observed magnetic moment of Mn (II) complex is 5.78 BM, which is within the limits of spin free values for five unpaired electrons indicating that the complex high spin octahedral. The observed magnetic moments 3.62 and 2.91 B.M., for the Co (II) and Ni (II) coordination polymers, respectively at room temperature is within the range for an octahedral geometry [23]. The reflectance spectrum of Co (II) coordination polymer shows bands at Δ17,690 and Δ21,690cm<sup>-1</sup>, which may be assigned to 4T<sub>1g</sub> (F) → 4A<sub>2g</sub> (F) and 4T<sub>1g</sub> (F) → 4T<sub>1g</sub> (P) respectively, of an octahedral geometry. The reflectance spectrum of the Ni (II) coordination polymer exhibits bands at Δ15,590, and Δ 22620 cm<sup>-1</sup> assignable to 3A<sub>2g</sub> → 3T<sub>1g</sub> (F) and 3A<sub>2g</sub> → 3T<sub>1g</sub> transitions respectively, in a square planar geometry. The reflectance spectrum of the Cu (II) coordination polymer displays a broad band at Δ15,200cm<sup>-1</sup> due to the 2E<sub>g</sub> → 2T<sub>2g</sub> transition and the observed magnetic moment is [1]83 B.M., which may be due to tetrahedral geometry Whereas tetrahedral geometry for Zn (II) and Cd(II) polymer coordination polymer is diamagnetic as expected for d10 system.

### Thermal Studies

Thermal analyses of the metal bis ligand coordination polymers were carried out up to the temperature 700°C. All the coordination polymers show a gradual mass loss indicating decomposition by fragmentation with increase in temperature. The perusal of thermograms of Mn(II), Co(II) and Ni(II) coordination polymers show weight loss of 6.42 (6.37%), 6.45(6.32%) and 6.40(6.32%), respectively in the temperature range 140–240°C. This weight loss corresponds to the loss of two coordinated water molecules. In the TG curve of Cu (II), Zn(II) and Cd(II) complex, there is no weight loss up to 245°C and these rules out the presence of any water molecule in these coordination polymers. After the loss of water molecules, TG curves shows continuous mass loss in a temperature range 250–650°C and attain a horizontal level above 650°C suggesting the formation of final decomposition product as stable metal oxides [24]. From the thermal decomposition data various kinetic parameters have been calculated by using both Coats-Redfern (CR) and Broido (B) methods [25] and comparable values obtained are given in Table 2.

### Solid State Conductivity

The solid state D.C. electrical conductivity of the synthesized ligand and its coordination polymers in compressed pellet form (5 ton cm<sup>-2</sup>) was measured in the temperature range (313–413 K) and a linear dependence of log σ = (10<sup>3</sup>/T) as evident from Arrhenius plot of electrical conductivity indicates the semiconducting behavior of these compounds [26]. The electrical conductivity (σ) varies exponentially with the absolute temperature according to the relation  $\sigma = \sigma^0 \exp(-E_a/KT)$ , Where σ<sup>0</sup> is constant, E<sub>a</sub> is the activation energy of electrical conduction, the absolute temperature and K, the Boltzmann constant. The D.C. electrical conductivity value at room temperature lies in the range 4.320x10<sup>-1</sup> to 7.211x10<sup>-10</sup> Ω<sup>-1</sup>cm<sup>-1</sup>. The conductivity of TDINH and its metal coordination polymers at 373 K followed the order Zn>Co> Ni> Mn>Ligand >Cu>Cd. The observed low value of electrical conductivity may be attributed to low molecular weight due to which the extent of conjugation becomes low or undesirable morphology due to pressing of the sample into hard brittle pellet form [27–30].

## III Conclusion

Here we have reported preparative and structural studies of metal coordination polymers of bis-ligand. All coordination polymers are insoluble in common organic solvents. It was not possible to characterize them by conventional methods, like osmometry, viscometry, conductometry, etc., as they are insoluble. The nature of ligand, high thermal stability, metal-ligand ratio (1:1) and insolubility of these compounds suggest their polymeric nature. An octahedral geometry has been suggested to Mn(II), Co(II),

Ni(II) and Cu(II) where as tetrahedral geometry for Zn(II) and Cd(II) polymers.

#### IV Acknowledgments

Authors are also thankful to Sophisticated Analytical Instrument facility, Punjab University, Chandigarh for providing elemental analysis, IR and <sup>1</sup>H NMR facility and SAIF, Lucknow for providing the element analysis, spectral and thermal analysis is also gratefully acknowledged.

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Ligand	Colour	Formula Weight	Colour	Elemental analysis found (Calcd.)				Ea (eV)
				C%	H%	N%	M%	
TDINH	Cream Colour	372.00	Cream Colour	64.0(64.02)	4.5(4.4)	21.7(22.0)	---	0.440
TDINH-Mn	Reddish Lemon	512.33	Reddish Lemon	49.2(50.2)	4.2(4.3)	14.6(14.99)	9.6(9.8)	0.755
TDINH-Co	Deep Scarlet	502.35	Deep Scarlet	47.2(47.8)	4.1.(4.4)	14.8(15.2)	9.5(9.7)	0.738
TDINH-Ni	Dark Umber	501.25	Dark Umber	42.8(43.0)	3.6(3.9)	14.0(14.1)	10.0(10.2)	0.929
TDINH-Cu	Chartreuse	485.36	Chartreuse	45.1(44.0)	3.8(3.5)	14.8(15.0)	12.3(12.7)	0.846
TDINH-Zn	Mustard	436.96	Mustard	50.5(50.2)	3.6(3.4)	17.4(17.2)	15.3(15.1)	0.553
TDINH-Cd	Avocado	435.75	Avocado	52.65(52.3)	3.5(3.2)	17.5(17.5)	15.2(15.0)	0.440

**Table: 1 Analytical and Physical studies of Coordination Polymers**

Ligand	Electrical Conductivity ( $\square\square\square\text{cm}^{-1}$ )	Activation Energy (eV)	DH ( $^{\circ}\text{C}$ )	Method	E ( $\text{Kj mol}^{-1}$ )	$\Delta\text{H}$ ( $\text{S}^{-1}$ )	$\Delta\text{S}$ ( $\text{JK}^{-1}\text{mol}^{-1}$ )
TDINH	$9.70 \times 10^{-12}$	0.31	140	F-C	29.49	90.44	-281.40
				C-R	27.95	160.40	-280.15
TDINH-Mn	$5.811 \times 10^{-8}$	0.190	320	F-C	24.14	204.57	-208.4
	$3.723 \times 10^{-8}$			C-R	28.09	375.81	-240.20
TDINH-Co	$3.126 \times 10^{-9}$	0.245	315	F-C	25.40	153.08	-280.67
	$1.010 \times 10^{-8}$			C-R	29.23	270.45	-280.54
TDINH-Ni	$2.392 \times 10^{-6}$	0.583	330	F-C	21.06	320.59	-273.38
	$7.735 \times 10^{-6}$			C-R	24.75	220.17	-281.42
TDINH-Cu	$6.001 \times 10^{-6}$	0.863	310	F-C	16.14	330.05	-280.14
	$9.410 \times 10^{-6}$			C-R	18.90	320.92	-276.48
TDINH-Zn	$1.362 \times 10^{-8}$	0.749	320	F-C	20.61	148.51	-264.27
	$2.023 \times 10^{-8}$			C-R	19.14	160.58	-258.91
TDINH-Cd	$1.699 \times 10^{-8}$	0.238	305	F-C	18.94	84.28	-210.45
	$4.948 \times 10^{-7}$			C-R	20.40	136.35	-215.28

**Table: 2 Thermal and Electrical conductivity data of Coordination Polymers**

F-C = Freeman-Carroll, C-R = Coats – Redfern and DH - Half Decomposition temp.