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Synthesis, Spectroscopic and Thermal Studies of Newly Synthesized Transition Metal Coordination Polymers

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ABSTRACT

The new Mn (II), Co (II), Ni (II), Cu (II), and Zn (II) coordination polymers of Schiff base ligand (TDINH) derived from Terephthaladehyde and Isoniazid have been synthesized in DMF media. The H2L ligand, is synthesized and characterized by using IR, 1H NMR and mass spectroscopy. The coordination polymers have been characterized by UV-Visible absorption spectra, Infra-Red spectra, elemental analysis and magnetic moments measurements. The thermal decomposition behaviors of all the polymers were studied using thermogravimetric analysis in nitrogen atmosphere. Freeman Caroll method was used to calculate the thermal activation energy (Ea), order of reaction (n), entropy change (ΔS), free energy change (ΔF), as well as apparent entropy change (S*) and frequency factor (Z).
Keywords: Coordination polymers, Schiff bases, Spectral studies, TG/DTA.

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INTRODUCTION

Schiff bases containing an azomethine group (–CH=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 supramolecules 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 [12-14] on the synthesis, characterization and thermal studies of coordination polymers. However, some additional equally good applications have been reported, such as solar energy converters [15] and removal of SOx and NOx from the environment [16]. One major goal in this area is the preparation of new compounds with interesting properties such as functional materials in molecular magnetism [17], catalysis [18], optoelectronic devices and gas sorption [19]. The study of polymeric ligands and their metal complexes is very useful as a catalyst in metal separation and in bio-inorganic chemistry [20–22]. Schiff bases and their complexes have a variety of applications in biological clinical and analytical fields [23]. Recently there has been a considerable interest in the chemistry of hydrazine and hydrazone compounds because of their potential pharmacological applications [24]. Isonicotinic acid hydrazide (Isoniazid, INH) has very high in vivo inhibitory activity towards M.tuberculosis H37Rv. Sah and Peoples synthesized INH hydrazide-hydrazones by reacting INH with various aldehydes and ketones. These compounds were reported to have inhibitory activity in mice infected with various strains of M. tuberculosis [25]. Some research developments on hydrazones compounds have been published recently on antimycobacterial substances [26-29].

EXPERIMENTAL

Materials and method

All the chemicals used were of analytical grade and used without further purification. The compound Terephthalaldehyde and metal acetate were purchased from E. Merck Ltd. (India). Isonazid was purchased from Himedia, India and used without further purification.

Synthesis of bis- ligand

Schiff base ligand has been synthesized by mixing ethanolic solution (100 ml) of Isonicotinic acid hydrazide 0.1 mol (15.3g), and ethanolic (50 ml) 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 h 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 $CaCl_2$. The reaction of ligand formation has been shown in following Fig. 1.
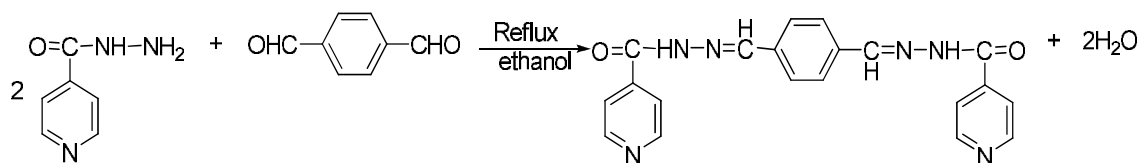
Fig 1: Structure of bis ligand

Synthesis of transition metal coordination polymers

All the coordination polymers isolated in the present study were prepared by following method:

Coordination polymers of Terephthalaldehyde di-isonicotinoylhydrazone (TDINH) (H_2L) with Mn (II), Co (II), Ni (II), Cu (II), and Zn (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 ^{o}C for 7 h. The products formed were filtered, washed thoroughly first with hot DMF and then with absolute alcohol and dried under vacuum on an anhydrous $CaCl_2$. The physicochemical and analytical data of the ligand and its coordination polymers are listed in table 1 and 2.

Table 1: Physicochemical data of TDINH and its coordination polymers

Polymers	Colour	Formula	Formula/Wt.	Yield %
TDINH	Cream colour	$C_{20}H_{16}N_6O_2$	372.00	74.0
TDINH – Co	Brick red	$CoC_{20}H_{22}N_6O_6$	501.35	60.2
TDINH – Ni	Green	$NiC_{20}H_{22}N_6O_6$	501.11	58.5
TDINH – Cu	Light brown	$CuC_{20}H_{20}N_6O_5$	487.93	60.5
TDINH – Zn	Light yellow	$ZnC_{20}H_{14}N_6O_2$	435.75	53.8

Table 2: Analytical data of TDINH and its coordination polymers

Ligand/ Coordination polymers	% C Obs(Calc)	% H Obs(Calc)	% N Obs(Calc)	% M Obs(Calc)	Magnetic moment (B. M.)
TDINH	64.0(64.4)	4.6(4.4)	21.8(22.0)	....	....
TDINH – Co	48.2(47.9)	4.0(4.3)	14.8(15.0)	9.5(9.7)	4.51
TDINH – Ni	42.9(43.0)	4.3(4.4)	14.0(14.1)	10.0(10.3)	3.10
TDINH – Cu	45.2(4.0)	3.6(3.8)	14.9(15.1)	12.3(12.5)	2.07
TDINH – Zn	50.4(50.3)	3.8(3.5)	17.4(17.2)	15.2(15.0)	....

CHARACTERIZATION

Spectral analysis and Magnetic moment measurements

Microanalysis for carbon, hydrogen, nitrogen and sulphur were analyzed on Eassuperuser, Elemental Analyser system GmbH, Access: VarioEL Superuser, BIT Mesra, Ranchi. Infrared spectra (4,000–400 cm^{-1}) were recorded on model FTIR-101A SHIMADZU using KBr pallets at Pharmacy Department, RTMNU, NAGPUR. ^{1}H NMR spectra were

recorded on model Bruker Avance II 400 MHz by usin DMSO-d6 as a solvent from SAIF, Punjab University Chandigarh. Reflectance spectra of the coordination polymers were recorded in the range of 1200-200nm (as MgO discs), from SAIF Kochi. The thermal studies of all the coordination polymers have been done at SAIF, Kochi, using TGA– SDTA-851, METTLER, TOLENDO. The thermocouple used was Pt-Pt-Rh, with a temperature range of 45–1,200 ^{0}C and the heating rate was 10^0C min^{-1}. The thermal Analysis was carried out in a nitrogen atmosphere. The activation energy (Ea) and the other thermodynamic parameters such as free energy change (F), entropy change (ΔS), apparent entropy change (S*) and frequency factor (Z) have also been evaluated on the basis of the data of Freeman-Carroll method. The magnetic moments were obtained by the Gouy's method at Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University Nagpur, India.

RESULTS AND DISCUSSION

Mass Spectra

In the mass spectrum of ligand, the molecular ion peak (M+) appeared at m/z 271.70 and base peak at 105.48 which was in confirmity with the molecular formula of ligand ($C_{20}H_{16}N_6O_2$).
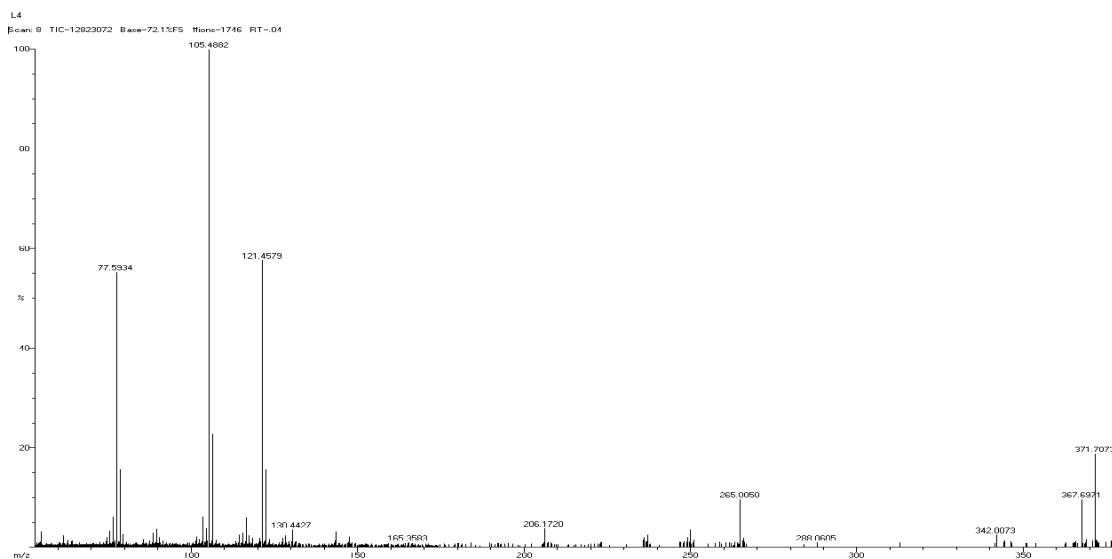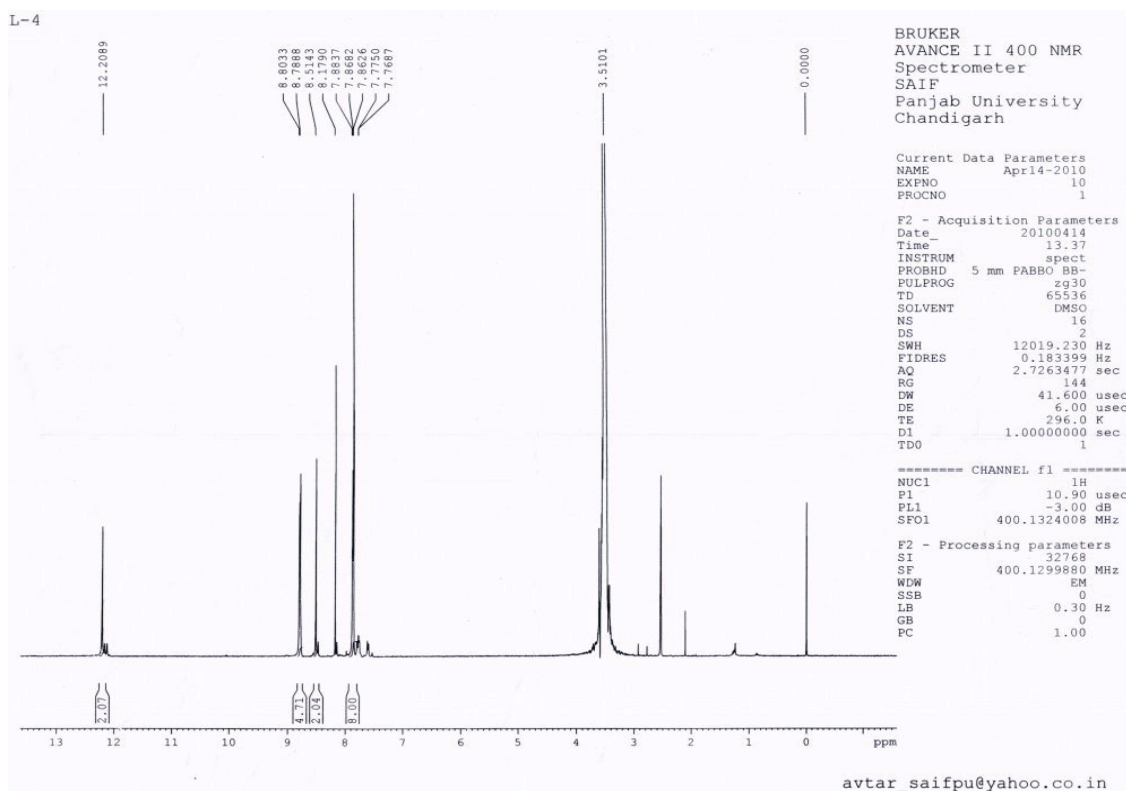

Fig 2: Mass spectrum of TDINH

NMR spectra

The ligand TDINH exhibits signals at 7.87, 8.51, 8.79 and 12.20 δ (ppm). A peak at δ 7.87 (ppm) may be assigned to ArH (pyridine ring) protons. The presence of sharp signal at δ 8.51 (ppm) may be attributed to the presence of proton of =CH-. A strong sharp signal at δ 8.79 (ppm) is attributed to the proton of aromatic ring and a peak at δ12.20 (ppm) is corresponding to -NH- protons.

Fig 3: 1H NMR spectrum of TDINH

IR spectra

IR spectrum of ligand depicts the band around 3250 cm^{-1} due to –NH- group of secondary amide [30]. However, after ligation with metal ions in coordination polymers, this frequency is disappearing indicating that the proton on the nitrogen atom is lost upon chelation with metal ions. The ligand also shows the IR absorption bands around 1655 cm^{-1} due to >C=O group and 1601 cm^{-1} due to –C=N-group, however the >C=O group bands is lower down 5 to 10 cm-1 in the 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 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 [31, 32]. The reflectance spectrum of Co (II) coordination polymer shows bands at ~17,690 and ~21,690cm^{-1}, which may be assigned to $^4T_{1g}$ (F) $\rightarrow$$^4A_{2g}$ (F) and $^4T_{1g}$ (F) $\rightarrow$$^4T_{1g}$ (P) respectively, of an octahedral geometry. The reflectance spectrum of the Ni (II) coordination polymer exhibits bands at~15,590, and~ 22620 cm^{-1} assignable to $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ transitions respectively, in an octahedral geometry. The reflectance spectrum of the cu (II) coordination polymer displays a broad band at ~15,200cm^{-1} due to the $^2E_g \rightarrow {}^2T_{2g}$ transition and the

observed magnetic moment is 1.83 B.M., which may be due to octahedral geometry [33]. The Zn (II) coordination polymer is diamagnetic as expected for d^{10} system.

Thermal studies

Following expression of Freeman-Caroll [34] method has been used to determine various kinetic parameters:

$$\Delta log(dW/dt)/\Delta \log Wr = (-Ea/2.303R) \Delta(1/T)/\Delta logW + n$$

Where dW/dt is the rate of change of weight with time,

$$Wr = Wc -W,$$

Where Wc is the weight loss at completion of reaction or at a definite time t, T is temperature, R is gas constant, n is the order of reaction. A typical curve of [Δ log (dW/dt)/Δ log Wr] versus [Δ (1/T)/Δ log Wr] for the Co (II) coordination polymer shown in Fig.2. The slope of the plot gave the value of Ea/2.303R and the order of reaction (n) was determined from the intercept.

Table 3: Kinetic parameters of the coordination polymers

Compounds	Ea(kJ mole-1)	Entropy change ΔS(J)	Free energy change ΔF(kJ)	Frequency factor Z (sec-1)	Apparent entropy S* (J)	Order of reaction found(n)
[Co(TDINH)(H$_2$O)$_2$]n·2H$_2$O	24.71	-156.54	77.62	2796.40	-47.62	1.19
[Ni(TDINH)(H$_2$O)$_2$]n·2H$_2$O	22.43	-155.50	74.99	2255.27	-45.51	1.21
[Cu(TDINH)(H$_2$O)$_2$]n·H$_2$O	24.24	-154.85	76.74	9680.54	-46.31	1.16
[Zn(TDINH)]n	30.46	-152.88	82.60	14763.86	-48.31	1.12

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 Co (II), Ni (II) and Cu (II) where as tetrahedral geometry for Zn (II) polymer.
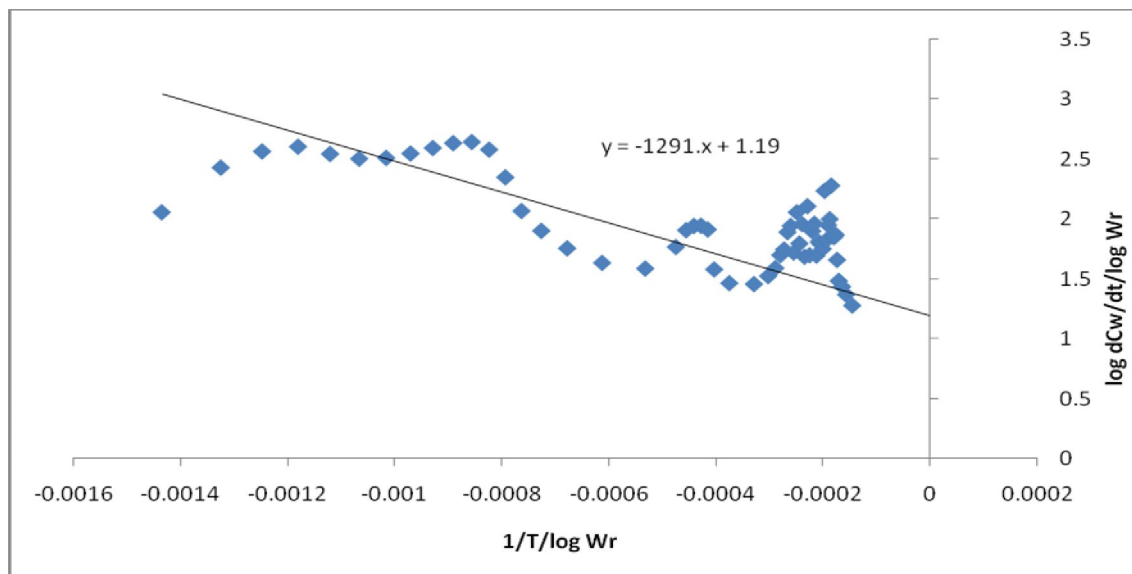
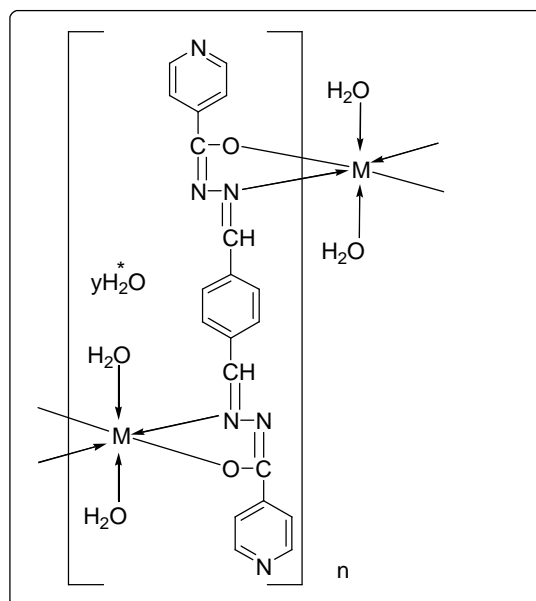Fig 4: Thermal activation energy plot of Co (II) coordination polymer

Fig 5: The proposed structure of the coordination polymers of Terephthalaldehyde Di-isonicotinoylhydrazone, M= metal ion, Co (II), Ni (II), Cu (II) and Zn (II). H2O □ lattice water. H_2O is absent in Zn (II) polymers. y = 2 for Co (II) Ni (II) and Cu (II) TDIH Coordination polymers and y = 0 for Zn (II) TDINH Coordination polymers.

ACKNOWLEDGEMENTS

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