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Synthesis and Characterization of Azodye Complexes of 4[(E)-(4 Chlorophenyl) Diazenyl]-3-Methyl-1-Phenyl-1H Pyrazol-5-ol

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ABSTRACT

Transition metal complexes of Cu(II), Co(II), Ni(II), Mn(II) and Zn(II) with azodyes of novel heterocyclic pyrazole derived from 3-methyl-1-phenylpyrazole and diazonium salt of chloroaniline have been synthesized and characterized based on elemental analysis, mass, IR,H^1 NMR, magnetic and thermogravimetric studies.

Keywords: 3-methyl-1-phenylpyrazole; Transition metal complexes; Chromophore

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INTRODUCTION

Azodye chromophores have been a special interest to many investigators due to their large molecular hyperpolarzability and delocalization of π-electronic cloud [1]. Azodyes are important class of organic colorant consisting at least one (–N=N-) conjugated chromophore, for many years and the azo compounds are most widely used class of dyes to their versatile application in various field such as dyeing of textile fiber, coloring of different materials, plastics and histological stains.[2] Azodyes are extensively studied because of rapid development in photoconductive materials, low cost, non-toxicity and architectural flexibility [3].observed photocurrents from thin layers of 1-(phenyl azo) naphthols [4] later used bisazo pigment in xerographic devices [5]. Azo pigments were widely studied as charge generation materials because of their technological advantages such as high sensitivity, wide spectral range (450-800 nm) and excellent stability [6]. Heterocycles are extensively used in disperse dye chemistry for textile, non-textile applications, photodynamic therapy and lasers [7]. Heterocyclic rings lead to brighter and deeper shades (8), hence azodyes of pyrazole derivatives are used [9]. Construction of metal organic coordination has become an area of intense research in recent years [10].

Derivatives of azo-chromophores with pyrazole or imidazole have four nitrogen atoms coupled in a conjugated system of π-bonds. Heterocyclic nitrogen plays an important role in coordination chemistry [11]; they are very useful as fungicides and bactericides [12]. Heterocyclic compounds are synthesized containing nitrogen and other hetroaromatic ring system [13]. Pyrazole has two coordinating sites such as –N=N-and –OH capable of coordination [14].

MATERIALS AND METHODS

The elemental analysis was carried out at sophisticated test instrumentation center (STIC) Cochin. Infrared spectra of azodyes and complexes were recorded in the region of 4000-400 cm^{-1} on a FT-IR Nicolet Impact 4100 n KBr pellets. The ^1H NMR was recorded in $CDCl_3$ on Bruker AVIII 400 MHz with tetramethylsilane as internal standard. The Mass spectrums were recorded with a LC-MSD-XCT plus mass spectrometer. UV-Visible spectra were recorded in MeOH and Chloroform with UV-Visible spectrometer 119 in wave length range of 230-500 nm. Thermal analysis was carried out in SHIMADZU TA-60WS Thermal analyzer in air at a heating rate of 50 °C min^{-1}.

Synthesis of 3-Methyl-1-Phenyl Pyrazole

Ethyl acetoacetate (0.01 mol) was mixed with phenyl hydrazine (0.01 mol) in 250 ml round bottomed flask, refluxed for 2 hours on water bath; the compound which was not true hydrazone was first formed. This under goes cyclisation with loss of ethyl alcohol, upon further heating forms heavy reddish syrup, which was allowed to cool, adds ether and stirred vigorously. The insoluble part gets solidified, filtered and recrystallized with equal volume of ethyl alcohol and water (Figure 1).

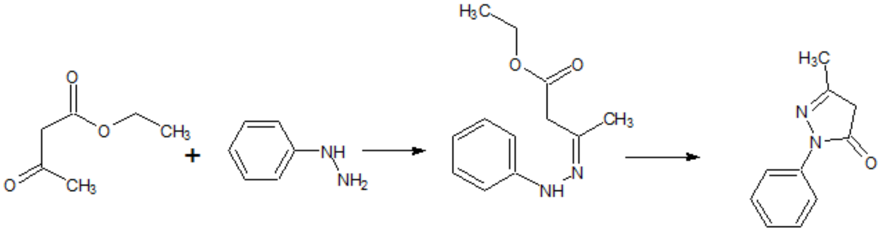


Figure 1: Synthesis of 3-methyl-1-phenyl pyrazole

Synthesis of Chloro-Benzene Diazonium Chloride

3-chloro aniline or 4-chloro-aniline (0.1 mole) was dissolved in hydrochloric acid (0.2 mole per 25 ml of distilled water). The hydrochloride derivative of chloro-aniline was diazotized below 50 ℃ with a was coupled with acidic solution of 3-methyl-1-phenyl pyrazole (0.1 mole Acetic acid), stirred for one hour at ice bath temperature, then sodium acetate was added (0.1 mole 20 ml) as a buffer to maintain PH between 4-5.5 and the mixture left overnight. The crude dyes were collected by filtration and recrystallized with ethyl alcohol and water.

Yield 96%. M.P; 123-1250 ℃. Anal Calcd for $C_{16}H_{13}N_4OCl$ (%) C, 61.44; H, 4.19; N, 17.9. Found C, 61.09; H, 4.40; N, 18.60. UV – Visible ($CHCl_3$), 239 (2.508), 402 (0.826) and in (MeOH) 252 (1.176), 396 (0.708), IR absorption bands (cm^{-1}) 838 w, 1155 s, 1549 s, 2922 m, 3442 b. LC-MSD 313 (Found, 312.75) ^1H NMR (400 MHz, $CDCl_3$) d (ppm) 2-3 (3H. S CH_3) 7.0-8.2 (9H. M 9CH).

Synthesis of Complexes

Synthesis of copper (II) complex derived from 4[(E)-(4 Chlorophenyl) diazenyl]-3-methyl-1-phenyl-1H pyrazol-5-ol 5 mmol of dye was dissolved in 20 ml of 1:1 mixture of methanol and chloroform in 250 ml round bottomed flask carrying reflux condenser. To this add 2 m mol of copper (II) acetate, and warmed on water bath maintained at 60-65°C for one hour, the mixture was kept overnight. The cake was ground and washed with ethyl alcohol, complex gets precipitated was filtered and dried. The formation of ligand and transition metal complexes are characterized by C.H.N, I.R, NMR, Mass spectra, UV-visible studies.

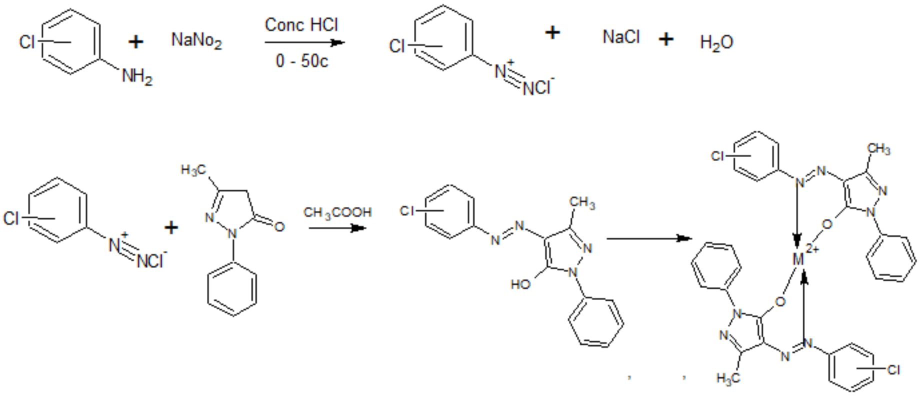


Figure 2: Synthesis of complexes

Thermal stability of dyes was examined by TGA-DTA studies and electrochemical nature of dyes was studied by cyclic voltmetry studies (Figure 2).

Yield 80%. Anal.Calcd. for $C_{32}H_{24}N_8Cl_20_2Cu$ (%) C, 55.94; H, 3.52; N, 16.31. Found C, 55.82; H, 3.64 N, 16.56. UV-Visible ($CHCl_3$), 244 (2.500), 395 (0.226) and (MeOH), 252 (1.802), 329 (0.823), 380 (0.901). IR absorption bands (cm^{-1}) 511 m, 667 w, 835 w, 1192 s, 1486 s, 1563 s, 2922 m, 3435 b. ^1H NMR (400 MHz, $CDCl_3$) d (ppm) 2-3(^6H, D $^2CH_3$), 5.8 (^1H, S ^1OH), 7-8.4 (16H, M 16CH).All the other metal (II) complexes were prepared by the above procedure using the respective azodyes and metal salts.

Synthesis of Cobalt (II) Complex Derived from 4[(E)-(4 Chlorophenyl) Diazenyl]-3-Methyl-1-Phenyl-1H Pyrazol-5-ol

Yield 83%. Anal.Calcd. for $C_{32}H_{24}N_8Cl_20_2Co$ (%) C, 55.94; H, 3.52; N, 16.33. Found C, 60.10; H, 3.33 N, 16.87. UV-Visible ($CHCl_3$), 242 (2.500), 235 (2.365) 402 (0.319) and (MeOH), 251 (1.799), 340 (1.038). IR absorption bands (cm^{-1}) 473w, 665w, 861m, 1157s, 1422s, 1562s, 2922m, 3435b. ^1H NMR (400 MHz, $CDCl_3$) d (ppm) 2-3 (^6H, D $^2CH_3$), 5.8 (^1H, S ^1OH), 7-8.4 (^{16}H, M ^{16}CH).

Synthesis of Manganese (II) Complex Derived from 4[(E)-(4 Chlorophenyl) Diazenyl]-3-Methyl-1-Phenyl-1H Pyrazol-5-ol

Yield 79%. Anal.Calcd. for $C_{32}H_{24}N_8Cl_20_2Mn$ (%) C, 56.62; H, 3.57; N, 16.52. Found C, 56.18; H, 3.32 N, 16.92. UV-Visible ($CHCl_3$), 239 (2.509), 402 (0.647) and (MeOH), 254 (1.043), 398 (0.859). IR absorption bands (cm^{-1}) 473 w, 682 m, 832 w, 1192 m, 1444s, 1561s, 2922m, 3421b. ^1H NMR (400 MHz, $CDCl_3$) d (ppm) 2-3 (^6H, D $^2CH_3$), 5.8 (^1H, S ^1OH), 7-8.4 (^{16}H, M ^{16}CH).

Synthesis of Zinc (II) Complex Derived from 4[(E)-(4 Chlorophenyl) Diazenyl]-3-Methyl-1-Phenyl-1H Pyrazol-5-ol

Yield 87%. Anal.Calcd. for $C_{32}H_{24}N_8Cl_20_2Zn$ (%) C, 55.79; H, 3.55; N, 16.29. Found C, 56.03; H, 3.48 N, 16.80. UV-Visible ($CHCl_3$), 240 (2.489), 235 (2.230), 400 (0.358) and (MeOH), 252 (2.218), 332 (1.280). IR absorption bands (cm^{-1}) 474 m, 687 m, 852 w, 1158 m, 1501 s, 1562 s, 2923 m, 3428 b. ^1H NMR (400 MHz, $CDCl_3$) d (ppm) 2-3 (6H, D $2CH_3$), 5.8 (1H, S 1OH), 7-8.4 (16H, M 16CH).

Synthesis of Nickel (II) Complex Derived from 4[(E)-(4 Chlorophenyl) Diazenyl]-3-Methyl-1-Phenyl-1H Pyrazol-5-ol

Yield 85%. Anal.Calcd. for $C_{32}H_{24}N_8Cl_20_2Ni$ (%) C, 56.34; H, 3.55; N, 16.40. Found C, 56.62; H, 3.43 N, 16.68. UV-Visible ($CHCl_3$), 242 (2.500), 235 (2.369), 402 (0.385) and (MeOH), 254 (2.248), 330 (1.280). IR absorption bands (cm^{-1}) 501 w, 688 m, 877 w, 1161 m, 1547 s, 2921 m, 3438 b. ^1H NMR (400 MHz, $CDCl_3$) d (ppm) 2-3 (6H, D $2CH_3$), 5.8 (1H, S 1OH), 7-8.4 (16H, M 16CH).

RESULTS AND DISCUSSION

Electronic Spectra of Azodyes Complexes

The spectrum of copper (II) complexes show (235,244,251,340, and 402) a broad band indicating the merging of three electronic transitions such as $^2B_1g \rightarrow ^2B_2g$; $^2B_1g \rightarrow ^2A_1g$ and $^2B_1g \rightarrow ^2E$. A square planar geometry was proposed for these complexes [15]. The electronic spectra of Co (II) complexes show (235,242,251,340, and 402) ^4T_1g (F)$\rightarrow ^4T_2g$ (F), and ^4T_1g (F)$\rightarrow ^4T_1g$ (P) These absorption bands are characteristic of high spin octahedral Co (II) complexes [16](Figure 3).

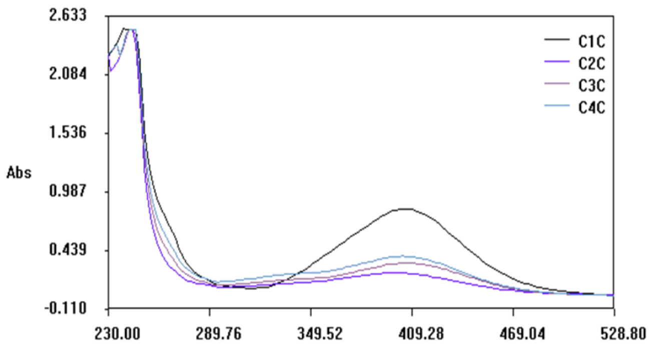


Figure 3: Electronic Spectra of Azodyes complexes

The electronic spectra of Mn (II) complexes exhibit very low intense bands (239,254, 398 and 402) are assigned to $^6A_1g \rightarrow {}^4T_1g(G)$, $^6A_1g \rightarrow {}^4A_1g(G)$, and $^6A_1g \rightarrow {}^4A_1g$ transitions, these may be attributed to number of forbidden transitions involving ^6A_1g ground state and several higher energy quartet states, which are consistent with octahedral geometry around Mn(II) ion[17]. The Zn (II) complexes with an electronic configuration of d^{10} did not show any d-d transitions. But the absorption bands 235,240,252,332 and 400) were due to charge transfer transitions which suffered from red and blue shift with hyper chromic effect [18]. The Ni (II) complexes exhibited (235,242,254,330 and 402) among them 254 nm and 388 nm which are attributed to the electronic transitions ^3A_2g (F) $\rightarrow {}^3T_2g$ (P) and ^3A_2g (F) $\rightarrow {}^3T_2g$ (F) respectively [19] (Figure 4).

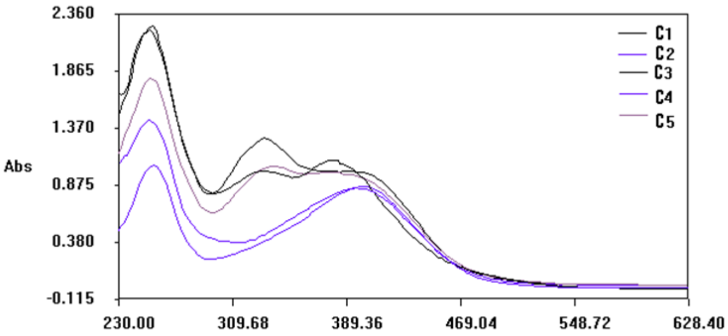


Figure 4: The electron transitions of electronic spectra of Mn (II) complexes

FT-IR Spectrum of Ligands and Complexes

The infrared spectral data reveal and broad bands in the range of 3250-3500 cm^{-1} attributed to the existence of coordinated and crystallized water molecules [20]. The absorption band at 3100-3050 cm^{-1} are assigned to aromatic stretching 2950-2900 cm^{-1} are due to methyl group, the band 1500-1560 cm^{-1} was assigned to C=N, the absorption band at 1438-1497 cm^{-1} are attributed to –N=N-bond involved in chelation [21] (Figure 5) The band at 650-880 cm^{-1} was assigned to coordinated water to metal ion [22]. The new bands arise at 690-630 cm^{-1} and 501-470 cm^{-1} is due to the presence of M-O and M-N bonds [23]. The band at 757-750 cm^{-1} was assigned to C-Cl bending vibrational modes.

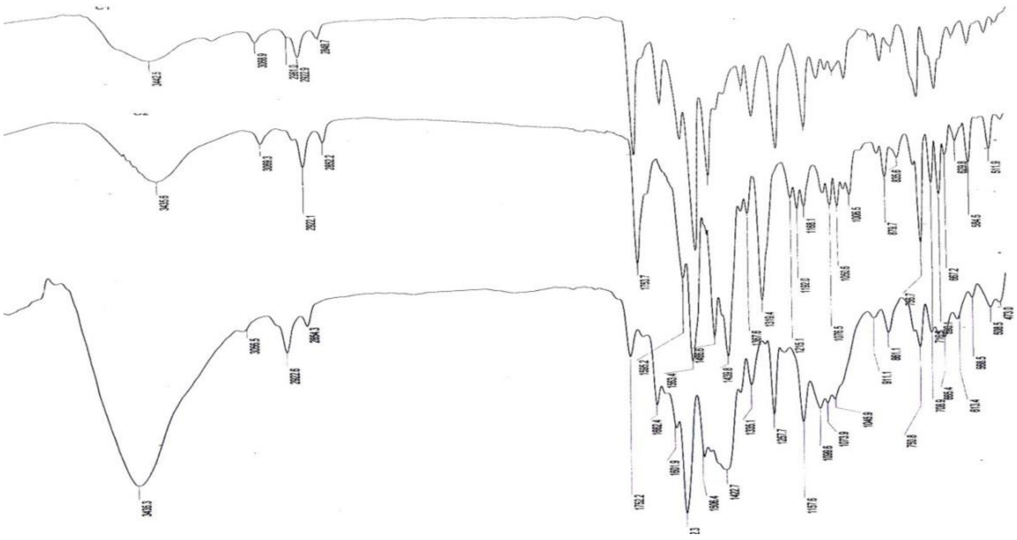


Figure 5: FT-IR Spectrum of ligands and complexes

^{1}H NMR Spectrum

The ^{1}H NMR is recorded on Bruker VIII (400 MHz, $CDCl_3$) at SAIF, Cochin, Kerala. The ^{1}H NMR spectra show multiples between 7-8.4 ppm assigned to aromatic ligand protons. The peak at 1.2-1.4 ppm was due to methyl protons and the peak 14.8 corresponds to –OH proton. Similarly, the peak at 7-8.5 ppm assigned to aromatic protons of complexes, the peak at 1.8 ppm was due to methyl protons and the peak at 14.8 ppm attributed to co-coordinated water molecule (Figures 6, 7).

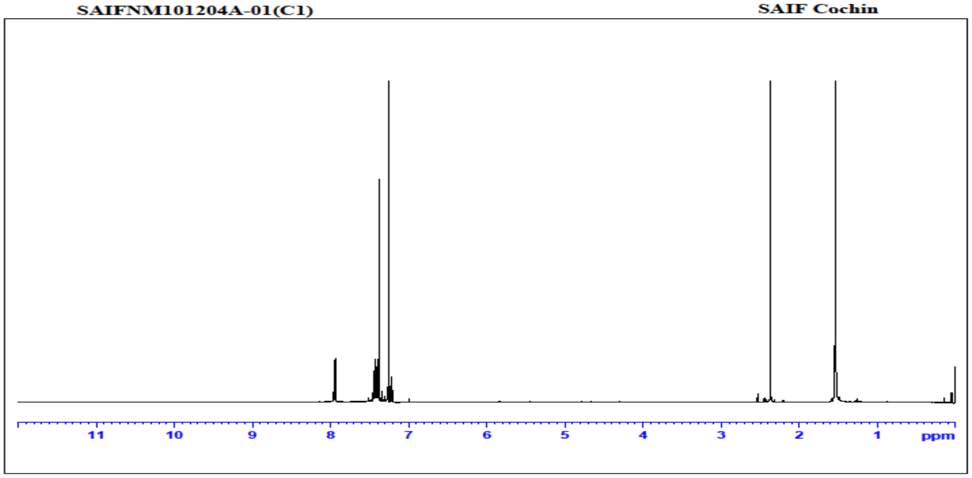
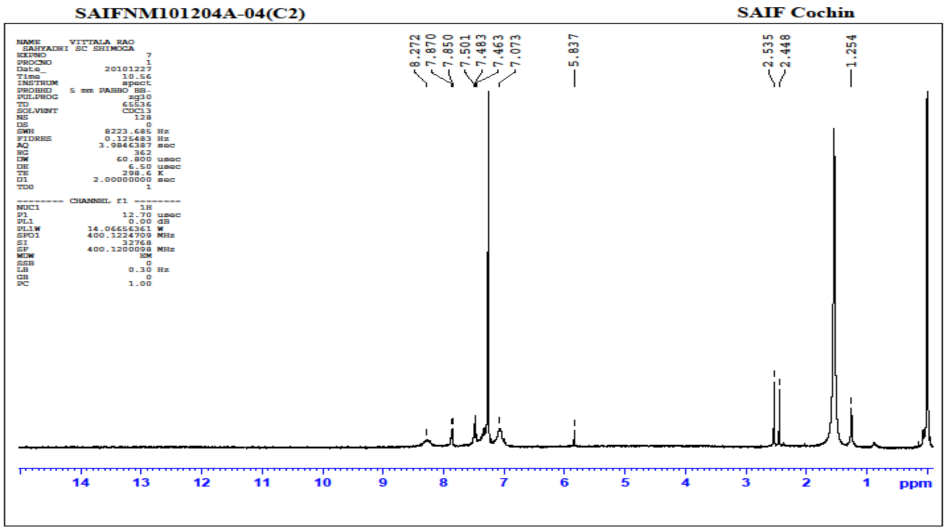


Figure 6: ^{1}H NMR is recorded on Bruker VIII



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 SAHYADRI SC SHIMOGA
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PROCNO                 1
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Time               10.56
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PULPROG             zg30
TD                 65536
SOLVENT            CDC13
NS                   128
DS                     0
SWH             8223.685 Hz
FIDRES          0.125483 Hz
AQ             3.9846387 sec
RG                   362
DW                60.800 usec
DE                  6.50 usec
TE                 298.6 K
D1            2.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 12.70 usec
PL1                 0.00 dB
PL1W         14.06656361 W
SFO1         400.1224709 MHz
SI                 32768
SF           400.1200098 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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Figure 7: ^{1}**H NMR is recorded on Bruker VIII in Cochin**

Powder XRD Studies

X-ray powder diffraction patterns in the 50<20<900 of the compounds were carried in order to obtain an idea about the lattice dynamics of the compound. By comparison of the obtained X-ray powder diffraction patterns shown in figure, the X-ray powder diffraction pattern throws light only on the fact that each solid represents a definite structure which was not contaminated with the starting materials. The identification of the complexes was done by known method. Such fact suggests that the prepared compounds are amorphous [24].

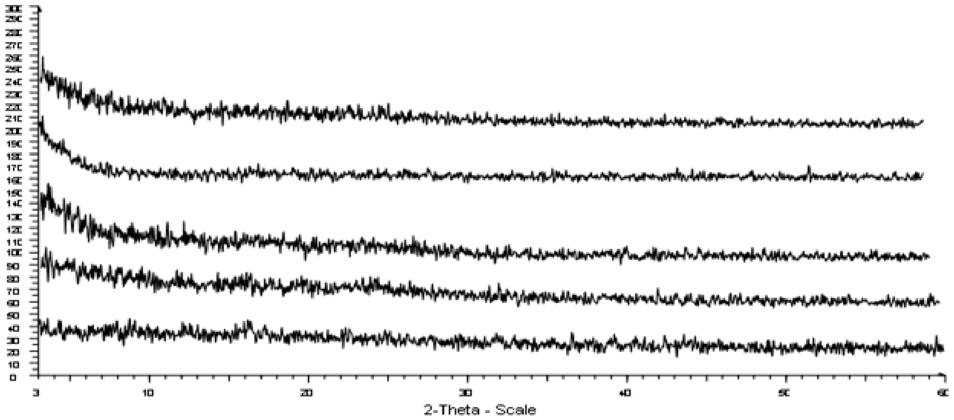

Figure 8: Powder XRD studies

Mass Spectra of Ligands and Complexes

The purity of the ligands A and B was checked from mass spectra (Figure 8). The spectra clearly showed base peaks (m/e) 313 as molecular weight, the calculated molecular weight was 312.75. The MALDI was carried out to few samples, which indicate the formations of metal complexes are in the ratio of 1:2.

Magnetic Susceptibility Studies of Complexes

Magnetic Susceptibility measurements of all the complexes were carried out at room temperature by Gouy method, Hg [Co (NCS) 4] used as calibrant. Molar susceptibilities were corrected for diamagnetism of component atoms using Pascal's constant. The magnetic moment of Cu (II) complexes are in the range of 2.19-2.31 B. M. at room temperature indicating square planar geometry [25]. The Magnetic moment of Co (II) complexes have 4.0-423 B.M. The higher value attributed to orbital magnetic moment with high spin configuration showing the octahedral geometry [26]. The magnetic moment of Mn (II) complexes was found to be 5.6-5.92 B.M. Mn (II) complexes are in good agreement with high spin configuration of d^5 electrons. This suggests that the complexes can be assigned with an octahedral geometry. The Zn (II) and Ni (II) complexes were bearing d^{10} and d^8 electrons, their magnetic moment are found to be diamagnetic.

Thermal Properties and Kinetic Parameters

The thermo analytical data from TG and DTA curves for all the compounds are given in Table 1. The typical TG curves of the compounds are illustrated in Figure. The data from thermo gravimetric analysis clearly indicated that the decomposition of the complexes proceeds in two steps. Water molecules were lost in between 90-2500 ℃. The metal oxides are formed above 4500 ℃ for Cu (II), Co (II), Mn (II), Zn (II) and Ni (II) complexes. For these complexes, the removal of water can proceed in two steps. All complexes lost hydration water between 90-2500 ℃, and then the coordinated water molecule was lost above 2000 °C. The decomposition was complete at 380-4500 ℃ for all complexes. Kinetic and thermodynamic parameters of the all the compounds have been evaluated by Broido's method [27]). Plots of In (In 1/Y) versus 1/T (where Y is the fraction of the compound undecomposed) were developed for the decomposition segment where loss of functional group occurs. From the plots of energy of activation (Ea) and frequency factor (InA) were evaluated. Enthalpy (ΔH), Entropy (ΔS) and free energy (ΔG) has been compared using standard equation. On the basis of the above observation and magnetic and solid reflectance measurements confirm the octahedral and square planar geometries are suggested for the investigated complexes [28].

Table 1: Kinetic parameters of complexes

Metal complex	**Decomposition temperature**	**Ea (activation energy)**	**-lna (frequency factor)**	**△ H**	**△ S(kJ)**	**△ G(KJ/mol)**
Cu	118	0.003781	-8.96609	-4489560	-35151.8	14492.39
	416					
	449	0.003146	-8.85295	-6360210	-35161	20537.96
	534					
Co	104	0.00105	-10.4351	-3757928	-35150.8	12130.82
	254					
	291	0.014448	-6.6891	-5354216	-35154.3	17285.14
	452					
Mn	105	0.00198	-4158.54	-4148686	-35151.3	13391.82
	348					
	348	0.012086	-6.91975	-5844742	-35156	188869.91
	513					
Zn	118	0.00376	-7.8148	-419005	-35150	14680
	413					
	452	0.003126	-11.6026	-562006	-35151	16280
	530					

CONCLUSION

The transition metal (II) complexes possess optical and high thermal stability hence used in memory storage devices. The ligand and complexes show potent biological activity. We conclude the formation of complexes is in the ratio of 1:2 from elemental and spectral analysis.

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