



Synthesis and Spectral Properties Studies of Novel Heterocyclic Mono Azo dye Derived from Thiazole and Pyridine with Some Transition Complexes

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ABSTRACT

A novel heterocyclic mono azo dye ligand 5-[2-(5-nitro thiazolyl)azo]-2-amino-4-methyl pyridine (NTAPy) was prepared by coupling reaction between 5-nitro thiazole diazonium chloride with 2-amino-4-methyl pyridine in alkaline alcoholic solution. A new series of some transition metal complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions were prepared forming seven chelate complexes. The prepared heterocyclic mono azo dye ligand and its metal complexes were checked by different spectral technique such as ¹H-NMR, ¹³C-NMR, FT-IR, electronic spectra, mass spectrum, C.H.N analysis, magnetic susceptibility, atomic absorption and molar conductivity. The analytical data show that the metal to ligand ratio [M:L] in all complexes are [1:2] and the mono azo ligand behavior as a bidentate chelating agent. The coordination number of all metal ions is found to be six in coordination through the nitrogen atom of azo group (N³) farthest of thiazole ring and nitrogen atom (N³) of thiazole molecule forming five member metallo-ring. All metal complexes of non-electrolytic and no conductive species exist excepted the Cr(III) and Fe(III) complexes are 1:1 electrolyte.

Keywords :- ligand 5-[2-(5-nitro thiazolyl)azo]-2-amino-4-methyl pyridine (NTAPy).

INTRODUCTION

Azo dyes of thiazole and pyridine compounds are very important class of chemical constituents having enormous applications in multiple fields such as polymer, paper, paint and coating industries as a dyeing pigments¹⁻⁴. Thiazolyl azo and pyridyl azo compounds are important in intermediates for the preparation of some applications such as biological activity^{5,6}, clinical fields^{7,8}, analytical reagents^{9,10} and

some drugs including discouraging the growth of germs^{11,12}. Most heterocyclic azo dyes such as pyridyl azo and thiazolylazo compounds of technical interest for application to textiles are derived from mono and diazo components consisting of five-membered metallo ring consisting of one sulphur or nitrogen hetero atom and to which a diazotisable amino group is directly attached, the ring may also possess one or two nitrogen hetero atoms such as pyridyl azo, imidazolylazo and benzimidazolyl azo¹³⁻¹⁵, or

one nitrogen and one sulphur hetero atoms such as thiazolylazo and benzothiazolylazo and be fused to another aromatic ring^{16,17}. The thiazolylazo and pyridyl azo reagents have an important role in spectral determination field to determine metal ions because of high sensitivity and selectivity^{18,19}. Thus azo dyes compounds from this intermediate have achieved significant commercial success for the dyeing of cellulose acetate fibers in which gas fastness is a higher priority than light fastness. In the present study, the synthesis of mono azo dye ligand (NTAPy) which contains two heterocyclic ring thiazole and pyridine and its metal complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ions are reported. Moreover spectral and analytical identification studies have been investigated for comparative purposes.

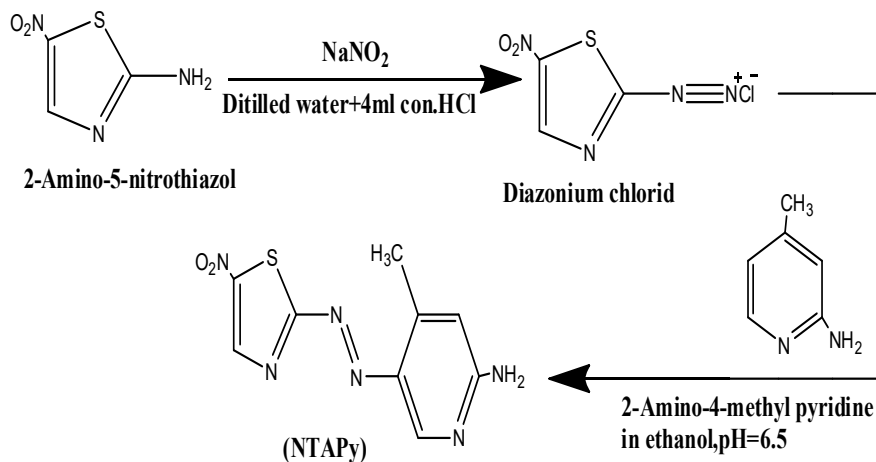
MATERIALS AND METHODS

2-Amino-4-methyl pyridine, 2-amino-5-nitro thiazole and other chemicals were equipped from Aldrich, BDH and sigma chemical companies and used without further purification. All chemicals and solvents used in the preparation and characterization were of analytical grade. ¹H-NMR and ¹³C-NMR spectra were obtained with a model Bruker AM(400MHz)spectrometer for using DMSO-d₆ solution in an appropriate deuterated solvent. The chemical shift are reported in ppm using tetra methyl silane(TMS)as the internal reference. Mass spectrum of azo ligand (NTAPy) were recorded on a Shimadzu Agilent Technologies 5975°C at 70ev and MSD

energy using a direct insertion probe (Acqmethod low energy) at 90-110°C temperature. Elemental analysis (C.H.N.S) was carried out using a C.H.N EA-99 mth instrument. The metal contents of metal complexes were measured by using atomic absorption technique by Shimadzu AA-6300. IR spectra were recorded as KBr discs in range (4000-400)cm⁻¹ on a Shimadzu 8400FT-IR spectrophotometer. The electronic spectra were measured in 1cm quartz cells on a spectrophotometer a UV-Visible T80-PG by using 10⁻³ M solution absolute ethanol at room temperature in the rang (200-1100) nm. Magnetic susceptibility measurements of the metal complexes in powder form were carried out on Balance Magnetic (MSB-MKi) apparatus by using farady method at room temperature Diamagnetic correction for the metal complexes was calculated using pascals constant. Molar conductivity measurements were recorded at room temperature in DMF solution (10⁻³M) by using a 31 A digital conductivity meter. Melting points of azo dye ligand and its metal complexes are uncorrected and were determined using open capillary tube method which uses Electrothermal melting point 9300 apparatus. The purity of the azo dya ligand was assessed by thin layer chromatography (TLC) using whatman 250 m silicelgel plates as the stationary phase and methanol as developing solvent.

Synthesis of Novel Heterocyclic Mono azo dye Ligand (NTAPy)

The novel heterocyclic mono azo dye ligand (NTAPy), (Scheme 1) was synthesized by dissolved 2-amino-5-nitro thiazole(1.45gm,0.01mol) in 50



Scheme 1 :- Synthesis of mono azo dye ligand 5-[2-(5-Nitro thiazolyl)azo]-2-amino-4-methyl pyridine(NTAPy)

ml distilled water and 4 ml hydrochloric acid. The solution was diazotized with (0.75 g, 0.01 mol in 25 ml distilled water) sodium nitrate (NaNO_2) was cooled and added drop – wise to solution of 2-amino-5-nitrothiazole. The resulting reaction mixture was stirred for 20 minutes, formed a clear yellow solution. In the resulting diazonium chloride solution, drop-wise, with cooled condition and stirring continuously at (0-5) °C, was added to solution of 2-amino-4-methylpyridine (1.08 g, 0.01 mol) dissolved in 100 ml ethanol. The color of the reaction mass was changed from yellow to brown red color. The reaction mixture was stirred for another 2 h at (0-5) °C in ice-bath. After completion of reaction, the reaction mixture was added to the ice cold water (200 ml) with stirring. The crude product was separated by filtration, washed with distilled water and dried. The solids obtained recrystallized with ethanol to get brown crystals colored. The purity of the azo dye ligand (NTAPy)

was determined by thin layer chromatography (TLC). The yield of the reaction was 76% and m.p., = 122 °C. The molecular structure of the azo dye ligand and was characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, mass spectrum, UV-Vis, FT-IR and C.H.N.S elemental analysis.

Synthesis of Metal Complexes

The metal complexes of mono azo dye ligand (NTAPy) were synthesized by adding 0.528 g (0.002 mol) of ligand dissolved in 50 ml hot ethanol in the form of drop-wise with stirring stoichiometric amount of 1:2, [M:L] mole ratio (0.001 mol) for Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) Chloride salts which dissolved in 30 ml hot buffer solution (ammonium acetate) at pH, 6-7.5 for each metal ions. The reaction mixture was heated and stirred for another 40 minutes at (60-70) °C until the precipitated product, than left over night,

Table 1: physical and analytical data of novel azo dye of ligand (NTAPy) and its metal complexes

Compound	pH	color	m.p °C	Yield %	Molecular formula	Found (caclcd) %				Metal
						C	H	N	S	
Ligand= NTAPy	6	Brown	122	76	$\text{C}_9\text{H}_8\text{N}_6\text{O}_2\text{S}$ -264.26	-40.9 40.68	-3.05 2.97	-31.8 31.35	-12.13 12.34	-
$[\text{Cr}(\text{L})_2\text{Cl}_2]$ Cl. H_2O	7.5	Purple	183	74	$\text{C}_{18}\text{H}_{18}\text{N}_{12}$ $\text{O}_5\text{S}_2\text{Cl}_3\text{Cr}$ (722.89)	(29.90) 30.09	(2.50) 2.39	(23.25) 23.60	(8.87) 9.11	(7.19) 7.48
$[\text{Mn}(\text{L})_2\text{Cl}_2]$ H_2O	7	Dark purple	168	63	$\text{C}_{18}\text{H}_{18}\text{N}_{12}\text{O}_5$ $\text{S}_2\text{Cl}_2\text{Mn}$ -672.5	-32.16 31.75	-2.69 2.75	-24.99 25.42	-9.536 9.84	-8.17 8.39
$[\text{Fe}(\text{L})_2\text{Cl}_2]$ Cl. H_2O	6.5	Reddish orange	194	58	$\text{C}_{18}\text{H}_{18}\text{N}_{12}\text{O}_5$ $\text{S}_2\text{Cl}_3\text{Fe}$ -708.86	-30.51 30.74	-2.55 2.46	-23.71 23.95	-9.04 8.83	-7.87 8.21
$[\text{Co}(\text{L})_2\text{Cl}_2]$ H_2O	7.5	Dark green	203	72	$\text{C}_{18}\text{H}_{18}\text{N}_{12}\text{O}_5$ $\text{S}_2\text{Cl}_2\text{Co}$ -676.45	-31.19 31.51	-2.68 2.56	-24.84 25.01	-9.48 9.75	-8.71 8.85
$[\text{Ni}(\text{L})_2\text{Cl}_2]$ H_2O	7	Purple	206	77	$\text{C}_{18}\text{H}_{18}\text{N}_{12}\text{O}_5$ $\text{S}_2\text{Cl}_2\text{Ni}$ -676.31	-31.98 32.44	-2.68 2.75	-24.84 24.99	-9.49 9.67	-8.67 8.78
$[\text{Cu}(\text{L})_2\text{Cl}_2]$ H_2O	6.5	Green	172	81	$\text{C}_{18}\text{H}_{18}\text{N}_{12}\text{O}_5$ $\text{S}_2\text{Cl}_2\text{Cu}$ -681.1	-31.75 31.93	-2.66 2.74	-24.46 24.79	-9.41 9.7	-9.32 9.75
$[\text{Zn}(\text{L})_2\text{Cl}_2]$ H_2O	7	pink	188	69	$\text{C}_{18}\text{H}_{18}\text{N}_{12}\text{O}_5$ $\text{S}_2\text{Cl}_2\text{Zn}$ -682.97	-31.67 31.91	-2.65 2.71	-24.61 24.77	-9.38 9.65	-9.58 9.79

NTAPy=L

The crude precipitate was filtered off and washed several time with distilled water, then washed by 10 ml absolute ethanol to remove any trace of unreacted organic material to get crystals product purple, orange, green and red solids, dried and preserved in desiccators over anhydrous CaCl_2 . The yields, melting points, color and analytical data are collected in Table 1

RESULTS AND DISCUSSION

Mass Spectrum of the Novel Azo dye Ligand (NTAPy)

The mass spectrum fragmentation of novel azo dye ligand (NTAPy) shown in scheme-2 and Figure 1. The base peak of azo dye ligand at $m/z^+ = 264.0$ is attributed to the original molecular weight of ligand $[\text{C}_9\text{H}_8\text{N}_6\text{O}_2\text{S}]^+$, 264.29. The peak at $m/z^+ = 234.0$ is due to loss of methyl and amine groups $[\text{C}_8\text{H}_4\text{N}_5\text{O}_2\text{S}]^+$ ion, while a peak at $m/z^+ = 188.0$ is attributed to the loss of nitro

group(NO_2) to give groups $[\text{C}_8\text{H}_4\text{N}_4\text{S}]^+$. The loss of azo group give a peak at $m/z^+ = 160.0$ $[\text{C}_8\text{H}_4\text{N}_2\text{S}]^+$. The peak at $m/z^+ = 84.0$ is analogous to the loss of $[\text{C}_5\text{H}_4\text{N}]^+$ (pyridine ring) and gives thiazole molecule $[\text{C}_3\text{H}_2\text{NS}]^+$,^{20,21}.

¹H-NMR Spectrum of Novel Azo dye Ligand (NTAPy)

The ¹H-NMR spectrum of novel azo dye ligand (NTAPy), Figure 2, was measured using in CDCl_3 solvent with TMS as an internal reference. The ¹H-NMR spectrum data of the azo dye ligand showed $\delta = 1.3$ ppm (S,3H, CH_3), $\delta = 6.8$ ppm (S,2H, NH_2) and $\delta = 7.1$ -8.1 ppm (m,3H,Ar-H)^{20,22,23}.

¹³C-NMR Spectrum of Novel Azo dye Ligand (NTAPy)

The ¹³C-NMR spectrum of novel azo ligand (NTAPy), Figure 3, was measured by using DMSO as solvent. The ¹³C-NMR spectrum of azo dye ligand show $\delta = 149.3$ ppm (C_2), $\delta = 124$ ppm (C_5),

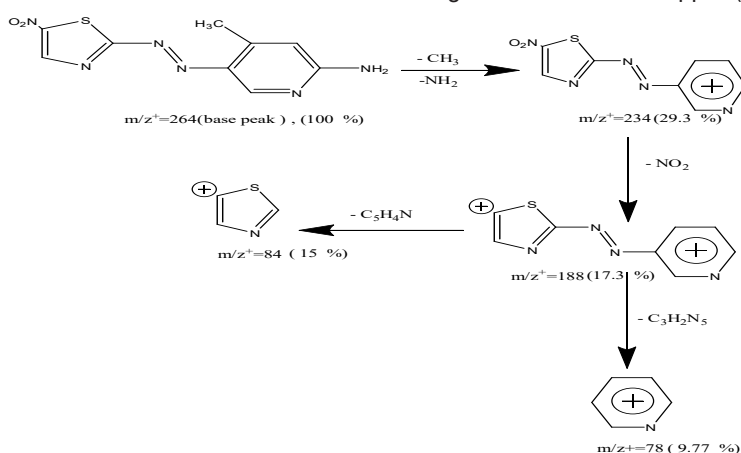
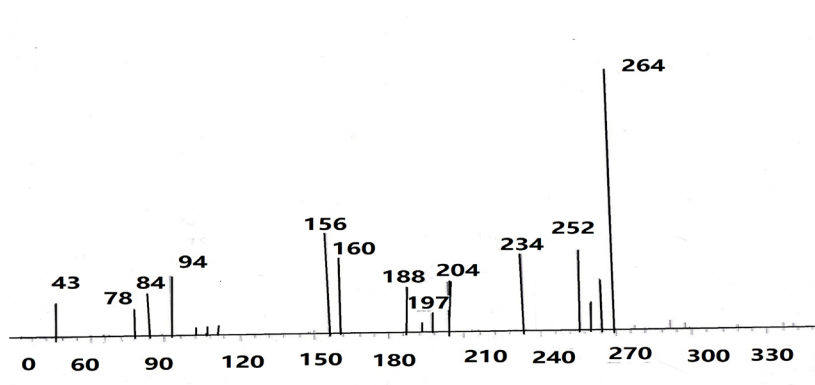


Fig. 1: Mass spectrum of novel azo dye ligand (NTAPy)



Scheme 2: Mass spectrum fragmentation of novel azo dye ligand (NTAPy)

$\delta=145$ ppm (C_4), $\delta=24.4$ ppm (C_7), $\delta=128$ ppm (C_4), $\delta=125$ ppm (C_5), $\delta=131$ ppm (C_6), $\delta=144$ ppm (C_2) and $\delta=114$ ppm (C_3)^{24,25}.

Infrared Spectral Studies

The IR spectral data of the prepared azo dye ligand (NTAPy) and their Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes (KBr disc) are presented in Table 2. The IR spectrum of the free azo dye ligand exhibited a band at 3402 cm^{-1} which is assigned to $\nu(-NH_2)$ group in the ligand (NTAPy).

This band does not change in position in all metal complexes because of non coordination with metal ion²⁶. The IR spectrum of azo dye ligand shows characteristic bands at 3263 cm^{-1} and 3101 cm^{-1} was attributed to $\nu(-CH_3)$ and $\nu(-CH)$ pyridine ring respectively²⁷. This band did not show any frequency shift in IR spectra of all metal complexes^{20,27,28}. The spectra of all metal complexes show a broad band around at (3440-3496) cm^{-1} indicated the presence of water molecule $\nu(H_2O)$ in these complexes^{14,15}. The strong band observed at 1628 cm^{-1} in the free

Table 2: Selected IR data (KBr disc, ν cm^{-1}) for novel azo dye ligand (NTAPy) and their metal complexes

Compound	$\nu(NH_2)$	$\nu(CH_3)$	$\nu(C=N)$	$\nu(NO_2)$	$\nu(N=N)$	$\nu(C=C)$	$\nu(C-S)$	$\nu(M-N)$
Ligand=(NTAPy)	3402 S.	3263 m.	1628 s.	1512 m.br 1365(s)	1473 m.	1335 w.	1257 m.	-
[Cr(L) ₂ Cl ₂].Cl.H ₂ O	3438* s.br.	3271 w.	1620 m.	1518 w. 1342	1458 w.	1157 w.	1248 w.	509 w.
[Mn(L) ₂ Cl ₂].H ₂ O	3425* w.	3217 w.	1620 m.sh	1512 m.sh 1345	1434 w.	1303 w.	1227 s.	486
[Fe(L) ₂ Cl ₂].Cl.H ₂ O	3406* w.	3214 w.	1620 w.	1519 m.sh 1335	1434 m.	1203 m.	1275 s.	508 w.
[Co(L) ₂ Cl ₂].H ₂ O	3440* s.br.	3224 w.	1620 m.sh	1516 m 1334 w.	1448 m.	1203 m.	1268 m.	493
[Ni(L) ₂ Cl ₂].H ₂ O	3428* m.br.	3215 w.	1604 m.	1527 w. 1357 w.	1443 m.	1296 w.	1228 w.	502 w.
[Cu(L) ₂ Cl ₂].H ₂ O	3340* m.(NH ₂) 3441 m.br.(H ₂ O)	3225 w.	1618 m.	1512 w. 1368 m.	1434 w.	1287 w.br.	1218 m.br.	485 w.
[Zn(L) ₂ Cl ₂].H ₂ O	3741 w.br (H ₂ O) 3332 m.br (NH ₂)	3226 w.	1605 m.sh	1520 m.br. 1358 m.br.	1442 w.	1296 w.	1203 m.sh	509 w.

*This band attributed to $\nu(NH_2)$ and $\nu(H_2O)$ molecule because of interference between this bands in this reagan ; w=weak , m=medium , s=strong , sh=sholder , b=broad .

azo dye ligand was attributed to ν (-C=N) stretching of the thiazole ring³⁰. This band shifted to a lower wave number side (1605- 1620) cm^{-1} in all metal complexes suggesting the participation of the ν (-C=N-) of thiazole ring in bonding with metal ions^{15,31}. A strong to medium intensity band at 1512 cm^{-1} in free ligand and 1512-1519 cm^{-1} in all metal complexes which is assigned to ν (-NO₂) group¹⁶. A medium intensity band at 1473 cm^{-1} in the free ligand was attributed to ν (-N=N) stretch of the azo group^{32,33}. The band shifts to lower wave number side (1458-1434 cm^{-1} in all metal complexes indicating the coordination with metal ions³⁴. Another

bands appeared at 1257 cm^{-1} in free ligand spectrum, attributed to ν (-C-S) of the thiazole ring^{15,20,27,35}. The existence of this band in all metal complexes means that the sulphur atom of thiazole ring does not participate in coordination³⁶. New absorption bands in the range of 512-493 cm^{-1} which are not present in the spectrum of the free ligand are due to ν (M-N) band of the metal complex³⁷. IR spectra data lead to suggest that the ligand behaves as a bidentate chelating agent coordinating through the nitrogen atom of thiazole ring and the nitrogen atom of azo group nearest to pyridine ring to give five membered metalo ring. Some representative spectra are given in Figures 4,5 and 6.

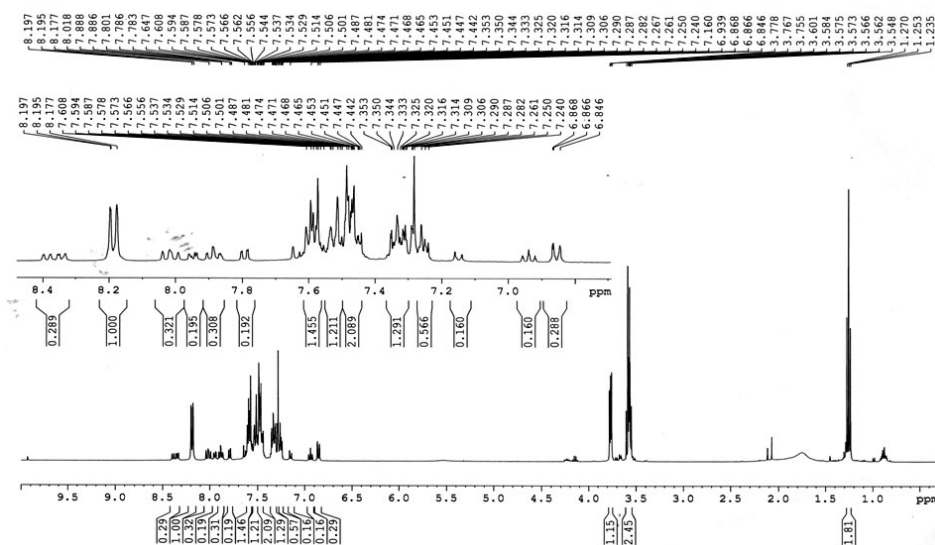


Fig. 2: ¹H-NMR spectrum of novel azo dye ligand (NTAPY)

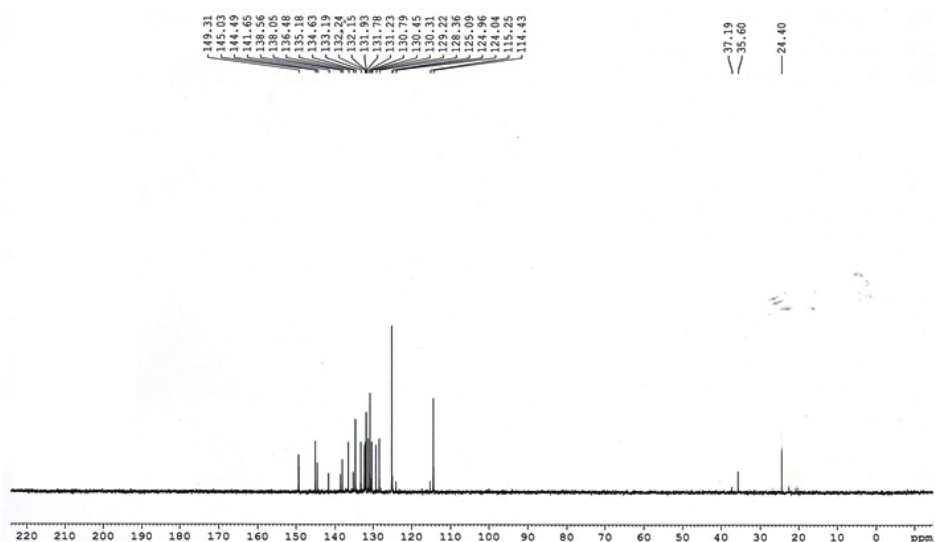


Fig. 3: ¹³C-NMR spectrum of novel azo dye ligand (NTAPY)

Electronic Spectral Studies

The electronic absorption spectra of the novel azo dye ligand (NTAPy) and its prepared metal complexes with some metal ions such as of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions were recorded in freshly absolute ethanol (10^{-3} M) at room temperature. The spectral data are summarized in Table (3) and show the spectra in Figures 7, 8, 9 and 10.

The electronic spectrum of the free ligand (NTAPy) exhibited two absorption bands at 384 nm

(26042 cm^{-1}) and 239 nm (41841 cm^{-1}) assignable to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively due to the azo group (-N=N-) and (C=C) groups of thiazole and pyridine rings^{20,38}. The absorption band of azo group showed a red shift because of coordination between ligand and metal ion^{15,39}. The electronic spectrum of the Cr(III) complex displayed three bands at 532 nm (18797 cm^{-1}), 412 nm (24272 cm^{-1}) and 349 nm (28653 cm^{-1}) which may be d-d transitions of Cr(III) ion, these bands are assignable to ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$, ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ transitions respectively²⁷. The electronic absorption

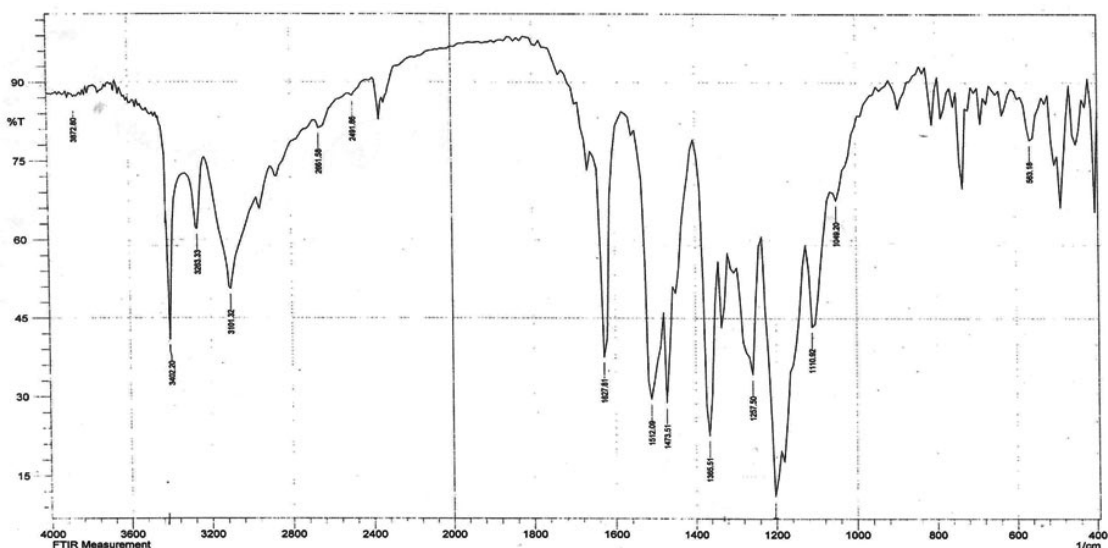


Fig. 4: IR spectrum of azo dye ligand (NTAPy)

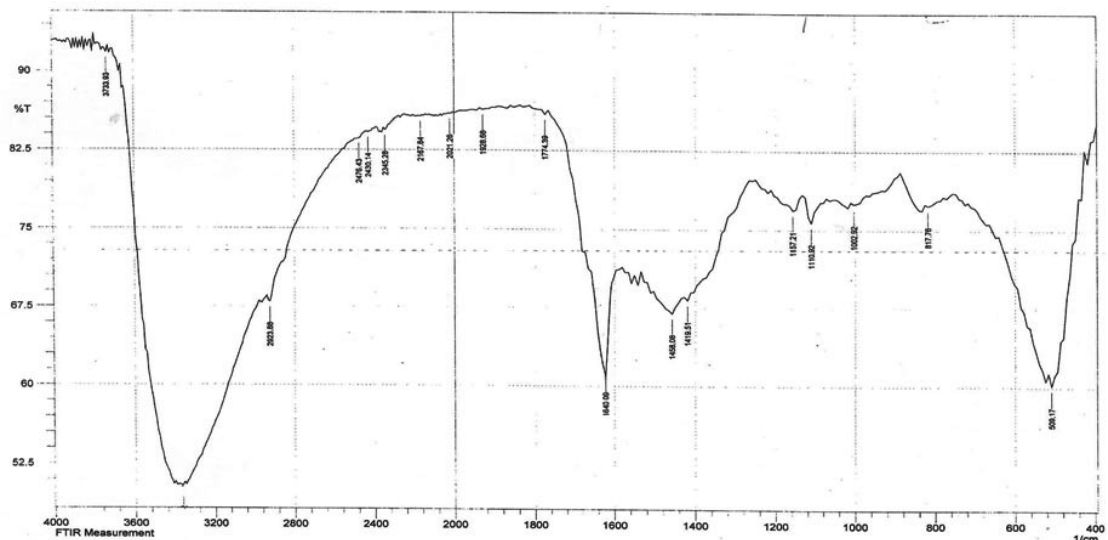


Fig. 5: IR spectrum of the $[Cr(L)_2Cl_2]Cl \cdot H_2O$ complex

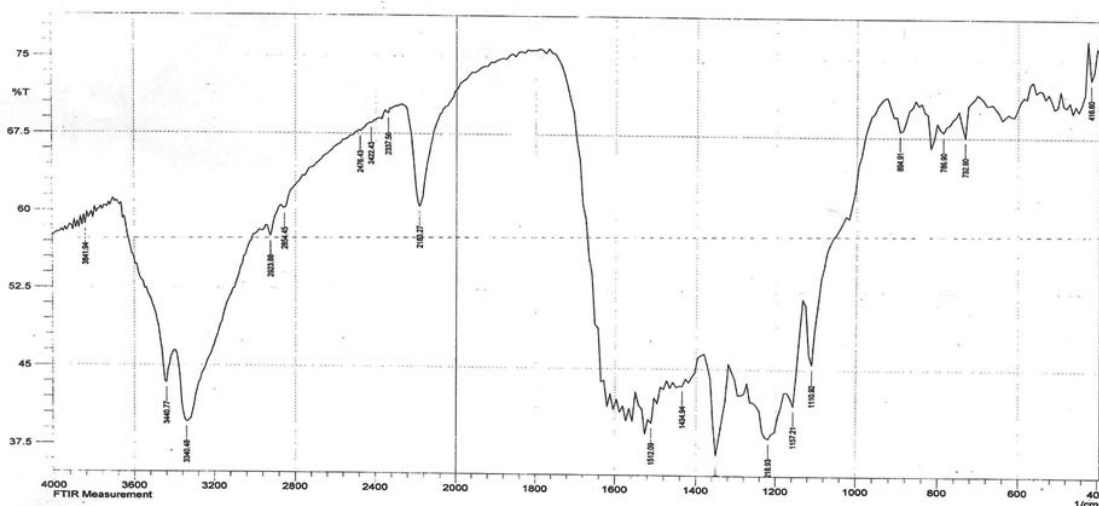


Fig. 6: IR spectrum of the $[\text{Cu}(\text{L})_2\text{Cl}_2]\cdot\text{H}_2\text{O}$ complex

Table 3: Electronic absorption spectra (nm, cm^{-1}), magnetic moments, geometry and hybridization

Compound	λ_{max} nm	Absorption bands(cm^{-1})	Transitions	M_{eff} (B.M)	Geometry	Hybridization
(NTAPy)(L)	384	26042	$n \rightarrow \pi^*$	-	-	-
$[\text{Cr}(\text{L})_2\text{Cl}_2]$ $\text{Cl}\cdot\text{H}_2\text{O}$	239	41841	$\pi \rightarrow \pi^*$	-	-	-
	532	18797	${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_2\text{g}(\text{F})(\nu_1)$	3.78	Octahedral	d^2sp^3
	412	24272	${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_1\text{g}(\text{F})(\nu_2)$		(Regular)	
	349	28653	${}^4\text{A}_2\text{g} \rightarrow {}^4\text{T}_1\text{g}(\text{P})(\nu_3)$			
$[\text{Mn}(\text{L})_2\text{Cl}_2]$ H_2O	907	11025	${}^6\text{A}_1\text{g} \rightarrow {}^4\text{T}_2\text{g}(\text{F})(\nu_1)$		Octahedral	Sp^3d^2
	537	18622	${}^6\text{A}_1\text{g} \rightarrow {}^4\text{Eg}, {}^4\text{A}_1\text{g}(\text{G})(\nu_2)$	5.63	(Regular)	(High spin)
$[\text{Fe}(\text{L})_2\text{Cl}_2]\text{Cl}$ H_2O	963	10384	${}^2\text{A}_2\text{g} \rightarrow {}^4\text{T}_1\text{g}(\text{G})(\nu_1)$		Octahedral	d^2sp^3
	468	21367	${}^2\text{A}_2\text{g} \rightarrow {}^4\text{Eg}, {}^4\text{A}_1\text{g}(\text{G})(\nu_2)$	1.84	distorted	(low spin)
	317	31546	${}^2\text{A}_2\text{g} \rightarrow {}^4\text{T}_1\text{g}(\text{P})(\nu_3)$		(Z-out)	
$[\text{Co}(\text{L})_2\text{Cl}_2]$ H_2O	637	15698	${}^4\text{T}_1\text{g} \rightarrow {}^4\text{T}_2\text{g}(\text{F})(\nu_1)$		Octahedral	Sp^3d^2
	500	20000	${}^4\text{T}_1\text{g} \rightarrow {}^4\text{A}_2\text{g}(\text{F})(\nu_2)$	4.23	(regular)	(High spin)
	402	24876	${}^4\text{T}_1\text{g} \rightarrow {}^4\text{T}_1\text{g}(\text{P})(\nu_3)$		z-out or z in	
$[\text{Ni}(\text{L})_2\text{Cl}_2]$ H_2O	968	10330	${}^2\text{A}_2\text{g} \rightarrow {}^2\text{T}_2\text{g}(\text{F})(\nu_1)$	3.04	Octahedral	Sp^3d^2
	535	18691	${}^2\text{A}_2\text{g} \rightarrow {}^2\text{T}_1\text{g}(\text{F})(\nu_2)$		(Regular)	(High spin)
	340	29412	${}^2\text{A}_2\text{g} \rightarrow {}^2\text{T}_1\text{g}(\text{P})(\nu_3)$			
$[\text{Cu}(\text{L})_2\text{Cl}_2]$ H_2O	618	16181	${}^2\text{B}_2\text{g} \rightarrow {}^2\text{A}_2\text{g}$	1.83	Octahedral distorted (Z in-z out)	Sp^3d^2
$[\text{Zn}(\text{L})_2\text{Cl}_2]$ H_2O	416	24088	$d\pi(\text{Zn})^{+2} \rightarrow \pi^*(\text{L})$	Dia	Octahedral (Regular)	Sp^3d^2

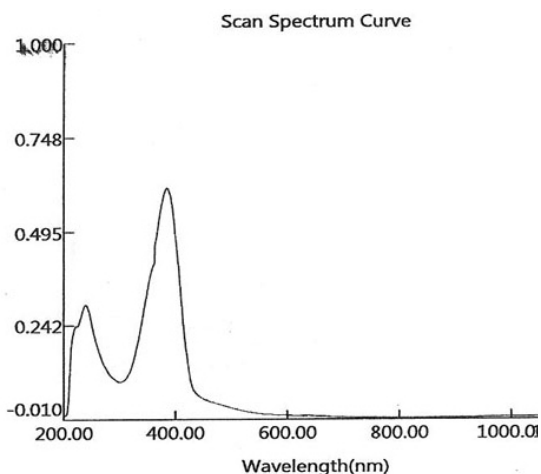


Fig. 7: UV-Visible spectrum of azo dye ligand (NTAPy)

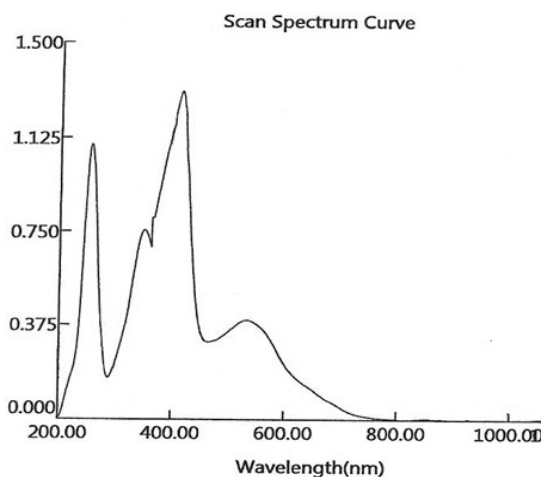


Fig 8: UV-Visible spectrum of Cr(III)-Complex

spectrum of Mn(II)-complex(d^5) exhibited one term apree ion (6s) in addition to several times dubline and quarter there for any transition between the crystal field cases will be prohibited multiplicity ,and as a result the spectra of ions(d^5) are very weak and the colors are faint⁴⁰. The Mn(II)- complex where showed two absorption bands at 907 nm (11025 cm^{-1}) and 537nm (18622 cm^{-1}) which may be attributed to $^6A_1g \rightarrow ^4T_2g$ and $^6A_1g \rightarrow ^4Eg, ^4A_1g(G)$ transitions respective⁴¹ . The absorption band at 238 nm(42017 cm^{-1}) is attributed to center ligand transition. The electronic spectrum of Fe(III)-complex showed three absorption band at 963 nm (10384 cm^{-1}), 468nm(21367 cm^{-1}) and 317 nm(31546 cm^{-1}) attributed to $^2A_2g \rightarrow ^4T_1g(G)$, $^2A_2g \rightarrow ^4Eg, ^4A_1g(G)$ and $^2A_2g \rightarrow ^4T_1g(p)$ transitions respectively²⁷. The Co(II)-complex exhibited three absorption band at 637 nm(15698 cm^{-1}), 500 nm (20000 cm^{-1}) and 402 nm (24876 cm^{-1}) assignable to $^4T_1g(F) \rightarrow ^4T_2g(F)$, $^4T_1g \rightarrow ^4A_2g$ and $^4T_1g(F) \rightarrow ^4T_1g(p)$ transition respectively^{40,43}, while the absorption bands at 296 nm (33784 cm^{-1}) and 251(39841 cm^{-1}) attributed to center ligand transitions. The electronic spectrum of the Ni(II)-complex exhibited three absorption bands at 968 nm(10330 cm^{-1}), 535 nm (18691 cm^{-1}) and 340 nm(29412 cm^{-1}) assignable to $^3A_2g(F) \rightarrow ^3T_2g(F)$ f, $^3A_2g(F) \rightarrow ^3T_1g(F)$ and $^3A_2g \rightarrow ^3T_1g(p)$ transition respectively while the absorption band at 252 nm(39682 cm^{-1}) attributed to center ligand transition^{32,43}. The green colored of Cu-complex exhibited a single broad asymmetric band around at 618 nm (1618 cm^{-1}), the broodiness of this band indicates the three transition $^2B_1g \rightarrow ^2A_2g(e_2)$, $^2B_1g \rightarrow ^2B_2g(e_2)$ and $^2B_1g \rightarrow ^3Eg(e_3)$, which are of similar energy and give rise to only one broad absorption

Table 4: stability constant values (β and $\log \beta$), molar conductivity optimal concentration , maximum wavelength (λ_{max}) and molar absorptivity (ϵ) of metal complexes

Ligand	Metal ion	Maximum Wavelength (λ_{max})nm	Optimal Molar Conc. $\times 10^{-4}$	Moler Absorptivity (ϵ) $\times 10^{-3}$ L.mol. cm^{-1}	Stability Constant $\beta, \text{L}^2.\text{mol}^{-2}$	Log β	Molar conductivity S.cm 2 .mol $^{-1}$
$\lambda_{max}=384\text{nm}$ $\epsilon=4.09 \times 10^3$ L.mol $^{-1}.\text{cm}^{-1}$ Conc.=1.50 $\times 10^{-4}\text{M}$	Cr(II)	532	1.75	2.25	3.77×10^9	9.58	73.85
	Mn(II)	537	1.5	0.39	4.18×10^9	9.62	16.08
	Fe(II)	468	2	8.64	2.49×10^9	9.4	79.37
	Co(II)	637	1.75	1.41	4.57×10^{10}	10.41	18.58
	Ni(II)	535	2	4.49	5.64×10^{10}	10.75	24.17
	Cu(II)	618	1.5	1.38	6.73×10^{10}	10.83	21.88
	Zn(II)	416	2.25	5.32	5.69×10^9	9.76	17.89

band due to ${}^2B_{2g} \rightarrow {}^2A_{2g}$ transition. The broadness of the band may be attributed to dynamic Jahn- Teller distortion^{20,23}. The electronic spectrum of the Zn(II)-complex did not show any d-d transition because it is saturated with electron (d^{10}). The absorption band at longer wavelength 416 nm (24038 cm^{-1}) is due to a charge transfer ($M \rightarrow L, CT$) transition. This transition where $d \pi(Zn^{+2}) \rightarrow \pi^*(L)$ is believed to be primarily dominated by the LUMO of the azoimine chromophory^{44,45}.

Magnetic Moments Studies

The magnetic moments obtained at room temperature for Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes are listed in table 3. The Cr(III)- Complex exhibited the magnetic moment value of 3.78 B.M, this value is too close to the theoretical of magnetic moment for the Cr(III) ion (${}^3t_{2g} e_g^0$), ($M_{\text{eff}}=3.87\text{ B.M}$) which indicates an octahedral geometry and d^2sp^3 hybridization²⁷. The magnetic moment value of Mn(II)-complex has

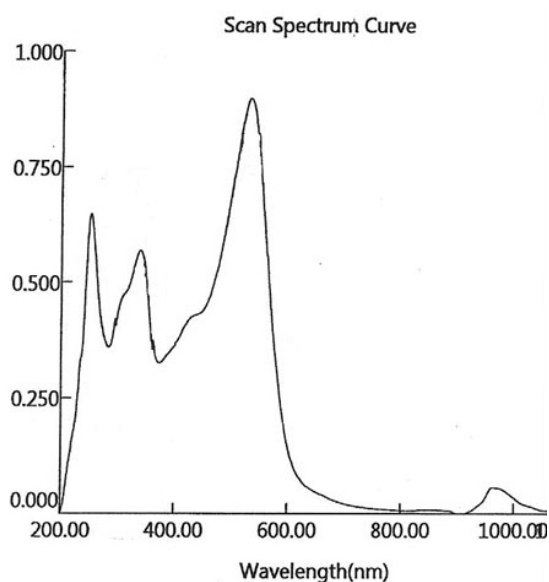


Fig. 9: UV-Visible spectrum of Ni(II)-Complex

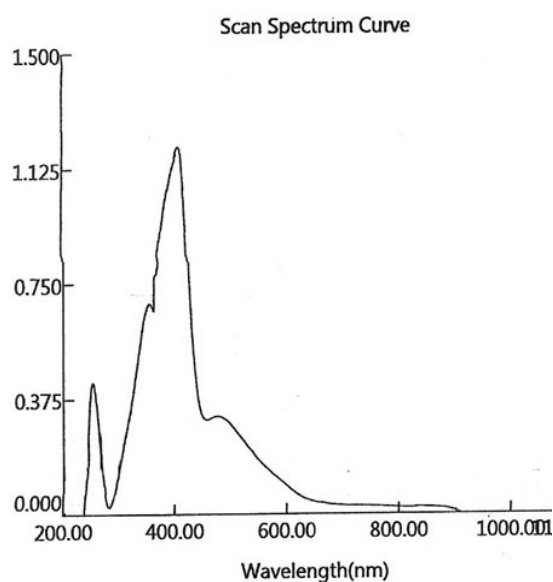
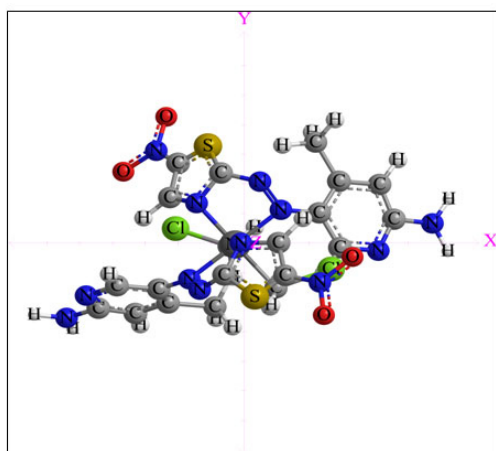
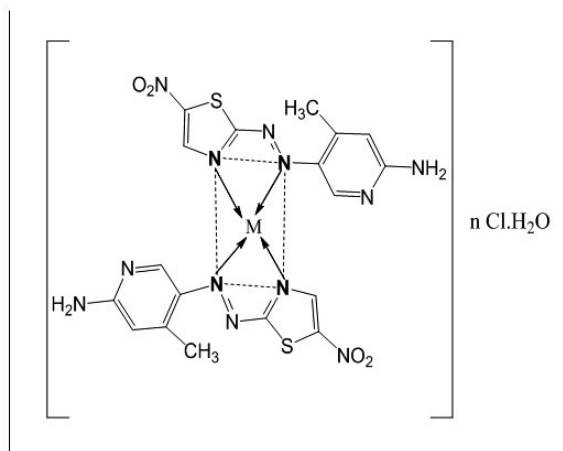


Fig. 10: UV-Visible spectrum of Zn(II)-Complex



Where $M = \text{Cr(III)}$ and Fe(II) ; $n=1$



$M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II) ; $n=0$

Fig. 11: The proposed structural formula of metal complexes

been found 5.63 B.M. The larger variation in the magnetic moment for a high spin has a d^5 , ($t_{2g}^3 e_g^2$) configuration depends on the magnitude of the orbital contribution. The high value of magnetic moment is because of five electrons unpaired which may suggest a regular octahedral geometry and sp^3d^2 hybridization^{27,46}. The Fe(III)-complex showed the magnetic moment value of 1.84 B.M due presence of one electron unpaired for low spin has a d^5 ($t_{2g}^5 e_g^0$) configuration which indicates a distorted octahedral geometry (Z-out) and d^2sp^3 hybridization⁴⁷. The Co(II)-complex exhibited three absorption bands at 637 nm (15698 cm^{-1}), 500 nm (20000 cm^{-1}) and 402 nm (24876 cm^{-1}) assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g} \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(p)$ transitions respectively^{40,42}, while the absorption bands at 296nm (33784 cm^{-1}) and 251 nm (39841 cm^{-1}) is attributed to center ligand transition. The Ni(II)-complex showed the magnetic moment value of 3.04 B.M with the range of 2.8-3.5B.M for high spin ($t_{2g}^6 e_g^2$) configuration suggesting a regular octahedral geometry and sp^3d^2 hybridization^{50,51}. The Cu(II)-complex has a $d(t_{2g}^6 e_g^3)$ configuration show magnetic moment of 1.83 B.M is slightly higher than the spin –only value of 1.73 B.M which offers possibility of an octahedral geometry because of the presence of one electron unpaired and sp^3d^2 hybridization⁵². The magnetic moment value of Zn(II)-complex is diamagnetic consistent d^{10} , ($t_{2g}^6 e_g^4$) configuration which indicates an octahedral geometry with sp^3d^2 hybridization⁵³.

Molar Conductivity Studies

The molar conductance (Λ_m) studies of the metal complexes were measured in DMF solvent in 10^{-3} M concentration at room temperature. The high values of molar conductivity of the Cr(III)- complex and Fe (III)-complex give $73.85\text{ S}\cdot\text{mol}^{-1}\cdot\text{cm}^2$ and $79.37\text{ S}\cdot\text{mol}^{-1}\cdot\text{cm}^2$ respectively which indicates that the complexes are 1:1 electrolyte with ionic nature because of the presence of the chloride ion (Cl⁻) which is located outside the coordination sphere^{20,27}, but showed the values of molar conductivity of the Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes ranged between (16.08-24.17) $\text{S}\cdot\text{mol}^{-1}\cdot\text{cm}^2$, this indicates that non –electrolyte and no conductive species exist because of the chloride ions (2Cl⁻) which are located in side the coordination sphere^{14,32,42,54}. The values of molar conductivity of this metal complexes are listed in Table 4.

Metal: Ligand Ratio

The metal : ligand ratio [M:L] of metal complexes were determined by molar ratio method at fixed concentration at wavelength maximum absorption (λ_{max}). The solution of prepared metal complexes increase the intensity of the colors as approach point of intersection ratio and color continues constant at passing the point which indicates that the metal complexes formed^{15,20,32,39}. The azo dye ligand (NTAPY) which was found to form 1:2 [M:L] mole ratio with all metal ions suggested the formation of metal complexes to give two five- membered chelate rings.

Calculation of Metal Complexes Stability Constant

The stability constant (β and $\log\beta$) of metal complexes are determined spectrophotometrically by measure the absorbance of mixture of solution of azo dye ligand (NTAPY) and metal ions at fixed wavelength (λ_{max}) and optimum concentration values. The degree of formation of metal complexes are calculated depending on the relationship $\beta = 1 - \alpha/4\alpha^3c^2$ and $\alpha = A_m - A_s/A_m$, (where..... respectively). The calculated β and $\log\beta$ values for prepared metal complexes are listed in Table 4. The listed stability constant follows the arrangement Cu(II) > Ni(II) > Co(II) > Zn(II) > Mn(II) > Cr(III) > Fe(III) the sequence of metal ions of the first row transition metals agree with Irving-Williams of stability constant^{55,56}.

The Proposed Structures of Metal Complexes

According to the results and discussion through different techniques, the proposed structures of the prepared metal complexes are suggested and shown in Figure 11. Depending on the analytical and spectral data, the novel azo dye ligand (NTAPY) behaves as a bidentate chelating agent coordination through the nitrogen atom (N³) of azo group nearest to pyridine ring and nitrogen atom (N³) of thiazole ring to give one-five membered chelate ring.

CONCLUSION

In this paper we report the synthesis and spectral properties studies of a bidentate azo dye ligand derived from thiazole and pyridine ring (NTAPY) and its metal complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and

Zn(II) ions. The azo dye ligand and its metal complexes were characterized by using several physical techniques such as elemental analysis, ¹H-NMR, ¹³C-NMR, Mass spectroscopy, IR, UV-Vis. and molar conductivity. The geometry proposed for all metal complexes were octahedral stereo

chemistry. All metal complexes are not effected by air, light and a moisture, suggesting high stability plus degrees of melting point that give another evidence of the stability of the prepared metal complexes .

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