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Spectral study and antimicrobial activity of Co (II), Cu (II), Mn (II), Ni (II) and Zn (II) Complexes of bisazo dye derived from Meta phenylene diamine

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ABSTRACT

In the present study, bisazo dye 2, 2¹ [benzene-1, 3-diyl di(E) diazene 2,1-diyl] bis (4-nitroaniline) has been synthesized by the diazotization and coupling of Meta phenylene diamine with 4-nitroaniline. Further azo metal (II) complexes of Co, Cu, Mn, Ni and Zn have been synthesized. The ligand and all the metal complexes were characterized by various physico-chemical techniques like elemental analysis, electronic, Infrared, Proton NMR and TGA. The metal chelates have metal to ligand ratio of 1:1. All the synthesized compounds were screened for antimicrobial activity.

Key words: bisazo dye, antimicrobial activity.

INTRODUCTION

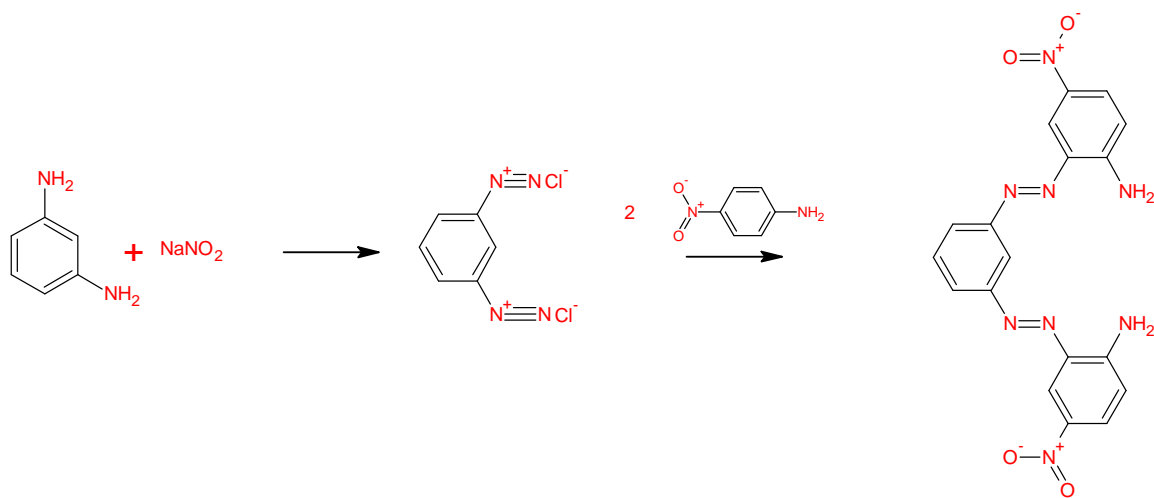
Azodyes are the versatile class of colored compounds having variety of shades. These are used in many optical signal recording processes like xerography, laser printing due to their excellent thermal and optical properties. Azo metal chelates have been studied due to their electronic and geometrical features for their non-linear optical application [1-3]. Photodynamic therapy (PDT) is a new type of treatment for tumors and certain other diseases. Indocyanine green, Procion blue, Sudan black have been suggested as possible photothermal sensitizers [4]. Recently the study of bisazo dyes has made much progress. Hence it was proposed to focus on ligation property of diazenyl derived from m-phenylenediamine coupled with 4-nitroaniline and its complexes with metal ion.

MATERIALS AND METHODS

All chemicals and solvents used were of analytical grade. All metal (II) salts were used as acetate. UV-VIS spectra were measured on a Perkin Elmer spectrophotometer in 200-800nm range in DMSO. IR spectra were recorded using SHIMADZU FT-IR spectrometer in the range of 400-4000 cm^{-1} range. ^1H NMR spectra were recorded in DMSO at room temperature. A mass spectrum of the ligand was recorded on Agilent 1200 series LC/MSD VL system. The molecular weights of metal complexes were determined by Rast camphor method. Melting points were determined by open capillary method using electric melting point apparatus and are uncorrected.

Synthesis of the ligand

Metaphenylenediamine (1.08g / 0.01mol) was dissolved in a mixture of 5 cm^3 of water and 10 cm^3 of concentrated hydrochloric acid. While 20ml concentrated hydrochloric acid was diluted with about 60g of crushed ice and cooled with a cooling mixture. To this a cold solution of sodium nitrite (2.5g/10 ml water) was added. Immediately metaphenylenediamine hydrochloride solution was added and stirred for about 1hr till a dark yellow colored solution was obtained. The coupling agent p-nitroaniline dissolved in DMF (0.02mol) was cooled and added to the tetrazo solution slowly with continuous stirring and maintaining the temperature 0-5 $^{\circ}\text{C}$. The resulting solution was stirred well and sodium acetate solution was added till neutralization. The dye was washed with cold water and collected by vacuum filtration.

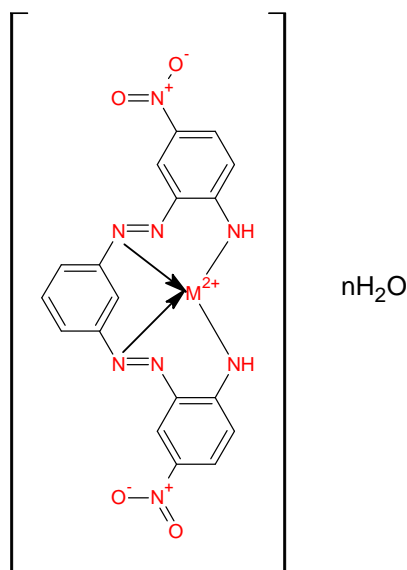


Scheme I

Ligand

Synthesis of metal (II) complexes

Solution of 4mmol of metal acetate in 10ml methanol was added to methanol-chloroform (1:1v/v) solution containing 8mmol of ligand and was refluxed for 2hrs. The obtained solution was left at room temperature. The precipitated complex was filtered, washed with methanol and then recrystallized from methanol-chloroform (1:3v/v) and dried in vacuum. The yields of all the complexes were almost quantitative and the probable structure of the complex is as predicted in Fig 1.



$M^{2+} = \text{Co, Cu, Mn, Ni, Zn}$

Figure1

Antimicrobial studies

The synthesized ligand and metal complexes were screened for their antimicrobial activity by well plate method in nutrient agar (antibacterial activity) and sabouraud dextrose agar (antifungal activity). The invitro antibacterial activity was carried against 24h old cultures of pathogenic bacteria like gram (+) *S-aureus* and gram (-) *Salmonella typhi*, *Klebisella pneumoniae* and *Bacillus subtilis* at 37° C. Antifungal activity was carried out against 72h old cultures of fungal strains like *Candida albicans*, *C.lipolytica*, *Cryptococcus neoformenas* and *Saccharomyces cerevisiae*. In order to ensure that solvent had no effect on bacteria or yeast growth, a control test was performed with only DMSO and found inactive in culture medium.

RESULT AND DISCUSSION

Characterization of the compound

All the synthesized compounds were intensely colored amorphous solids. The ligand decomposes between 110-280°C and metal complexes in the range of 240-360°C. The ligand was soluble in methanol, chloroform and DMSO and metal complexes were soluble in DMF and DMSO. The micro analytical data of all the compounds were summarized in Table1.

Thermal behavior of the azo ligand and its metal complexes were studied by thermo gravimetric techniques in the temperature range of 0-600°C and the data were also summarized in table1. The thermal stabilities of metal complexes were higher than the corresponding azo ligand. The final residue in all the metal complexes was corresponding to its metal oxide. The decomposition was complete at 480°C for all complexes [5] and the decomposition pattern was in Fig-2.

All the spectral data were consistent with the assigned structure of the compounds. In the IR spectra, the ligand azo dye showed a weak band in the region 1558cm^{-1} which gets shifted to higher frequency in the complexes ($1568\text{-}1596\text{cm}^{-1}$). Both the ligand and its metal complexes show a band for $-\text{NO}_2$ (symm) at $1333\text{-}1338\text{cm}^{-1}$ [6]. It was found from the IR spectra of complexes that there were strong and wide bands at $457\text{-}491\text{cm}^{-1}$ for M-N bonding and $788\text{-}791\text{cm}^{-1}$ for co-ordinated water [7-10]. The ^1H NMR spectral data of azo ligand and complexes showed signal between $\delta 6.58\text{-}8.297$ for aromatic protons and $\delta 1.90\text{-}1.92$ for N-H protons. The peak at $\delta 2.49\text{-}3.49$ would be due to DMSO protons. Spectra of complexes showed an additional signal at $\delta 13$ which was attributed to co-ordinated water molecules [11]. The spectral data were listed in Table 2. The spectra of azo ligand and complexes were shown in Figures 3-6.

The electronic spectra of synthesized azo dye and its metal complexes were measured in DMSO (10^{-4} to 10^{-6}M) at room temperature. All the compounds exhibited dye character since their molar extinction coefficients (ϵ) were over $40000\text{ mol}^{-1}\text{cm}^{-1}$. The synthesized compounds showed two bands between $264\text{-}291\text{nm}$ and $397\text{-}434\text{nm}$. The first band may be due to $\pi\text{-}\pi^*$ transition within the aromatic ring and the second band would be due to $n\text{-}\pi^*$ transition of $\text{N}=\text{N}$ group. The formation of metal (II) azo complexes was also confirmed by their UV-VIS spectra. It can be seen that λ_{max} of azo dye was at around 264 and 398nm . While the λ_{max} of complexes were red shifted which arise from the energy change of intense $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transition of the conjugated chromophore due to the chelation between metal ions and azo ligand [12-19]. The ability of metal ions to make red shift was in the order $\text{Ni (II)} > \text{Cu (II)} > \text{Zn (II)} > \text{Mn (II)} > \text{Co (II)}$. This can be explained on the basis of positive electricity ability of metal ion and so the difference of absorption maximum of metal (II) azo complexes ($0.563\text{-}1.751$) to its azo ligand ($0.333\text{-}1.341$) [20]. All the spectral data were summarized in Table 3 and the spectra in Fig-7.

The powder X-ray diffraction patterns of the azo metal complexes were taken in the range of angles $3\text{-}2\theta\text{-}60^\circ$ indicating simple scattering of the X-ray beam to give a continuous baseline and showed very poor crystallinity [21].

Table1: Micro analytical data of ligand and metal complexes

S.No.	Name of compound	Carbon Found (Calc.)	Hydrogen Found (Calc.)	Nitrogen Found (Calc.)	M.P. ($^\circ\text{C}$)	Mass (M^{+1})	Color	Yield %	Decomposition temperature($^\circ\text{C}$)
1.	Ligand (L)	53.06 (53.20)	3.28 (3.47)	26.96 (27.58)	94	406.3 (405.9)	Reddish brown	68	110-280
2.	L- Co^{2+}	(43.30) (44.25)	(3.23) (4.17)	(22.44) (20.67)	>280	499.3	Deep brown	72	240-380
3.	L- Cu^{2+}	(42.90) (43.83)	(3.20) (4.79)	(22.24) (20.95)	>300	503.9	Black brown	70	240-380
4.	L- Mn^{2+}	(43.65) (42.34)	(3.26) (4.37)	(22.62) (23.56)	>280	495.3	Reddish brown	75	240-360
5.	L- Ni^{2+}	(43.22) (42.17)	(3.23) (4.08)	(22.45) (21.67)	>290	499.0	Deep brown	78	240-390
6.	L- Zn^{2+}	(42.74) (41.93)	(3.19) (4.87)	(22.15) (24.26)	>300	505.7	Blackish brown	74	240-360

L-azo ligand,; $L\text{-M}^{2+} = \text{Co}^{2+}, \text{Cu}^{2+}, \text{Mn}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$.

Table 2: Characteristic IR and ¹H NMR spectral data of the ligand and its metal complexes

Comp	IR spectra cm ⁻¹						¹ H NMR spectra ppm	
	M-N	N=N	N-H	-NO ₂	Ar-H	Coordinated water	Ar-H	N-H
Ligand (L)	-	1558.38	3583.49	1338.51	2921.96	-	6.589-8.286	1.909
L-Co ²⁺	489.89	1568.02	3387.71	1346.22	3001.03	790.76	6.585-8.235	1.903
L-Cu ²⁺	491.81	1596.95	3338.55	1334.65	3126.40	788.83	6.597-8.297	1.920
L-Mn ²⁺	457.32	1587.94	3385.40	1333.95	3099.39	789.34	6.585-8.249	1.922
L-Ni ²⁺	459.03	1596.95	3383.98	1336.50	3072.39	788.62	6.586-8.285	1.904
L-Zn ²⁺	493.74	1596.95	3337.95	1334.65	2925.81	791.25	6.588-8.283	1.902

Table 3: UV-VIS Spectra in DMSO

compound	Ligand (L)	L-Co ²⁺	L-Cu ²⁺	L-Mn ²⁺	L-Ni ²⁺	L-Zn ²⁺
λ _{max} (nm)	264.47	270.01	291.37	274.07	284.62	272.18
	397.97	399.58	422.85	399.58	434.92	422.85
Absorbance	0.335	0.774	0.776	0.563	1.081	0.640
	1.341	1.402	1.604	1.492	1.751	1.654

Table 4: Antibacterial and antifungal activities (mm)

Sl no	Test Bacteria	Zone of inhibition in mm						
		L-Co ²⁺	L-Cu ²⁺	L-Mn ²⁺	L-Ni ²⁺	L-Zn ²⁺	(L)Ligand	control
1	<i>Samonella typhi</i>	12	12	12	13	13	13	-
2	<i>Staphylococcus aureus</i>	14	11	14	12	13	13	-
3	<i>Bacillus subtilis</i>	-	-	10*	11*	11	-	-
4	<i>Klebsella pneumonia</i>	13	12	14	13	12	11*	

* Less growth

	Test Yeasts	Zone of inhibition in mm						
		L-Co ²⁺	L-Cu ²⁺	L-Mn ²⁺	L-Ni ²⁺	L-Zn ²⁺	(L)Ligand	control
1	<i>C.albicans</i>	-	-	-	09	-	-	-
2	<i>C.lipolytica</i>	12	-	-	13	-	10	-
3	<i>Saccharomyces cerevisiae</i>	17	20		18		20	-
4	<i>C. neoformens</i>	-	-	-	-	-	-	-

All the compounds were evaluated for their antibacterial activity by using zone inhibition technique against four bacteria namely gram (+) *S.aureus* and gram (-) *Salmonella typhi*, *Klebisella pneumoniae* and *Bacillus subtilis* and were found to be active. The compounds were also evaluated for antimicrobial activity against four fungi namely *Candida albicans*, *C.lipolytica*, *Cryptococcus neoformenas* and *Saccharomyces cerevisiae* and were found to be active towards *C.lipolytica* and *Saccharomyces cerevisiae* [22]. The results obtained were presented in table 4.

¹H NMR spectra of azo ligand (fig 3) and complexes (fig 4-6)

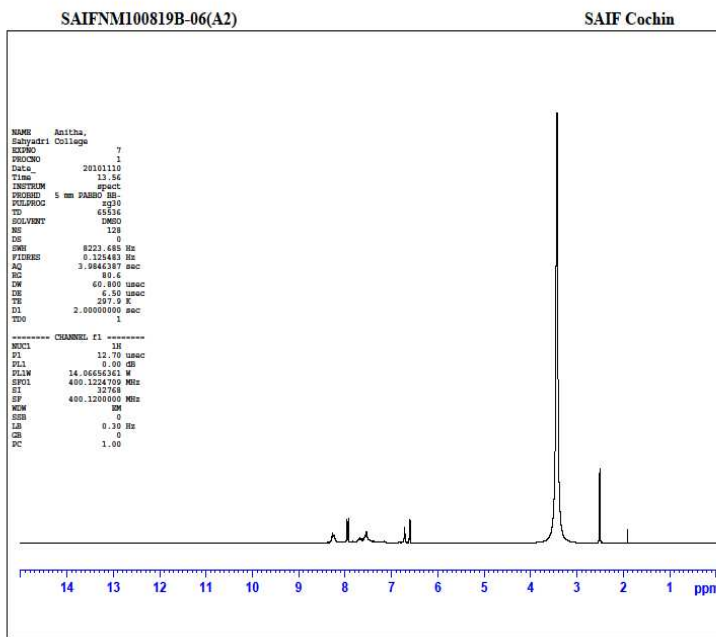


Fig 3

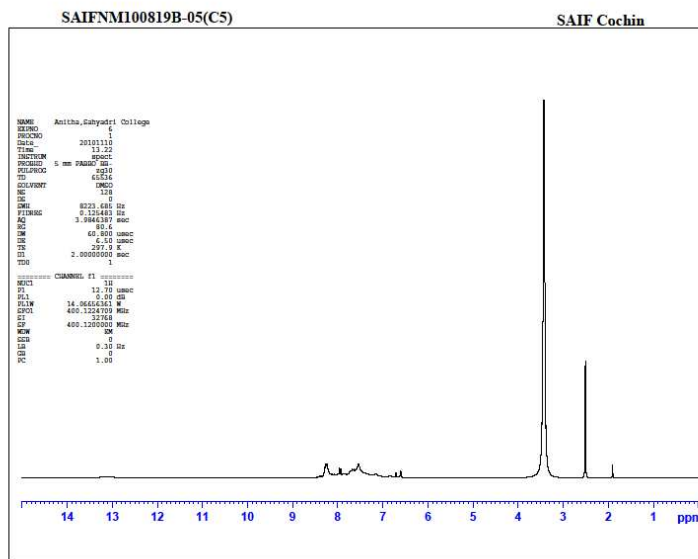


Fig 4

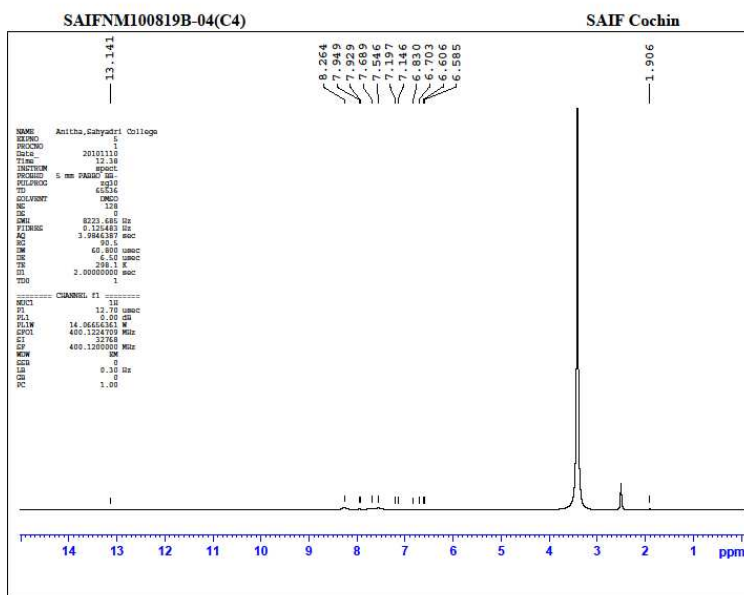


Fig 5

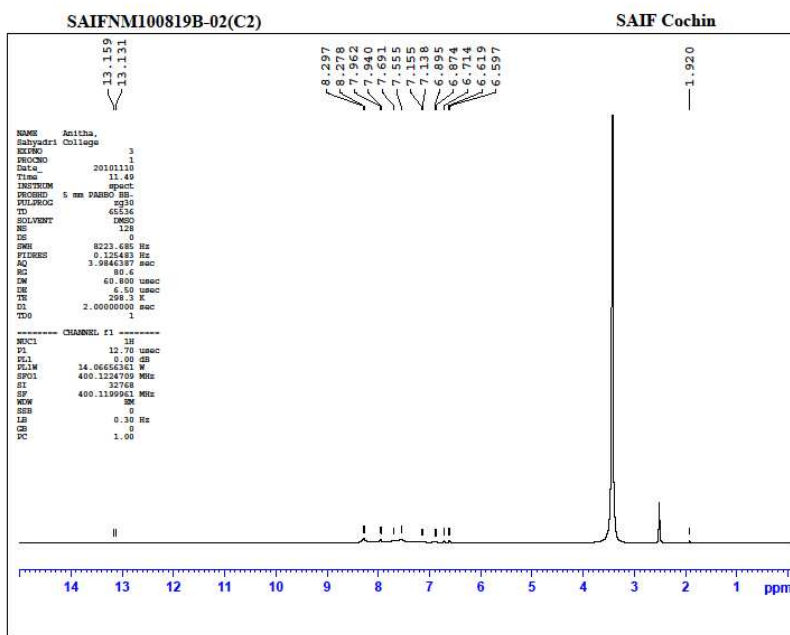
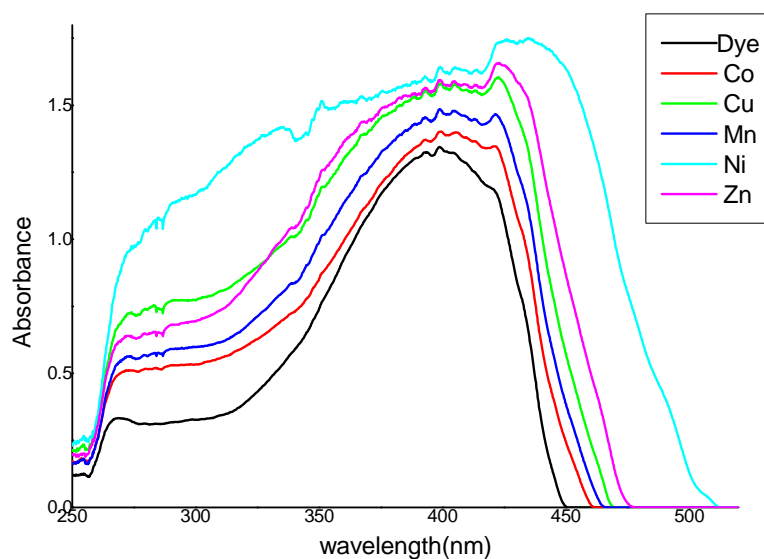
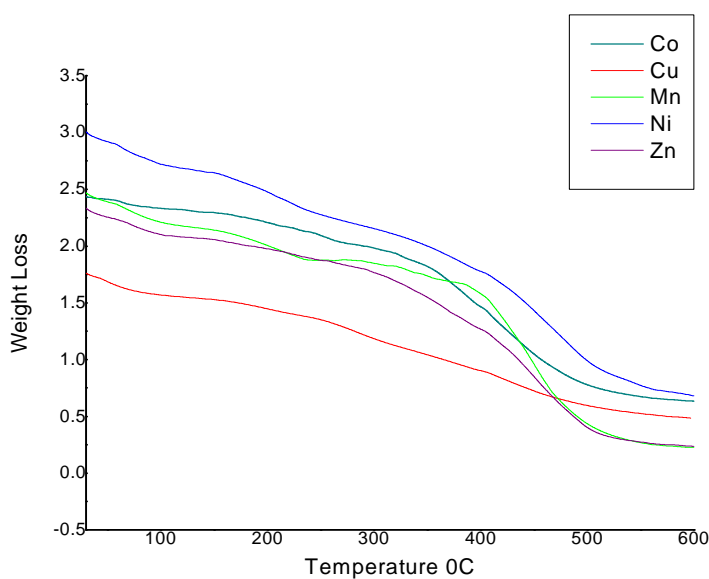


Fig 6

Fig 7: UV-VIS Spectra of ligand and complexes**Fig 2: TGA curves of metal complexes**

CONCLUSION

The synthesized azo metal (II) complexes have potential application for high density optical recording media due to their absorption spectra and high thermal stability. The ligand and metal complexes act as potent bactericidal agent. From the elemental analysis and spectral observations

we can conclude that the ligand is co-ordinated to metal atom as monodentate in the ratio of 1:1. Further work with analogs is needed.

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