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Synthesis and antimicrobial evaluation of metal (II) complexes of a novel bisazo dye 2, 2^1 [benzene-1, 3-diyl di (E) diazene 2, 1-diyl] bis (4-chloroaniline)

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ABSTRACT

Transition metal complexes of Co(II), Cu(II), Mn(II), Ni(II) and Zn(II) with a novel bisazo dye 2, 2^1 [benzene-1, 3-diyl di(E) diazene 2,1-diyl] bis (4-chloroaniline) derived from m-phenylenediamine and p-chloroaniline were synthesized. Characterization of these compounds has been done on the basis of elemental analysis, electronic data, FT-IR, ^{1}H NMR, powder X-ray diffraction and thermal analysis (TGA) and magnetic data. From the analytical and thermal data, the stoichiometry of the complexes has been found to be 1:1 (metal: ligand). On the basis of physicochemical data octahedral, tetrahedral and square planar geometries were assigned for the complexes. The ligand and metal complexes were screened for their antimicrobial activity.

Key words: 1: bisazo dye, 2: thermal, 3: antimicrobial activity.

INTRODUCTION

Azo compounds, with two phenyl rings separated by an azo (-N=N-) bond are versatile molecules and have received much attention in research areas both fundamental and application. The strong electronic absorption maximum can be tailored by ring substitution to fall anywhere from the ultraviolet to red visible regions, allowing chemical fine-tuning of color. This combined with the fact that these azo groups are relatively robust and chemically stable, has prompted extensive study of dyes and colorants.

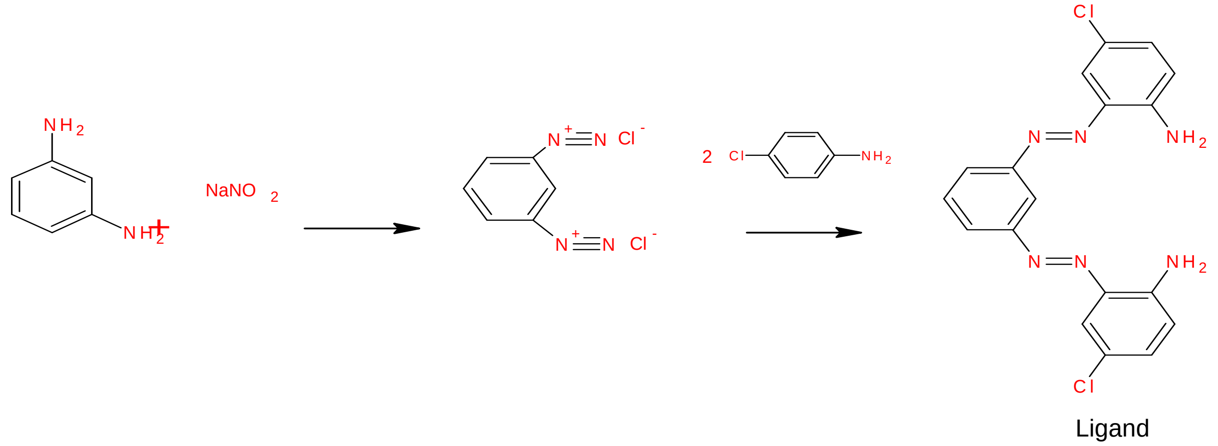
Because of the good thermal stability of azo compounds they are useful in the optical data storage devices. In recent years metal-azo complex dyes are used for DVD-R (digital versatile disc recordable) as recording layer. Most recently some azo dyes have been studied for nonlinear optical (NLO) applications. 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.[1-4] Although, many researchers have described the synthesis of monoazo dyes, very few comparable investigations have been made with disazo dyes. In this study, the synthesis of disazo dye derived from m-phenylenediamine and p-nitroaniline as coupling component and its metal (II) complexes is described. The structural investigation and antimicrobial activity of the synthesized compounds are discussed.

EXPERIMENTAL SECTION

All chemicals 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 400-4000cm^{-1}range.^{1}H NMR spectra were recorded in DMSO at room temperature. The mass spectrum of the ligand was recorded on Agilent 1200 series LC/MSD VL system. The molecular melting points were determined by open capillary method using electric melting point apparatus and are uncorrected.

Synthesis of the ligand

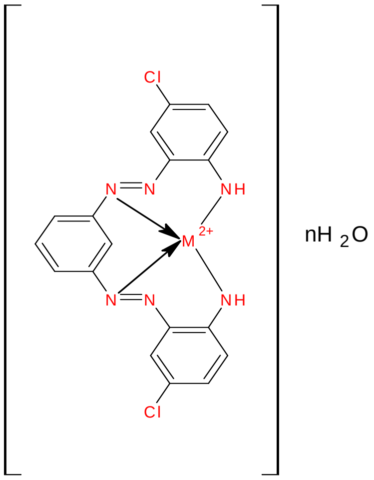
Metaphenylenediamine (1.08g / 0.01mol) was dissolved in a mixture of 5cm^3 of water and 10cm^3 of concentrated hydrochloric acid. While 20ml concentrated hydrochloric acid was diluted with about 60g of crushed ice and cooled with a cooling mixture. To this a cold solution of sodium nitrite (2.5g/10 ml water) was added. Immediately m-phenylenediamine hydrochloride solution was added and stirred for about 1hr till a dark yellow colored solution was obtained [8]. The coupling agent p-chloroaniline dissolved in DMF (0.02mol) was cooled and added to the tetrazo solution slowly with continuous stirring and maintaining the temperature 0-5^{o}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. The probable route for the synthesis of the azo ligand and the complex were as depicted in scheme I.



Scheme I: General route for the synthesis of azo ligand and the complexes

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 complexes were almost quantitative.



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

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 DMSO and found inactive in culture medium.

RESULTS AND DISCUSSION

Characterization of the compound

All the synthesized compounds were intensely colored amorphous solids. The ligand was soluble in methanol, chloroform and DMSO while the metal complexes in DMF and DMSO. The data were summarized in Table1

Infrared spectral studies

The IR data of the ligand and its metal complexes were presented in Table 2. The IR spectra of complexes were compared with that of the free ligand in order to determine the co-ordination sites involved in chelation. There were some guide peaks in the spectra of ligand, the position of these peaks were expected to change upon chelation. Upon comparison, it was found that the (N=N) stretching vibration in free ligand was at 1629 cm^{-1} which gets shifted to 1602-1611 cm^{-1} in complexes, indicating the participation of azo nitrogen in co-ordination (M-N).

New bands found in the spectra of complexes in the region 553-587 cm^{-1} have been assigned to (M-N) mode, [5-10] the bands at 827-830 cm^{-1} were assigned to co-ordinated water molecule. [17]

Table1: Microanalytical data of ligand and metal complexes

S. No.	Name of compound	Carbon Found (Calc.)	Hydrogen Found (Calc.)	Nitrogen Found (Calc.)	M.P. (°C)	Color	Yield %
1.	Ligand(L) $C_{18}H_{14}Cl_{12}$ N_6	56.12 (54.87)	3.66 (3.47)	21.81 (22.58)	90±2	Reddish brown	68
2.	Co(II) complex $C_{18}H_{12}Cl_{12}Co$ N_6	47.53 (48.89)	3.01 (2.74)	20.68 (19.01)	>300	Deep brown	76
3.	Cu(II) complex $C_{18}H_{12}Cl_{12}Cu$ N_6	48.95 (48.39)	2.92 (2.71)	17.95 (18.81)	>300	Black brown	80
4.	Mn(II) complex $C_{18}H_{12}Cl_{12}Mn$ N_6	50.25 (49.34)	2.55 (2.76)	20.68 (19.18)	>280	Reddish brown	75
5.	Ni(II) complex $C_{18}H_{12}Cl_{12}Ni$ N_6	49.78 (48.92)	3.12 (2.74)	18.74 (19.02)	>300	Deep brown	78
6.	Zn(II) complex $C_{18}H_{12}Cl_{12}Zn$ N_6	47.75 (48.19)	3.02 (2.7)	19.23 (18.73)	>290	Pale brown	79

Table 2: Characteristic IR spectral data of the ligand and its metal complexes in cm^{-1}

Comp	υ(M-N)	υ(N=N)	υ(N-H)	υ(Ar-Cl)	υ(Ar-H)	Co-odinated water	υ(C-N)
Ligand (L)	-	1629	3383	735	1890	-	1302
L-Co^{2+}	553	1607	3337	755	1890	830	1374
L-Cu^{2+}	555	1611	3340	748	1890	827	1365
L-Mn^{2+}	595	1602	3329	738	1887	829	1390
L-Ni^{2+}	564	1604	3328	737	1895	830	1379
L-Zn^{2+}	587	1602	3313	746	1890	830	1378

^{1}H NMR spectra

The ^{1}H NMR spectral data of azo ligand was recorded in DMSO-d_6 solution. A multiplet at δ6.58-8.29 was due to aromatic protons and δ1.90-1.92 for N-H protons. The peak at δ2.49-3.49 would be due to DMSO protons. The ^{1}H NMR signals are in correlation with the expected structure of azo ligand. The spectra of azo ligand and Ni (II) complex were shown in Figures 1 & 2.

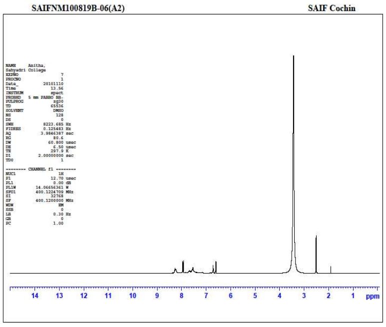


Fig 1:^{1}H NMR spectra of azo ligand L

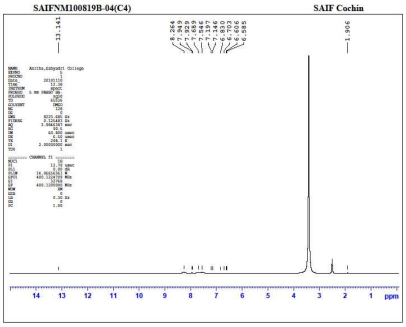


Fig 2:^{1}H NMR spectra of Ni (II) complex

Electronic spectra

The UV-VIS spectra of synthesized azo dye and its metal complexes showed two bands between 265-269nm and 422-425nm in DMSO, 238-247 and 421-424nm in methanol. The first band may be due to π-π*transition within the aromatic ring and the second band would be due to n-π* transition of N=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 slightly blue shifted which arise from the energy change of intense π-π* and n-π*transition of the conjugated chromophore due to the chelation between metal ions and azo ligand. The complexation of the dye with the metal ion was responsible for a significant hypochromic shift at both π-π* and n-π*transition region. [12-16]. The electronic absorption data were shown in Table 3 and the spectra were shown in Figures 3-4.

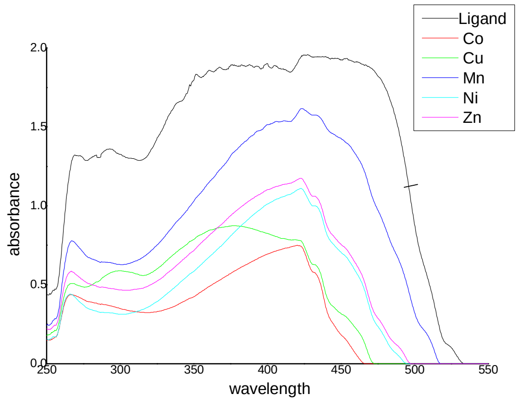


Fig 3: Electronic spectra of ligand and complexes in DMSO

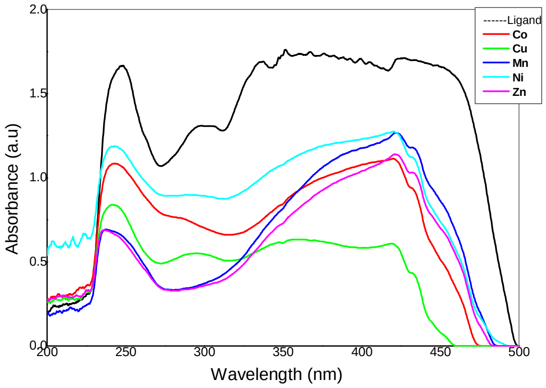


Fig 4: Electronic spectra in Methanol

Table 3: Absorption data of the ligand and complexes

compound	DMSO		Methanol	
	λ_{max}(nm)	absorbance	λ_{max}(nm)	absorbance
Azo ligand (L)	269 351 425	1.317 1.821 1.961	247 336 421	1.665 1.689 1.708
L-Co^{2+}	266 422	0.504 0.778	243 421	1.084 1.109
L-Cu^{2+}	265 422	0.436 1.109	242 418	0.839 0.607
L-Mn^{2+}	267 422	0.773 1.614	242 481	0.664 1.27
L-Ni^{2+}	265 423	0.442 1.114	243 422	1.188 1.267
L-Zn^{2+}	266 422	0.582 1.182	238 421	0,684 1.138

The Mn^{2+} complex with d^5 configuration exhibits absorption bands in the region 17642 & 36835 cm^{-1}. These bands may be attributed to number of spin forbidden transitions involving $^6A_{1g}$

ground and several higher energy quartet states, which were in consistent with octahedral geometry around Mn (II) metal ions.

The spectrum of Co(II) complex shows two bands at 11398 & 17595 cm^{-1} these bands were assigned to $^4A_{2g}\rightarrow{}^4T_{1g}$ (F) and $^4A_{2g}\rightarrow{}^4T_{1g}$ (P) transitions respectively. These transitions were consistent with the proposed tetrahedral geometry of this complex.

The spectrum of Cu (II) complex shows a broad band in the region 9760- 24826 cm^{-1}. The position and shape of this band suggests the merging of three electronic transitions. A square planar geometry was proposed for this complex. The black color of the complex also supports its proposed stereochemistry.

The spectrum of Ni (II) complex shows absorption bands in the region 10000 and 25208 cm^{-1}. The bands at 10000 cm^{-1} was assigned to $^3A_{2g}\rightarrow{}^3T_{2g}$ while the band at 25208 was assigned to $^3A_{2g}\rightarrow{}^3T_{1g}$ (F) transitions in an octahedral geometry.

Powder XRD study

The powder X-ray diffraction patterns of the azo metal complexes were taken in the range of 2θ angles 3-60^0 indicate simple scattering of the X-ray beam to give a continuous baseline and showed very poor crystallinity. Thus no definite structure can be described for metal complexes.[17] However spectroscopic data and elemental analysis of CHN enable us to predict possible structures.

Magnetic susceptibility measurements

The magnetic moments are measured at room temperature. The magnetic moments are 4.1, 5.85, 2.16 and 3.41 B.M. for Co(II), Mn(II), Cu (II) and Ni(II) respectively. They correspond to d^7, d^5, d^9 and d^8 configurations of the complexes respectively. Metal-metal interactions were not visualized. The Cu (II) complex shows a magnetic moment of 2.16 B.M. This value supports the square planar geometry.

Thermal studies

Thermal behavior of the azo ligand and its metal complexes were studied by thermo gravimetric techniques in the temperature range of 25-600^{0}C. The thermal stability data were listed in Table 5. The data clearly indicated that the decomposition of the complexes proceeds in two steps. Water molecules were lost between 50^{0}C and 250^{0}C and metal oxides were formed above 500^{0}C. For these complexes, the removal of water can proceed in two steps. All complexes lost hydration water 50^0 and 200^{0}C and then the co-ordinated water molecule was lost above ≥250^{0}C. The decomposition was complete at >500^{o}C for all complexes. The degradation pathway for all complexes may be represented as follows.

$$[ML(H_2O)]\,n\,H_2O \rightarrow [ML(H_2O)] + nH_2O \qquad (1)$$

$$[ML(H_2O)] \rightarrow H_2O + [MO \text{ or } MO_2] \qquad (2)$$

Where MO= CuO, CoO, NiO, ZnO and MO_2= MnO_2.

All the complexes have good thermal stability and hence can be used for optical recording media. .The TGA curves were shown in Figure 5.

The thermodynamic activation parameters of decomposition of dehydrated complexes, namely activation energy (E), enthalpy (ΔH), entropy (ΔS) and Gibbs free energy change of decomposition (ΔG) were evaluated graphically by using Coats- Redfern relation.

$$Log\ [log\ \{W_f/(W_f-W)\}/T^2] = log\ [AR/\theta E-(1\text{-}2RT/E)]\text{-}\ E/2.303RT \qquad (3)$$

where W_f is the mass loss at the completion of the reaction, W is the mass loss up to temperature T, R is the gas constant, E is the activation energy in kJmol−1, θ is the heating rate and [1-(2RT/E)]~= 1. A plot of the left-hand side of equation (3) against 1/T (shown in Figure 6) gave a slope from which E was calculated and lnA (Arrhenius factor) was determined from the intercept. The entropy of activation (ΔS), enthalpy of activation (ΔH) and the free energy change of activation (ΔG) were calculated.

Table 4: Thermodynamic data and kinetic parameters of azo metal complexes

\Complex	Decomposition Temp. (^oC)	E_a kJ/mol	Frequency factor (lnA)	ΔH kJ/mol	ΔS kJ/mol	ΔG kJ/mol
Co^{2+}	285-501	4.375	8.616	5.53	-160.56	106.93
Cu^{2+}	250-520	7.861	7.625	5.46	-156.74	103.13
Mn^{2+}	282-510	8.547	7.704	5.55	-162.91	108.98
Ni^{2+}	308-493	5.303	8.437	5.59	-162.81	109.57
Zn^{2+}	250-571	4.514	8.655	5.67	-162.70	111.19

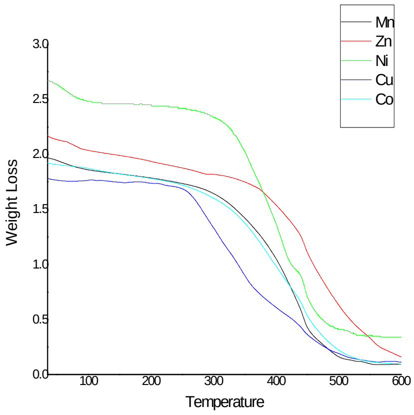


Fig 5: TGA curves for metal complexes

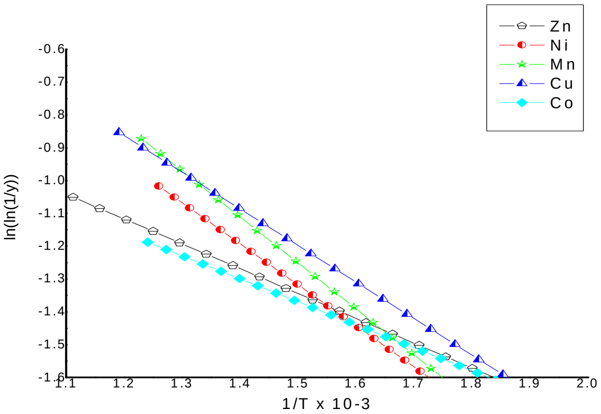


Fig 6: Plot of ln[ln(1/y)] vs 1/T x 10^{-3} for azo metal (II) complexes

The data were summarized in Table 4. The activation energies of decomposition were in the range 4.375-8.547 kJ mol−1.The high values of the activation energies reflect the thermal stability of the complexes. [*18*-21] The entropy of activation had negative values in all the complexes, which indicates that the decomposition reactions proceed with a lower rate than normal ones.

Antimicrobial activity

The azo ligand and all the metal complexes showed good activity against gram (+) *S-aureus* and gram (-) *Salmonella typhi, Klebisella pneumonia*. While Mn(II), Ni(II) and Zn(II) complexes have a moderate effect on *Bacillus subtilis.*

The fungi *Saccharomyces cerevisiae* was affected vigorously by azo ligand, Co(II), Cu (II) and Zn(II) complexes whereas *C.Lipolytica* was moderately affected by the ligand, Cu(II) and Ni(II) complexes.[22-24] The synthesized compounds have no effect on *C.albicans and C.neoformens*. The results in Table 5 reveal that the synthesized compounds were potent as bacteriostatic agents and have a good inhibitor effect on the growth of fungi *Saccharomyces cerevisiae.*

Table 5: Antimicrobial and antibacterial activity

	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	C.albicans	-	-	-	09	-	-	-
2	C.lipolytica		-	-	13	-	10	-
3	S. cerevisiae	17	20		18		20	-
4	C. neoformens	-	-	-	-	-	-	-
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	Samonella typhi	12	12	12	13	13	13	-
2	Staphylococcus aureus	14	11	14	12	13	13	-
3	Bacillus subtilis	-	-	10*	11*	11	-	-
4	Klebsella pneumonia	13	12	14	13	12	11*	

**Less growth*

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 its metal complexes act as potent bactericidal agent. Further work with analogs is needed.

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