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Synthesis, Characterization, and Antimicrobial Studies of Some Metal (II) Complexes of Some Azo Dyes

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ABSTRACT

Azo compounds possess the R-N=N-R' functional group are used as dyes and from the literature survey, their biological activities are enhanced when coupled with other transition metal complexes of Co(II), Cu(II), Mn(II), Ni(II) and Zn(II) with a novel bis azo dye 2, 2 1 [benzene-1, 3-diyl di(E) diazene 2,1-diyl] bis (4-chloroaniline) derived from mphenylenediamine and p-chloroaniline were synthesized. Data were supported by characterizations using UV-Vis spectroscopy and these compounds have been done based on elemental analysis, electronic data, Fourier Transform Infra-Red (FT-IR), 1H Nuclear Magnetic Resonance (NMR), powder X-ray diffraction and thermal analysis, and magnetic data. From the analytical and thermal data, the stoichiometry of the complexes is 1:1 (metal: ligand). Based on physicochemical data octahedral, tetrahedral, and square planar geometries were assigned for the complexes. The ligand and metal complexes were screened for their antimicrobial activity. The azo of 2-aminopyridine with its cobalt (II) complex exhibited antimicrobial activity at higher and lower concentrations.

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1. INTRODUCTION

Coordination chemistry of transition metal complexes is an important and fascinating branch of chemistry this is because the unique properties of the transition metals cause them to form numerous compounds with different ligands thereby expanding their usefulness and applications in industry, technology, and life processes (Luo *et al*., 2021; Yam, 2015; Cotton, 2000). Azo ligands are of significant importance in pharmaceuticals, food, textile, and technology thereby playing a pivotal role in the industry, technology, and life processes. As a result of the potential applications of these azo ligands in various fields, chemists around the world have always been fascinated and inspired to further research in the coordination chemistry of transition metal complexes of azo ligands. As a result of the -N=N-group present in the azo compound, azo compounds possess suitable bonding sites and can thus combine with a variety of transition metals to form coordination complexes of magnetic and unusual structural properties (Madkour *et al*.,2022).

The evidence of this further research can be seen in the recent, numerous, and diverse research papers on the subject of azo complexes with their various applications in different fields of chemistry, biology, and industry (Alsantali *et al*., 2022; Van der Zee & Cervantes, 2009). These azo groups from which the azo compounds are formed are usually highly colored, as a result, some of these azo compounds are used as dyes, pigments, and indicators (Ali *et al*., 2018). Their excellent optical properties enhanced their applications in optical data storage, photoswitching, and nonlinear optical materials. As a result of the vast applications of azo compounds, scientists especially chemists have explored the detailed and advanced study of the azo compounds and the coordination complexes of the azo compounds Xue *et al*., (2018). Azo compounds can be characterized using various spectroscopic techniques to determine their structures. The literature survey suggests that the structural chemistry of transition metal complexes of azo dyes containing nitrogen donor atoms exhibits large variations in structural chemistry. The variation in the structural aspects can be related to the nature of the donor atom, the structure of the ligand, and also the metal-ligand interaction. Azo compounds also have the potential tendency to act as bridging agents which form a variety of networks with transition metal complexes (Manjunatha & Bodke, 2021; Shimizu *et al*., 2009). The increasingly wide applications of azo compounds raise the need for continuous and further research on azo compounds and their metal complexes.

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In this study, Azo compounds possess the R-N=N-R’ functional group are used as dyes and from the literature survey, their biological activities are enhanced when coupled with other transition metal complexes of Co(II), Cu(II), Mn(II), Ni(II) and Zn(II) with a novel bis azo dye 2, 2 1 [benzene-1, 3-diyl di(E) diazene 2,1-diyl] bis (4-chloroaniline) derived from mphenylenediamine and p-chloroaniline were synthesized. Data were supported by characterizations using UV-Vis spectroscopy and these compounds have been done based on elemental analysis, electronic data, Fourier Transform Infra Red (FT-IR), 1H Nuclear Magnetic Resonance (NMR), powder X-ray diffraction and thermal analysis, and magnetic data.

2. METHODS

Reagents and solvents used include Sodium nitrite, 2-aminopyridine, benzylamine, 2,4-diamino pyridine, Hydrochloric acid, 1-naphthol, Sodium hydroxide, Sodium chloride, Silica gel, metal (II) salts Ethyl acetate, n-hexane, distilled water, methanol, diethyl ether, ethanol, and general laboratory purpose solvents. All were of analytical grade obtained from Sigma Aldrich chemicals and BDH chemicals. Some apparatuses used include a Buchner flask/funnel, Electric pump, UV-lamp, Hot plate with a magnetic stirrer, weighing balance, Gallen-Kamp melting point apparatus, glassware, etc.

2.1. Synthesis of the azo compound

The diazonium of the azo compounds was synthesized using the direct method and then coupled with the 1-naphthol.

2.2. Synthesis of the 2-aminopyridine coupled with 1-naphthol

The synthesis is shown in **Figure 1**. 5 mmol of 2-aminopyridine with 5.5 mmol of $NaNO2$ in 1.5 mL of distilled water was added to 3 mL of 1:1 conc. HCl water solution in an ice bath and stirred for 10 minutes, the resulting solution was added into a round bottom flask containing a solution of 2.5 M NaOH with 5mmol of 1-naphthol and stirred for 10 minutes in the ice bath, conc. HCl was be added with 1g of NaCl, the flask was be heated till the NaCl was be dissolved. After heating, the reaction system was be allowed to cool to room temperature. It was placed in the ice bath for 15 minutes, and the resulting mixture obtained was be filtered under vacuum, using the Buchner and electric pump.

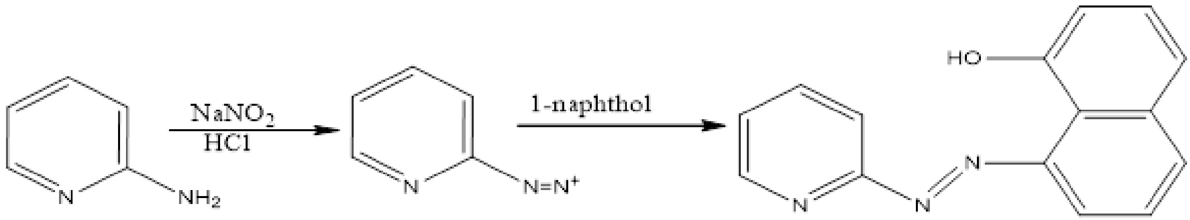

Figure 1. Synthesis route 1.

2.3. Synthesis of the 2,4-diamino pyridine coupled with 1-naphthol

The synthesis is shown in **Figure 2**. 5 mmol of 2,4-diamino pyridine with 5.5 mmol of $NaNO2$ in 1.5 mL of distilled water was added to 3 mL of 1:1 conc. HCl water solution in an ice bath and stirred for 10 minutes, the resulting solution was added into a round bottom flask containing a solution of 2.5 M NaOH with 5 mmol of 1-naphthol and stirred for 10 minutes in the ice bath, conc. HCl was added with 1 g of NaCl, the flask was heated till the NaCl was dissolved. After heating, the reaction system was allowed to cool to room temperature. It was placed in the ice bath for 15 minutes, the resulting mixture obtained was filtered under vacuum, using the Buchner and electric pump.

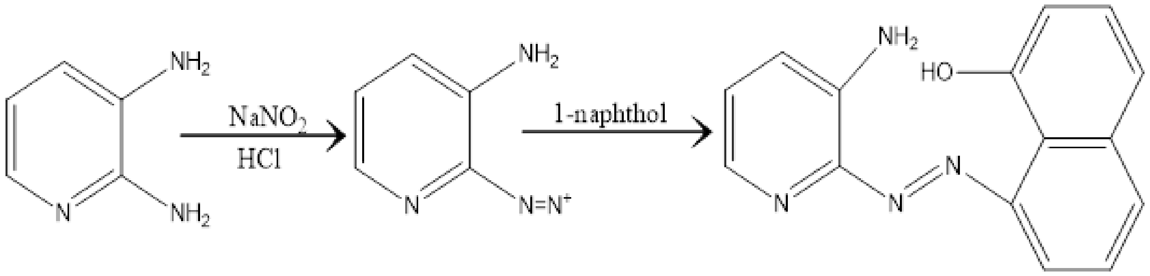

Figure 2. Synthesis route 2.

2.4. Synthesis of the 3-aminoacetophenone coupled with 1-naphthol

The synthesis is shown in **Figure 3**. 5 mmol of 3-aminoacetophenone with 5.5 mmol of NaNO2 in 1.5 mL of distilled water was added to 3 mL of 1:1 conc. HCl water solution in an ice bath and stirred for 10 minutes, the resulting solution was added into a round bottom flask containing a solution of 2.5 M NaOH with 5mmol of 1-naphthol and stirred for 10 minutes in the ice bath, conc. HCl was added with 1g of NaCl, the flask was heated till the NaCl was dissolved. After heating, the reaction system was allowed to cool to room temperature. It was placed in the ice bath for 15 minutes, and the resulting mixture obtained was filtered under vacuum using the Buchner and electric pump.

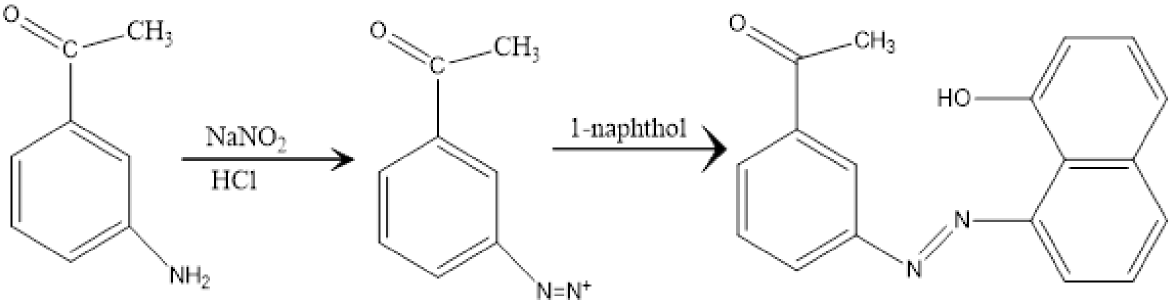

Figure 3. Synthesis route 3.

2.5. Synthesis of the Benzylamine coupled with 1-naphthol

The synthesis is shown in **Figure 4**. 5 mmol of Benzylamine with 5.5 mmol of NaNO2 in 1.5 mL of distilled water was added to 3 mL of 1:1 conc. HCl water solution in an ice bath and stirred for 10 minutes, the resulting solution was added into a round bottom flask containing a solution of 2.5 M NaOH with 5 mmol of 1-naphthol and stirred for 10 minutes in the ice bath, conc. HCl was added with 1g of NaCl, the flask was heated till the NaCl was dissolved. After heating, the reaction system was allowed to cool to room temperature. It was placed in the ice bath for 15 minutes, the resulting mixture obtained was filtered under vacuum, using the Buchner and electric pump.

2.6. Synthesis of the metal (ii) complex

The complexes were synthesized using the conventional reflux method (Abdallah, 2010). Detailed information is in the following:

(i) Complexation of the azo of 2-aminopyridine using a ratio of 1:1. 0.5 mmol of the hydrated metal (II) salts (cobalt, nickel, cadmium, and zinc) were prepared in 30 mL of 50% of

Ethanol solution and added to 30 mL of a solution of 0.5 mmol of 2-aminopyridine azo 50% of Ethanol solution and refluxed for 3 hours.

(ii) Complexation of the azo of 2-aminopyridine using a ratio of 1:2. The 0.25 mmol of the hydrated metal (II) salts were prepared in 30 mL of 50% of Ethanol solution, and added to 30 mL of a solution of 0.5 mmol of 2-aminopyridine azo 50% of Ethanol solution and refluxed for 3 hours.

(iii) Complexation of the azo of 2,4-diamino pyridine at a ratio of 1:1. The 0.5 mmol of the hydrated metal (II) salts were prepared in 30 mL of 50% of Ethanol solution and added to 30 mL of a solution (50% of Ethanol solution) of 0.5 mmol of 2,4-diamino pyridine azo and refluxed for 3 hours.

(iv) Complexation of the azo of 2,4-diamino pyridine at a ratio of 1:2. The 0.25 mmol of the hydrated metal (II) salts was prepared in 30 mL of 50% of Ethanol solution and added to 30 mL of a solution of 0.5 mmol of 2,4-aminopyridine azo in 50% of Ethanol solution and refluxed for 3 hours.

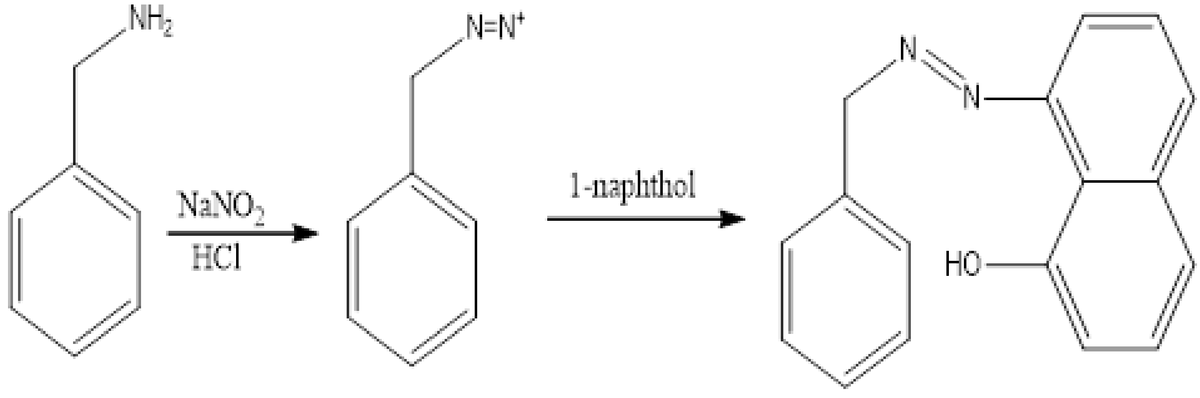

Figure 4. equation of reaction for azo of benzylamine.

2.7. Antimicrobial Activity

The varying mass of the synthesized azo compounds and their complexes was dissolved appropriately to concentrations between 100 mg/mol and 3.125 mg/mol. The solvent methanol and gentamycin were used as antibacterial and tioconazole as antifungal control of the experiment, this was to determine the minimum inhibition zone of the azo and their complexes on some specified microorganisms (Staphylococcus aureus, Bacillus subtilis, Streptococcus pyogenes, and Enterococcus feacilis, Pseudomonas aeruginosa, Escherichia coli, Candida talcatum, Aspergillus niger, Candida albicans, and Penicillium notatum). The pour plate method was used for the bacteria while the surface plate method was used for the fungi. The plates were incubated for 48 hours at 30 - 35˚C.

3. RESULTS AND DISCUSSION

The ligands and the complexes were characterized using elemental analysis, UV-Visible spectroscopy, and FT-IR spectroscopy which showed complexation of the ligand with $CoCl_2$, $NiCl_2$, $CdCl_2$, and $ZnSO_4$ using different stoichiometric rates. All the metal complexes showed similar color ranges with the ligand (brown). After purification, the synthesized compounds showed single spots. A good percentage yield of the ligands and their complexes was obtained.

Results from solubility tests are shown in **Tables 1 and 2**. The physicochemical properties of the compounds are shown in **Table 3**. Results of the UV-Vis Spectroscopy are shown in **Table 4**. From **Table 4**, it can be observed that the free ligand, 2-(2-pyridyl azo)-1-naphthol has one prominent peak at 320nm assigned to $n – \pi^*$ transition in the UV-region while the higher wavelength in the complexes as shown in **Table 3**. 4 are as a result of the metal present which gave the $\pi - \pi^*$ transitions.

Table 1. Solubility of 2-(2-pyridyl azo)-1-naphthol.

Solvent	Cold	Hot
Water	Insoluble	Insoluble
Methanol	Soluble	Soluble
Ethylacetate	Soluble	Soluble
Diethyl ether	Soluble	Soluble
n-Hexane	Insoluble	Soluble

Table 2. Solubility of 2-(2,4-dipyridyl azo)-1-naphthol.

Solvent	cold	Hot
Water	insoluble	Insoluble
Methanol	soluble	Soluble
Ethylacetate	soluble	Soluble
Diethyl ether	soluble	Soluble
n-Hexane	soluble	Partly-soluble

Table 3. Physiochemical properties of the ligand and the complexes.

Synthesized compound	Appearance	Yield (%)	Melting point (°C)
2-(2-pyridyl azo)-1-naphthol	reddish brown	72.7	99
Co (1:1)	Pinkish brown	71.0	
Co (1:2)	Dirty brown	50.0	
Ni (1:1)	Purplish brown	57.0	
Ni (1:2)	Brown	56.0	
Cd (1:1)	Light brown	55.0	
Cd (1:2)	Light brown	68.0	
Zn (1:1)	Light brown	55.0	
Zn (1:2)	Dirty brown	67.0	

Results from FT-IR Spectroscopy are shown in **Table 5**. Results from the CHN analysis of the 2-(2-pyridyl azo)-1-naphthol are shown in **Table 6**.

For results from the microbial evaluation, the bacteria plates were observed after 24 hours of incubation, it was observed that there were clear zones of inhibition of some plates of higher concentrations and no zones of inhibition at the lower concentration. The fungi plates were also observed after 48hrs of incubation. The microorganisms used include *Staphylococcus aureus, Bacillus subtilis, Streptococcus pyogenes, and Enterococcus feacilis* as gram-positive bacteria*, Pseudomonas aeruginosa,* and *Escherichia coli* as gram-negative bacteria*, Candida talcatum, Aspergillus niger, Candida albicans,* and *Penicillium notatum* as fungi. Detailed data are shown in **Tables 7, 8, 9,** and **10**.

Table 4. UV-Vis spectroscopy data of ligand ad complexes.

Compound	Λ_{max} (nm)	Energy (cm^{-1})	Absorbance	Assignment
2-(2-pyridyl azo)-1-naphthol	320		2.518	$n-\pi^*$
Co (1:1)	330		2.528	$n-\pi^*$
	380		3.620	$\pi-\pi^*$
	510		0.529	
Co (1:2)	325		2.404	$n-\pi^*$
	470		0.161	$\pi-\pi^*$
Ni (1:1)	320		2.420	$n-\pi^*$
	680		0.437	$\pi-\pi^*$
Ni (1:2)	325		2.465	$n-\pi^*$
	365		1.169	$\pi-\pi^*$
	735		0.074	
Cd (1:1)	325		2.492	$n-\pi^*$
	425		0.237	$\pi-\pi^*$
Cd (1:2)	320		2.380	$n-\pi^*$
	360		0.387	$\pi-\pi^*$
Zn (1:1)	320		2.518	$n-\pi^*$
	375		3.592	$\pi-\pi^*$
	380		1.001	
	735		0.037	
Zn (1:2)	330		2.530	$n-\pi^*$
	380		1.049	$\pi-\pi^*$
	730		0.057	

Table 5. Data from FTIR spectroscopy of ligands and complexes.

compounds	ν (N-H)	ν (O-H)	ν (C-N)	ν (C-O)	ν (N=N)	ν (C-H) aromatic	ν (C=C)	ν (M-O)	ν (M-N)	ν (M-Cl)
2-(2-pyridyl azo)-1-naphthol	3298	-	1292	-	1518	3049	1518 1456	-	-	-
Co (1:1)	3385	3385	1271	-	1518	3055	1458	484	418	-
Co (1:2)	3289	-	1309		1518	3049	1458	-	-	-
Ni (1:1)	3296	-	1309	-	1518	3051	1518 1458	-	-	-
Ni (1:2)	3404	3404	1301	-	1514	3059	1514 1458	-	414	-
Zn (1:1)	3298	-	1309	-	1518	3049	1518 1458	-	-	-
Zn (1:2)	3311	3311	1309	-	1518	3053	1518 1458	-	-	-

Table 6. Data from CHN analysis of the ligand, 2-(2-pyridyl azo)-1-naphthol.

Element	C	H	N
% Theory	73.57	5.70	13.19
% Found	73.58	5.66	13.21

Table 7. Data from a microbial evaluation of the ligand.

[mg/ml]	**Gram-positive Bacteria**				**Gram-negative Bacteria**		**Fungi**			
	S.a	***B.sub***	***S.pyo***	***E.tac***	***Ps.g***	***E.c***	***C.tal***	***A.n***	***C.alb***	***Pen. not***
100	24	22	24	20	20	22	16	18	16	14
50	20	18	20	18	16	18	14	16	14	12
25	18	16	16	16	14	14	12	14	12	10
12.5	14	14	14	14	12	12	10	10	10	-
6.25	12	10	10	10	10	10	-	-	-	-
3.125	10	-	-	-	-	-	-	-	-	-
Control	38	40	40	40	40	38	28	28	28	28

Table 8. Data from a microbial evaluation of ligands at L^2.

[mg/ml]	**Gram-positive bacteria**				**Gram-negative bacteria**		**Fungi**			
	S.a	***B. sub***	***S.pyo***	***E.tac***	***Ps. g***	***E.c***	***C.tal***	***A.n***	***C. alb***	***Pen. not***
100	22	20	22	18	18	22	18	18	18	16
50	18	18	18	16	16	18	14	16	14	14
25	16	16	16	14	14	16	12	14	16	10
12.5	14	14	14	10	12	14	10	12	10	-
6.25	12	10	10	10	10	10	-	-	-	-
3.125	10	-	-	-	-	-	-	-	-	-
Control	38	40	40	40	40	38	28	28	28	28

Table 9. Data from a microbial evaluation of Co (1:1).

[mg/ml]	**Gram-positive Bacteria**				**Gram-negative Bacteria**		**Fungi**			
	S.a	***B. sub***	***S.pyo***	***E.tac***	***Ps.g***	***E.c***	***C.tal***	***A.n***	***C.alb***	***Pen.not***
100	28	24	26	28	24	26	18	20	18	16
50	24	21	22	24	21	22	16	18	16	14
25	21	18	18	21	18	18	14	16	14	12
12.5	18	16	14	16	16	14	12	14	12	10
6.25	14	14	12	14	14	12	10	12	10	-
3.125	10	10	10	10	10	10	-	-	-	-
Control	38	40	40	40	40	38	28	28	28	28

Table 10. Data from microbial evaluation Co (1:1) complex at $[Co]^2$

[mg/ml]	**Gram-positive bacteria**				**Gram-negative bacteria**		**Fungi**			
	S.a	***B. sub***	***S.pyo***	***E.tac***	***Ps. g***	***E.c***	***C.tal***	***A.n***	***C.alb***	***Pen. not***
100	26	22	22	22	22	24	18	18	18	16
50	22	18	18	18	18	20	16	16	16	14
25	20	16	16	16	16	18	14	14	14	10
12.5	16	14	14	14	14	16	12	12	12	10
6.25	14	12	12	10	12	12	10	10	10	-
3.125	10	10	10	10	10	10	-	-	-	-
Control	38	40	40	40	40	38	28	28	28	28

4. CONCLUSION

The synthesized azo metal (II) complexes are good for high-density optical recording media due to their absorption spectra and high thermal stability. The ligand and its metal complexes act as bactericidal agents.

5. ACKNOWLEDGMENT

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6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. Authors confirmed that the paper was free of plagiarism.

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