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Design and synthesis of copper metal complexes of azo compound containing 1-Naphthol moiety

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Abstract
As per continuations of our findings in the field of azo compounds and their different derivatives such as thymol derivatives, carvacrol derivatives and many more, they show number of different properties. In this work we focus on the azo compounds containing 1-naphthol and their metal complexes. 7 ligands L_1, L_2, L_3, L_4, L_5, L_6 and L_7 are synthesized from 4-nitro aniline, 2,6-xylidene, 2-amino benzoic acid, 4-amino benzoic acid, 2-methyl aniline, 4-chloro aniline and 2-amino phenol respectively. All these newly synthesized 7 azo ligands were characterized and confirmed by IR and ^{1}H NMR spectral studies, and finally use in the formation of 7 different Copper metal complexes where they are characterized by IR. Further study and Characterizations is also needed for exploring of different properties of these metal complexes.

Keywords: Azo compounds, 1-naphthol, cu metal complexes

Introduction

According to the continuation of our findings, in the subject area of azo compounds, their ligands and their metal complexes with different transition metal, these compounds and their derivatives show enormous properties such as antibacterial, antifungal, drug carriers, cancer treatments, anti-oxidants, anti-inflammatory and analgesic [1, 2, 3]. A bis azo dye ligand 2, 2 1 [benzene-1, 3-diyl di(E) diazene 2,1 diyl] bis (4-chloroaniline) derived from mphenylenediamine and p-chloroaniline complexes with Co(II), Cu(II), Mn(II), Ni(II) and Zn(II) show good antimicrobial activity against species such as *Staphylococcus aureus, Bacillus subtilis, Streptococcus pyogenes, and Enterococcus feacilis, Pseudomonas aeruginosa, Escherichia coli, Candida talcatum, Aspergillus niger, Candida albicans, and Penicillium notatum* [4]. Azo ligand contains 4-(2-Hydroxyphenylazo)-1 naphthol and complex formation with Mn (II), Fe (III) and Cr (III) exhibits remarkable antibacterial and antifungal activity against different types of species (*Pseudomonas aeruginosa, Staphylococcus aureus, Escherichia coli, Aspergillus flavus, Trichophyton rubrum, and Candida albicans*), Mn (II) complex shows highest binding affinity to amino acid residue (protein) receptor of *E. coli* growth (PDB ID: 1hnj) [5]. Tupys (2016) et. al. reported a new azo reagent 1-[(5-benzyl-1,3-thiazol-2-yl) diazenyl] naphthalene-2-ol having thermal stability up to 171°C, used as selective analytical reagent for the determination of transition metal ions such as Cd (II), Hg (II), Pd (II), also used as an indicator in acid-base titrations [6]. Gold catalyzed ortho C-H bond fictionalization of 1-naphthol with α-aryl-α-diazoester exhibits possible applications in synthesis of bioactive compounds, natural products and late-stage modification of medicine containing a naphthol moiety, this reveals the site selectivity in 1-naphthol [7]. The synthesized ligands (*E*)-1-(((2,6-dichlorophenyl) imino) methyl) naphthalen-2-ol (L1) and (*E*)-1-(((4-bromo-2,6-dichlorophenyl) imino) methyl) naphthalen-2-ol complexes with Cu (II) displayed the better antidiabetic, antioxidant, and antibacterial potential than parent ligands; in addition to this they also show the moderate to good antioxidant activity [8]. Acetic acid derivatives of naphthalene-based rings report the cytotoxic potency towards diverse cancer cell lines better than the reference compound employed [9]. Azo compounds namely, 2-(phenylazo)-1-naphtllol (Sudan I), 4-(phenylazo)-1-naphthol and 2,4-bis(phenylazo)-1-naphthol complexes with Fe (III), Co (II) and Cu (II) exhibits considerable anti-inflammatory activity [10]. The ligand 4-(naphthalen-1-yl)-1-((quinolin-2-yl) methylene) thiosemicarbazide and its metal complexes with Co (III), Ni (II) and Cu (II) gives good anti-tubercular activity against *Mycobacterium* strain, M. *H37Rv in-vitro*. It also shows cytotoxic activity over human embryonic kidney cells (HEK293) by inhibiting tuberculosis bacteria [11].

By considering the above-mentioned vast types of properties of azo ligand complexes with 1-Naphthol prompted us to undertake the synthesis of Copper metal complexes containing azo compound linked 1-Naphthol moiety.

Materials and Methods

The chemicals were used in this work is of synthetic grade (S.D. Fine Chem. Ltd, Mumbai, India), recrystallized/redistilled before use it. After synthesis the newly obtained products were characterized by ^{1}H NMR and IR. The physical constants (melting point) were determined and recorded by open capillary method and are uncorrected. The IR spectra (Table 1) were recorded on a Perkin-Elmer spectrum-one FTIR instrument in the form of KBr pallet. ^{1}H NMR spectra (Table 2) were recorded in $CDCl_3$ on a Varian Mercury-YH-300 spectrometer using TMS as an internal standard. The purity of compounds was checked by TLC. The crude products were recrystallized from ethanol as solvent.

Preparation of Ligands L_1 i.e.[(*E*)-2-((4-nitrophenyl) diazenyl) naphthalene-1-ol]:
4-nitro aniline (i.e. primary aromatic amine) (1.38 g, 0.01 mole) was mixed with Conc. HCl (2.5 mL) to the resultant suspension crushed ice (25 g) and $NaNO_2$ (2.5 mL, 4N) was added with stirring. Diazotization was carried out over 30 mins at 5° - 7°C and then diazonium salt solution was added drop wise at 5° - 10°C to the alkaline (i.e. NaOH) solution of 1-Naphthol. The coupling reaction was stirred for 45 mins and the pH of the resultant mixture was adjusted to pH 7. The formed ligand product was filtered, washed with water and dried. Crude products were recrystallized with proper solvent.

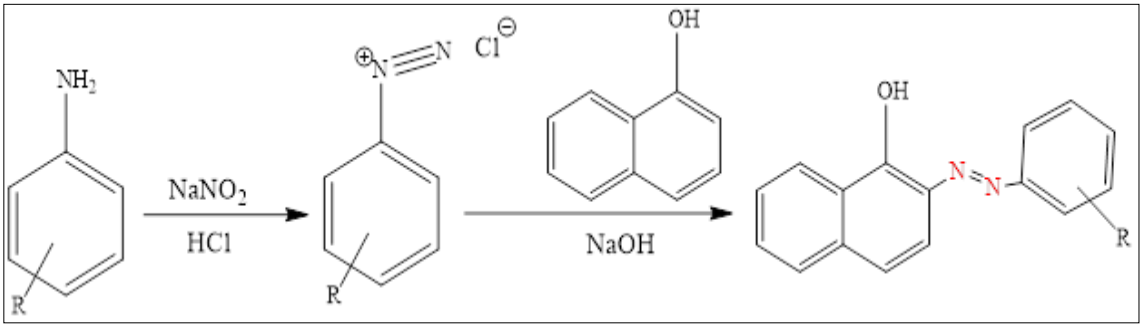


Fig 1: Synthesis of azo compound ligands containing 1-Naphthol moiety

By using above procedure and scheme total 7 ligands L_1, L_2, L_3, L_4, L_5, L_6 and L_7 were prepared from 4-nitro aniline, 2,6-xylidene, 2-amino benzoic acid, 4-amino benzoic acid, 2-methyl aniline, 4-chloro aniline and 2-amino phenol respectively. All the obtained azo ligands are colored and crystalline in nature. The colour ranges from Merlot red to Ruby red. All synthesized ligands show the characteristic peak of –N=N- linkage in IR spectra ranges from 1435.69 cm^{-1} to 1572.29 cm^{-1} (Reference range 1400-1500 cm^{-1}).

Table 1: IR spectra values in $cm^{-1}$of newly synthesized ligands

Sr. No.	Ligand	-N=N-	-C=C-Aro.	-OH Aro.	-C-H Aro.	-C-N=Aro.	-C-H Bending
1.	L_1	1536.40	1595.68	3244.45	2971.42	1315.40	754.32
2.	L_2	1572.29	1697.97	3221.68	2968.36	1377.91	808.98
3.	L_3	1435.69	1594.38	3244.45	2976.65	1365.32	1067.80
4.	L_4	1572.29	1697.97	3265.24	2969.25	1362.21	887.62
5.	L_5	1438.69	1594.38	3185.21	2971.42	1325.63	793.69
6.	L_6	1536.40	1594.25	3189.25	2972.65	1315.40	752.25
7.	L_7	1572.29	1637.97	3178.98	2978.32	1377.91	821.98

^{1}H NMR spectra of all newly synthesized ligands L_1 to L_7 also reveals that, the linking of azo group (-N=N-) is takes place at the *ortho* position of –OH group in 1-Naphthol, because the absence of peak at 6.73 δ (d, 1H) due to *ortho* hydrogen of –OH. In addition to this all the remaining hydrogens present on naphthol ring shows the peak at slightly downfield also suggested that the introduction of electron withdrawing group i.e. –N=N- group in naphthol ring.

Table 2: ^{1}H NMR spectra values in δ of newly synthesized ligands

Sr. No	Ligand	Colour	M. P.	^{1}HNMR
1.	L_1	Merlot Red	138°C	1.68 δ (s, 1H of -OH), 7.40 δ (dd, 1H of 1-Naphthol), 7.42 δ (dd, 1H of 1-Naphthol), 7.49 δ (d, 1H of 1-Naphthol), 7.70 δ (dd, 1H of 1-Naphthol), 7.88 δ (d, 1H of 1-Naphthol),7.90 δ (dd, 1H of 1-Naphthol), 8.14 δ (d, 2H meta to -NO_2), 8.28 δ (d, 2H ortho to –NO_2).
2.	L_2	Crimson red	162°C	1.57 δ (s, 1H of -OH), 2.38 δ (s, 6H of 2 –CH_3), 7.40 δ (dd, 1H of 1-Naphthol), 7.16 δ (d, 2H of aro. ortho to both –CH_3), 7.30 δ (d, 1H of aro. meta to both –CH_3),7.42 δ (dd, 1H of 1-Naphthol), 7.48 δ (d, 1H of 1-Naphthol), 7.74 δ (dd, 1H of 1-Naphthol), 7.88 δ (d, 1H of 1-Naphthol), 7.96 δ (dd, 1H of 1-Naphthol),
3.	L_3	Lipstick red	144°C	1.54 δ (s, 1H of -OH), 7.41 δ (dd, 1H of 1-Naphthol), 7.43 δ (dd, 1H of 1-Naphthol), 7.49 δ (d, 1H of 1-Naphthol), 7.74 δ (dd, 1H of 1-Naphthol), 7.83 δ (d, 1H of 1-Naphthol), 8.00 δ (dd, 1H of 1-Naphthol), 7.61 δ (dd, 1H meta to -COOH), 7.71 δ (dd, 1H para to -COOH), 8.10 δ (dd, 1H meta to –COOH but ortho to –N=N-), 8.24 δ (dd, 1H meta to -COOH),
4.	L_4	Apple red	128°C	1.67 δ (s, 1H of -OH), 7.40 δ (dd, 1H of 1-Naphthol), 7.43 δ (dd, 1H of 1-Naphthol), 7.50 δ (d, 1H of 1-Naphthol), 7.73 δ (dd, 1H of 1-Naphthol), 7.87 δ (d, 1H of 1-Naphthol), 7.96 δ (dd, 1H of 1-Naphthol), 8.09 δ (d, 2H meta to -COOH), 8.24 δ (d, 2H ortho to -COOH).
5.	L_5	Wine red	132°C	1.63 δ (s, 1H of -OH), 2.36 δ (s, 3H), 7.27 δ (dd, 1H ortho to –CH_3), 7.29 δ (dd, 1H para to –CH_3), 7.35 δ (dd, 1H meta to –CH_3), 7.40 δ (dd, 1H of 1-Naphthol), 7.42 δ (dd, 1H of 1-Naphthol), 7.49 δ (d, 1H of 1-Naphthol), 7.74 δ (dd, 1H of 1-Naphthol), 7.84 δ (dd, 1H ortho to –N=N- but meta to –CH_3), 7.87 δ (d, 1H of 1-Naphthol), 7.96 δ (dd, 1H of 1-Naphthol),
6.	L_6	Rose red	166°C	1.64 δ (s, 1H of -OH), 7.40 δ (dd, 1H of 1-Naphthol), 7.43 δ (d, 2H ortho to -Cl), 7.44 δ (dd, 1H of 1-Naphthol), 7.50 δ (d, 1H of 1-Naphthol), 7.76 δ (dd, 1H of 1-Naphthol), 7.82 δ (d, 2H meta to -Cl), 7.86 δ (d, 1H of 1-Naphthol), 7.96 δ (dd, 1H of 1-Naphthol).
7.	L_7	Ruby red	148°C	1.59 δ (s, 1H of -OH), 6.90 δ (dd, 1H ortho to -OH of Phenol), 6.97 δ (dd, 1H para to -OH of Phenol), 7.20 δ (dd, 1H meta to -OH of Phenol but ortho to –N=N-), 7.24 δ (dd, 1H meta to -OH of Phenol), 7.40 δ (dd, 1H of 1-Naphthol), 7.42 δ (dd, 1H of 1-Naphthol), 7.50 δ (d, 1H of 1-Naphthol), 7.74 δ (dd, 1H of 1-Naphthol), 7.86 δ (d, 1H of 1-Naphthol), 7.96 δ (dd, 1H of 1-Naphthol), 9.49 δ (s, 1H of OH of Phenol).

Preparation of Metal complexes

Take 0.20 gm of ligand azo compound in 100 ml beaker; add 15 ml alcohol and 15 ml of water in it. In another beaker 15 ml alcohol and 5 ml of water mixture was taken and dissolves the $CuCl_2$ $6H_2O$ salt in it. After this add the metal chloride solution into the solution of ligand azo compound with constant stirring (Magnetic stirrer). After 30 to 35 mins metal complex crystals were precipitate out. For digestion purpose this reaction mixture was refluxed for 120 mins, on magnetic stirrer (precaution was taken that, the temperature of reaction mixture is not exceeds 80°C and stirring speed dose not exceeds 750 rpm). Finally, cool the reaction mixture and filter the obtained metal complex product and dry it.

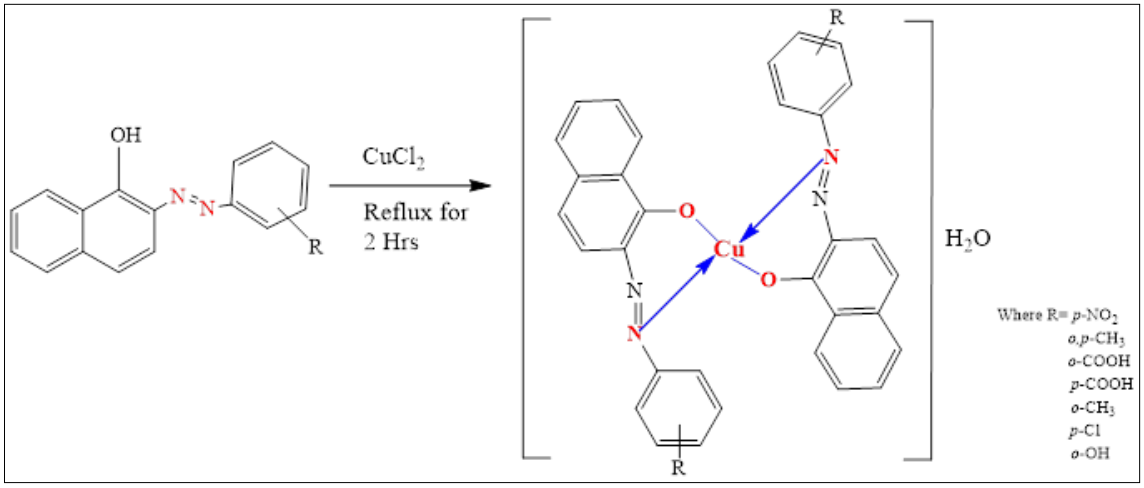
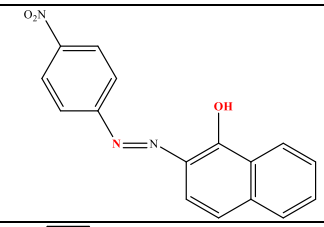
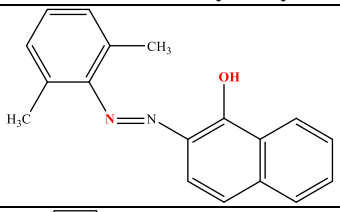
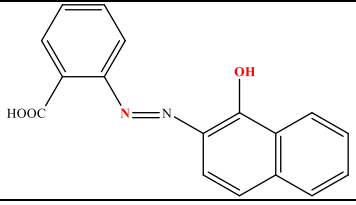


Fig 2: Synthesis of metal complexes of Cu and azo compound ligands containing 1-Naphthol moiety

All the new synthesized metal complexes are dark in colour, having luster and crystalline in nature. Colours are ranges from Garnet red to wine red (Table 3). After complex formation the newly obtained metal complexes were characterized by IR. The physical constants (melting point) were determined and recorded by open capillary method and are uncorrected. The IR spectra (Table 4) were recorded on a Perkin-Elmer spectrum-one FTIR instrument in the form of KBr pallet.

Some more characterization techniques are needed to explore the different properties of these synthesized copper metal complexes such as ^1H NMR spectral studies, x-ray diffraction studies, Magnetic susceptibility, Thermal analysis, Molar conductance etc. Including this some important investigations such as antitumor activity, antibacterial, antifungal, antiviral, antidiabetic etc also be needed for such type study to focusing on metal complexes of such type.

Table 3: The physical properties of the complexes

Sr. No.	Ligand	Molecular formula and Molecular weight of Complex	Colour	M.P.	Yield
1.		$C_{32}H_{22}N_6CuO_7$ 667.55	Garnet red	212°C	90 %
2.		$C_{36}H_{31}N_4CuO_3$ 630.55	Brick red	220°C	85 %
3.		$C_{34}H_{24}N_4CuO_7$ 665.55	Mahogany red	242°C	82 %

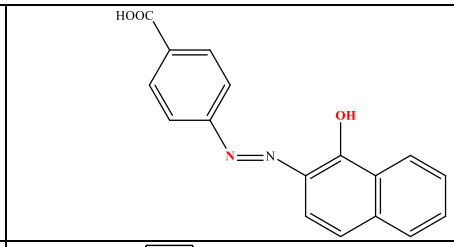
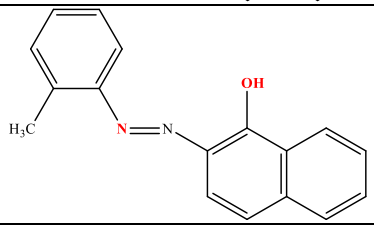
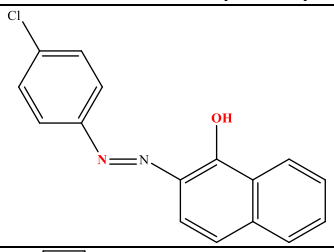
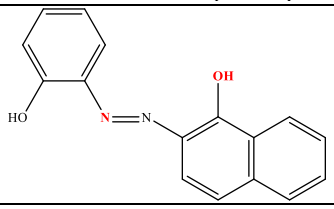
4.		$C_{34}H_{24}N_4CuO_7$ 665.55	Jam red	222°C	90 %
5.		$C_{34}H_{28}N_4CuO_3$ 603.55	Blood red	210°C	92 %
6.		$C_{32}H_{22}N_4CuO_2Cl_2$ 628.45	Currant red	268°C	88 %
7.		$C_{32}H_{24}N_4CuO_2$ 559.55	Wine red	250°C	86 %

Table 4: The IR spectra bands (cm^{-1}) of the complexes

Sr. No.	Complex		-N=N- Stretching	-C=C- Aro. stretching	-C-N- Stretching	Aro. –OH stretching	-C-H Aro. stretching
1.	ML_1	$[Cu(L_1)_2(H_2O)]$	1522.58	1578	1300.65 1564.74	3225.32	2959.62
2.	ML_2	$[Cu(L_2)_2(H_2O)]$	1584.58 1505.66	1671.64 1602.35	1359.37 1313.45 1290.10	3200.58	2948.84
3.	ML_3	$[Cu(L_3)_2(H_2O)]$	1418.58	1548.32	1345.54	3208.68	2959.32 1051.32 (Bending)
4.	ML_4	$[Cu(L_4)_2(H_2O)]$	1528.24 1505.66	1649.62 1602.35	1351.28	3231.98	2969.25
5.	ML_5	$[Cu(L_5)_2(H_2O)]$	1401.65	1557.23	1302.87	3142.98	2971.42 772.65 (Bending) 754.70 1092.79
6.	ML_6	$[Cu(L_6)_2(H_2O)]$	1499.65	1523.68	1289.14 1264.74	3170.74	2972.65
7.	ML_7	$[Cu(L_7)_2(H_2O)]$	1535.23 1506.66	1607.63 1602.53	1355.74 1313.45 1290.10	3155.69 3060.16	2978.32

Conclusion

Azo compounds containing 1-Naphthol moiety was fruitfully synthesized by using 7 different primary aromatic amines. They were characterized and confirmed by IR and ^1H NMR. Further, these newly synthesized azo compounds containing 1-Naphthol moiety were used as ligand for the formation of metal complexes of Cu metal ions. No doubt further research needed for complete optimization and to explore various properties of such type of metal complexes. But this type research may open the new era or gateway to new researcher in the field of coordination chemistry.

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Conflict of Interest

There are no conflicts of interest in this research study.

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