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Design and synthesis of nickel metal complexes of azo compound of 1-naphthol

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Abstract
According to our ongoing 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. This work focuses on the azo compounds containing 1-naphthol and their Ni metal complexes. Ligands L_a, L_b, L_c, L_d, L_e, L_f and L_g 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 azo ligands were characterized and confirmed by IR and ^{1}H NMR spectral studies, and finally use in the formation of 7 different Nickel metal complexes and they were characterized by IR. Continued investigations and Characterizations are also required for exploring of different properties of these metal complexes.

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

Introduction

We all know that, the azo compounds not only used as dyeing agents, but also, they are used in various fields such as food industry, pharmaceutical industry, in cosmetics etc. Some studies show that the azo compounds exhibit wide range of medicinal applications including antibacterial, antifungal, antiviral, and cytotoxic effects. They can also be used as drug carriers through prodrug approach. Metal complexes of some azo compounds were also be synthesized and also show different kinds of medicinal and pharmaceutical applications. The Fe (III), Co (II) and Cu (II) metal complexes containing azo compound 2-(phenylazo)-1-naphtllol (Sudan I), 4-(phenylazo)-1-naphthol and 2,4-bis(phenylazo)-1-naphthol exhibits good anti-inflammatory activity [1]. Ni (II) metal complexes of 2-benzoylpyridine-N_4-methyl-3-thiosemicarbazone shows square planar azido-nickel (II) complex structure and also show generates supramolecular 1D chain [2]. Ni (II) metal complexes of five different ligands such as dichloro-bis-4-picolyl, dichoro-bis-(4-[(pyridin-4-yl) methoxy] aniline), dichloro-bis(pyridin-4ylmethyl-4nitrobenzoate), dichloro-bis(pyridin-4ylmethyl-4aminobenzoate) and dichoro-bis-4-(4-nitrophenoxy) methyl) pyridine shows antibacterial activity against Gram-negative bacterium species S. aureus and all are highly stable to thermal studies [3]. Ni metal complexes are biologically active because Ni is an essential metal ion, it regulates metabolism, fight against oxidative stress and strengthen immune system. Ni metal complexes are used in the treatment of cancers [4]. Some metal complexes of 2-hydroxy-4,5-dimethylacetophenone of Ni (II) shows octahedral geometry that controls the interaction of drug molecule, this also affects the drug behavior, stability, interaction with biological targets (including proteins and enzymes) [5]. Awasthi and his co-workers explore the medicinal properties of metal complexes of transition elements especially Cu (II), Co (II), Ni (II) and Zn (II), they also reported that, these transition metal complexes exhibit good antimicrobial activity against various bacterial and fungal species such sa E. coli, K. pneumoniae, P. aeruginosa, S. aureus, A. niger and C. albicans. Among all Cu (II) metal complexes shows highest antimicrobial activity [6]. Some metal complexes of Cu (III), Fe (III), Pt (IV) Ru (III/II), Os (II) and Ir (II) show redox mediator anti-cancer activity, metal complexes of vanadium show insulin mimetic activity, metal complexes of gallium (III) exhibits moderate anticancer activity [7]. Some mononuclear Nickel (II) metal complexes of 1-((4-hydroxybutylimino) methyl) naphthalen-2-ol, 1-((5-hydroxypentylimino) methyl) naphthalen-2-ol and 1-((6-hydroxyhexylimino) methyl) naphthalen-2-ol show active electrocatalysts for hydrogen evolution reactions using acetic acid and trifluoroacetic acid as the substrates in DMF [8]. Among the Ni^{2+}, Cu^{2+}, Ag^{+}, and Hg^{2+} metal complexes, Ni^{2+} metal complex with ligand N (4-chlorophenyl)-2-(phenylglycyl) hydrazine-1-carbothioamide show good antibacterial activity against Escherichia coli and Klebsiella pneumonia than gentamicin (standard), Staphylococcus aureus and Streptococcus mutans than ampicillin [9]. Nickel (II) metal complexes with three derivatives of carbazolone-based benzhydrazone ligands displayed enhanced cytotoxicity against the cervical and colon cancer cells [10].
By considering the above-mentioned vast types of properties of Nickel metal complexes prompted us to undertake the synthesis of Nickel (II) metal complexes containing azo compound linked 1-Naphthol moiety.

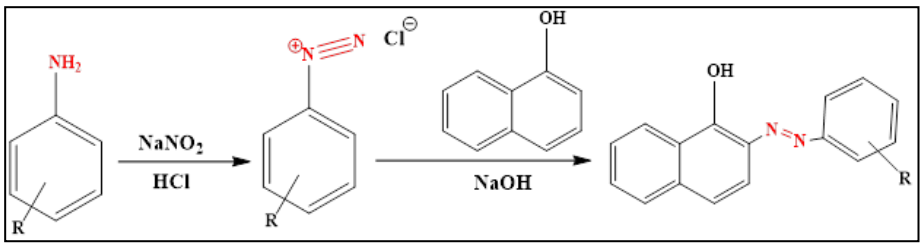
Materials and methods

The chemicals were used in this work is of synthetic grade (S.D. Fine Chem. Ltd, Mumbai, India), recrystallized/redistilled before use it. After the complete 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_a 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.



By using above procedure and scheme total 7 ligands La, L_b, L_c, L_d, L_e, L_f and L_g 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_a	1535.35	1592.72	3244.45	2971.42	1313.40	752.38
2.	L_b	1572.29 1505.66	1697.97 1602.35	3218.38	2948.36	1377.91 1313.45 1290.10	802.92
3.	L_c	1435.69	1594.38	3244.45	2976.65	1365.32	1092.80 1067.80
4.	L_d	1572.29 1505.66	1697.97 1602.35	3265.24	2969.25	1377.91 1313.45 1290.10	885.62
5.	L_e	1435.69	1594.38	3185.21	2971.42	1325.63	1092.79 793.69 754.70
6.	L_f	1536.40	1595.00	3189.25	2972.65	1315.40 1264.74	752.25
7.	L_g	1572.29 1506.66	1637.97 1602.53	3178.98 3060.16	2978.32	1377.91 1313.45 1290.10	829.98

^{1}H NMR spectra of all newly synthesized ligands L_a to L_g 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.

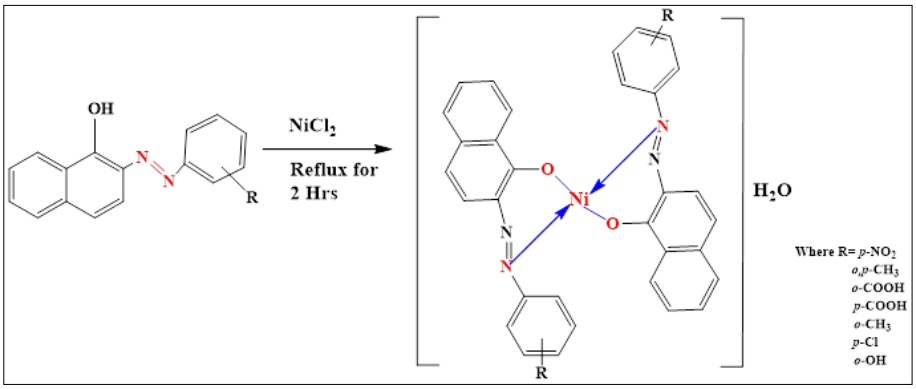
Table 2

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

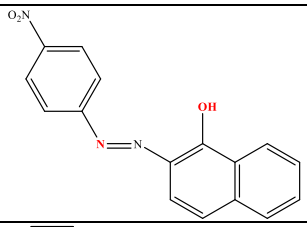
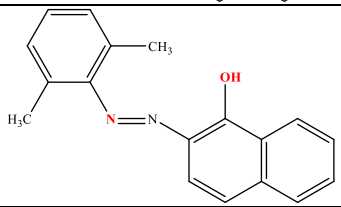
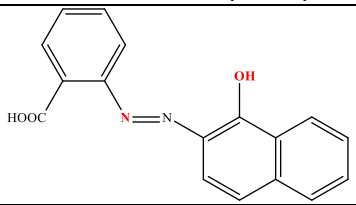
Take 0.20 gm of ligand azo compound in 100 ml beaker; add 15 ml alcohol and 15 ml of water in it. In another beaker 15 ml alcohol and 5 ml of water mixture was taken and dissolves the $NiCl_2$ $6H_2O$ salt in it. After this add the metal chloride solution into the solution of ligand azo compound with 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 were 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.



All the new synthesized metal complexes are dark in colour, having luster and crystalline in nature. Colours are ranges from orange to 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 essential to investigate the different properties of these synthesized nickel 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	Subtotal Mass	Colour	M.P.	Yield
1.		$C_{32}H_{22}N_6NiO_7$ 661.25	C=58.12 % H=3.35 % N=12.71 % Ni=8.88 % O=16.94 %	International orange	198°C	80 %
2.		$C_{36}H_{31}N_4NiO_3$ 626.35	C=69.03 % H=4.99 % N=8.94 % Ni=9.37 % O=7.66 %	Orange red	202°C	79 %
3.		$C_{34}H_{24}N_4NiO_7$ 659.27	C=61.94 % H=3.67 % N=8.50 % Ni=8.90 % O=16.99 %	Cardinal red	212°C	78 %

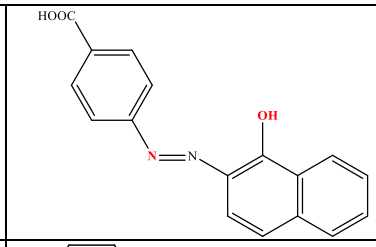
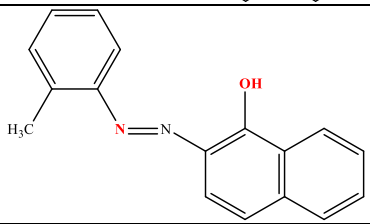
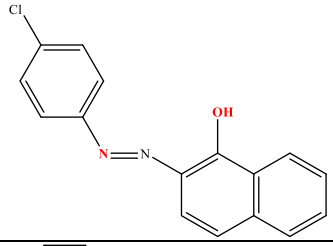
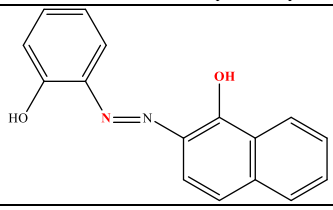
4.		$C_{34}H_{24}N_4NiO_7$ 659.27	C=61.94 % H=3.67 % N=8.50 % Ni=8.90 % O=16.99 %	Mahogany	210°C	75 %
5.		$C_{34}H_{28}N_4NiO_3$ 599.30	C=68.14 % H=4.71 % N=9.35 % Ni=9.79 % O=8.01 %	Pumpkin	192°C	82 %
6.		$C_{32}H_{22}N_4NiO_2Cl_2$ 624.14	C=61.58 % H=3.55 % N=8.98 % Ni=9.40 % O=5.13 % Cl=11.36 %	Persian	212°C	80 %
7.		$C_{32}H_{24}N_4NiO_2$ 555.25	C=69.22 % H=4.36 % N=10.09 % Ni=10.57 % O=5.76 %	Chili red	202°C	79 %

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_a	$[Ni(L_a)_2(H_2O)]$	1519.48	1578 1582	1302.95	3220.40	2958.64
2.	ML_b	$[Ni(L_b)_2(H_2O)]$	1579.40	1669.24	1357.30	3204.08	2946.04
3.	ML_c	$[Ni(L_c)_2(H_2O)]$	1420.42	1542.62	1342.54	3212.84	2954.41 1048.61 (Bending)
4.	ML_d	$[Ni(L_d)_2(H_2O)]$	1522.56 1507.99	1653.62	1349.54	3228.41	2971.51
5.	ML_e	$[Ni(L_e)_2(H_2O)]$	1404.65	1555.54	1300.14	3143.84	2968.84 770.50 (Bending)
6.	ML_f	$[Ni(L_f)_2(H_2O)]$	1497.38	1524.84	1287.84 1260.04	3178.87	2969.05
7.	ML_g	$[Ni(L_g)_2(H_2O)]$	1538.23 1502.96	1606.79	1356.84 1315.10	3153.09 3062.06	2975.90

Conclusion

Azo compounds i.e. ligands containing 1-Naphthol structure was successfully 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 structure were used as ligand for the formation of metal complexes of Ni metal ions. Definitely further research looked-for complete optimization and to discover various properties of such type of metal complexes, however 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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