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Synthesis and Antimicrobial Activities of Cobalt (II) and Nickel (II) Schiff Base Complexes Derived from 3,4-Methylenedioxy Naphthaldehyde (Naphtho [1,2-D][1,3] Dioxole-5-Carbaldehyde)

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ABSTRACT

Schiff base complex of cobalt(II) and nickel(II) with 3,4-methylenedioxy naphthaldehyde (naphtha[1,2-d][1,3] dioxole-5-carbaldehyde have been synthesized in methanol medium. The formation of the complexes is endothermic processes. The ligand was characterized by melting point, elemental analysis, absorption spectra and antimicrobial activity while the complexes were characterized by melting point, absorption spectra. A simple and sensitive spectrophotometric method was developed for Schiff base complex of cobalt (II) and nickel (II) with 3,4-methylenedioxy naphthaldehyde (naphtha[1,2-d][1,3] dioxole-5-carbaldehyde. The optimum condition for complete colour development has been established. The stability constant, dissociation constant & change in free energy of cobalt (II) and nickel (II) have been determined by Job's variation & mole ratio method indicates that the M:L is 1:2. Tolerance limit of diverse ions in the determination of copper (II) and nickel (II) with 3,4-methylenedioxy naphthaldehyde (naphtha[1,2-d][1,3] dioxole-5-carbaldehyde is investigated.

INTRODUCTION

Schiff base metal complexes play an important role of coordination chemistry. It has a lot of applications in different fields. It also has various applications in biology, industries, role in catalysis and also used in the synthesis of organic compounds[1-4]. Complex of Schiff base also has importance as biomedical, analytical, antimicrobial reagents[5-6]. The biofunctional activity of metal bonded complexes in medicine and chemotherapy has to spur the growth of interest in the scientific world in the past decades after the successful clinical use of cisplatin as an anticancer drug[7-10]. Most of the metal being unnatural to human body because of having no effective mechanism for its rejection and toxic behavior there has been rapid expansion in research and development of novel metal based drugs with improved pharmacological properties[11-12]. Metal complex also has interest in research in medicinal science for immense biological activities[13-14] . Novel antimicrobial drugs are demand for various diseases[15-17]. They have also various catalytic functions due to chelating nature[18]. Azomethine linkage in Schiff base is the responsible part of biological activity. Drug has better activity in complex form[19,20]. Schiff bases and their first row transition metal complex such as Cu(II), Co(II) has fungicidal, bactericidal, antiviral and antitubercular activity[21-27]. Due to the biological role of cu(II) & its synergetic activity with drug[30]. The antifungal & antibacterial properties of a range of cu(II) complexes have been evaluated against several pathogenic fungal & bacteria[31-33]. There has been tremendous interest in studies pertaining to inter action of transition metal complexes with nucleic acid[34-36]. Copper(II) plays a significant role in naturally occurring biological systems as well as pharmacological agents[37-39].

Thiosemicarbazone is an analog of a semicarbazone which contain S atom in place of oxygen atom. Thiosemicarbazones are known to have anti-viral & anti-cancer usually mediated through binding to copper or iron in cells. Thiosemicarbazone is of special importance because of their versatile biological and pharmacological activities. They have the application in drug development for the treatment of central nervous disorders of bacterial infection as well as analgesic and anti-allergenic agent. Thiosemicarbazones are potent intermediate for the synthesis of pharmaceutical and bioactive materials and they are used extensively in the medicinal chemistry. Thiosemicarbazone derivatives have wide range of biological activity antimicrobial[40-46], antitumour[47-49], sodium channel blocker[50], anticancer[51-52], antitubercular[53-54], antiviral[55], antifungal[56-58], antibacterial[59]. It also has herbicidal and anti acetylcholinesterase activities[60]. It has fungicidal and pesticidal properties[61-62].

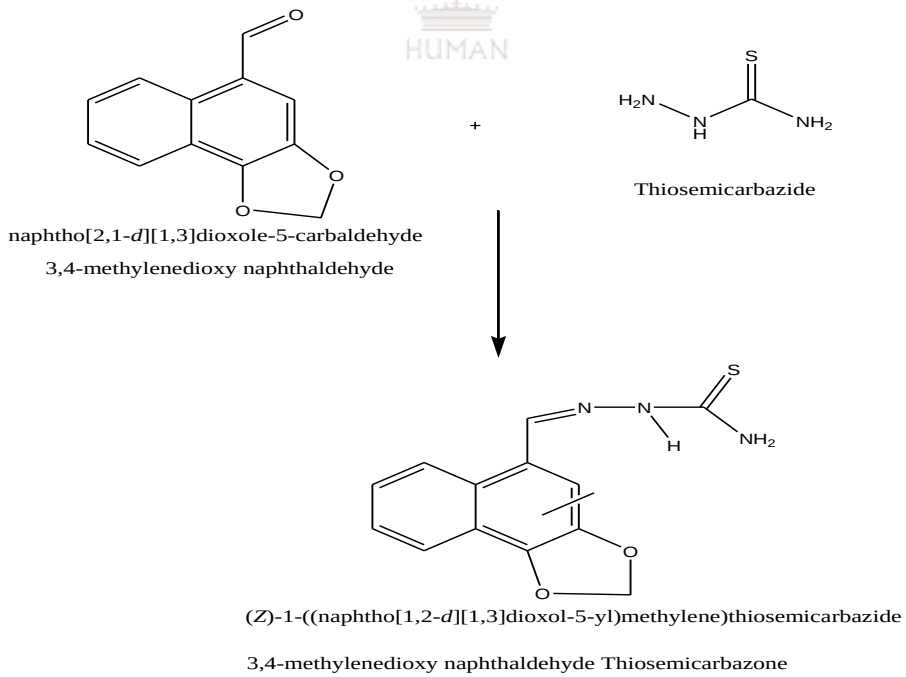
Thiosemicarbazones are used as influenza drugs[63]. Thiosemicarbazone also find wide applications as an analytical reagent for various metal ions[64]. Thiosemicarbazones are complexing reagent because they form highly stable and intensely coloured complexes. 2-Hydroxy-5-methyl acetophenone thiosemicarbazone has been used as an analytical reagent for metal ions[65].

MATERIALS AND METHODS

All chemical and solvents used were of analytical grade. An Elico pH meter LI-610 is used for the pH measurements. An Elico UV-visible spectrophotometer model UV-SL-164 equipped with 1 cm quartz cell used for spectrophotometric measurements taken on the instrument. Elemental analysis and antimicrobial activity were done in Laboratory approved by central government for AGMARK.

SYNTHESIS AND CHARACTERISATION OF 3,4-METHYLENEDIOXY NAPHTHALDEHYDE

Synthesis of 3,4-Methylenedioxy Naphthaldehyde (3,4-MNAP)



naphtho[2,1-*d*][1,3]dioxole-5-carbaldehyde

3,4-methylenedioxy naphthaldehyde

Thiosemicarbazide

(*Z*)-1-((naphtho[1,2-*d*][1,3]dioxol-5-yl)methylene)thiosemicarbazide

3,4-methylenedioxy naphthaldehyde Thiosemicarbazone

The crude product is crystallized in methanol. The recrystallized product is yellowish solid has melting point 145ºC and molecular weight by formula is 273.

Characterization of 3,4-METHYLENEDIOXY NAPHTHALDEHYDE

Absorption Spectra of 3,4-Methylenedioxy Naphthaldehyde (3,4-MNAP)

Absorption Spectra of 3,4-MNAP was recorded against a blank solution containing buffer (pH4) . Absorption spectra was recorded in the wave length range 220 nm to 500 nm. It shows an absorption maximum at 360 nm wavelength the molar absorptivity of 3,4-MNAP is 0.977301 x 10^3 $L.mol^{-1}.cm^{-1}$.

Elemental Analysis of 3,4-Methylenedioxy Naphthaldehyde (3,4-MNAP)

The elemental analysis of 3,4-MNAP was done in Laboratory approved by Central Government for AGMARK. It shows the result of elemental analysis in **Table 1**.

Validity of Beer's Law and Composition of Complex

For the study of Beer's law, the solutions were prepared which containing different amounts of

Cu (II) ,same amount of ligand pH 5 and different amounts of Ni (II) ,same amount of ligand pH 6 The composition of the Cu (II)-metal complex & Ni (II)-metal complex is found to be 1:2. It was determined by studying Job's method. The ratio of metal ion to ligand molecule in the coloured complex was found to be 1:2 composition of complex.

Antimicrobial Activity of 3,4-Methylenedioxy Naphthaldehyde (3,4-MNAP)

The Antimicrobial activity of 3,4-MNAP was done in Laboratory approved by Central Government for AGMARK. It shows the result of Antimicrobial activity in **Table 2.**

Physico-chemical Characteristic of 3,4-Methylenedioxy Naphthaldehyde (3,4-MNAP)

Physico-chemical and analytical characteristic of transition metal complex of ligand was studied and given in **Table 4** and Tolerance limit of diverse ions in the determination of ligand shown in **Table No. 5**

RESULT AND DISCUSSION

Table No. 1. Elemental Analysis of 3,4-MNAP

Sr. No.	Chemical Analysis	Percentage Found	Percentage Expected
1)	Carbon	57.14 %	56.99 %
2)	Hydrogen	04.03 %	03.84 %
3)	Oxygen	11.72 %	12.05 %
4)	Nitrogen	15.38 %	16.34 %
5)	Sulphur	11.72 %	10.86 %

Table No. 2. Antimicrobial Activity of 3,4-MNAP

Sr. No.	Antimicrobial	Activity
1)	Klebsiella Pneumoniae	Nil
2)	Vibriae Cholerease	Nil
3)	Bacillus Megaterium	Nil
4)	Salmonella Typhi	Nil
5)	Shigella Flexneri	Nil

Table 3. Experimental Result & Physical data of Cu (II) & Ni (II)- 3,4-MNAP

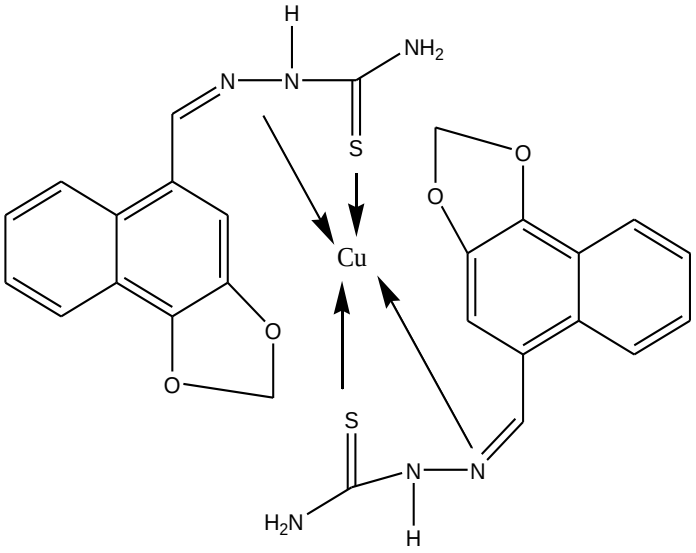
Code No	Compound M.P. (°C)	Colour	Molecular weight by formula gm/mole	Yield
3,4-MNAP	145 °C	Yellow	273.00	78 %
Cu (II)- 3,4-MNAP	167 °C	Bluish white	336.55	70 %
Ni (II)- 3,4-MNAP	175 °C	Greenish White	331.69	67 %

Table. 4. Physico-Chemical and Analytical Characteristic of Cu (II) & Ni (II)- 3,4-MNAP

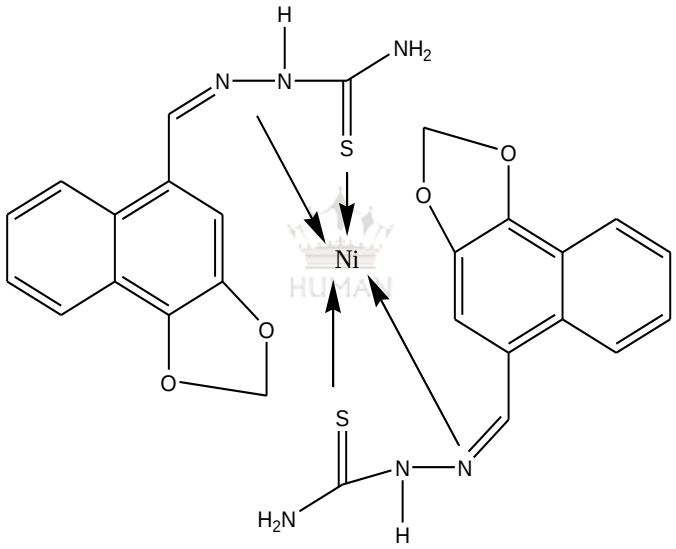
Sr. No.	Characteristics	Result	
		Cu (II)- 3,4-MNAP	**Ni (II)- 3,4-MNAP**
1)	Absorption Spectra	400 nm	380 nm
2)	Molar absorptivity	0.99243×10^{3} Lit. mol^{-1}. cm^{-1}	0.80351×10^{3} Lit. mol^{-1}. cm^{-1}
3)	pH range (optimum)	4.0	6.0
4)	Reagent required for maximum complexation	0.275 ml	0.325
5)	pKa	5.9384×10^{8}	4.99928×10^{8}
6)	Beer's law validity range (ppm)	5 ppm	8 ppm
7)	Composition of complex (M: L)	1:2	1:2
8)	Stability Constant	4.9043031×10^{7}	5.32097×10^{7}
9)	Dissociation Constant	5.92576×10^{-8}	5.00215×10^{-8}
10)	Change in free energy	- 45.97 KJ/mole	- 51.03 KJ/mole
11)	Sandell's Sensitivity (µg/cm^2)	0.003194 µg /cm^2	0.004114µg /cm^2

Table No. 5 Tolerance limit of diverse ions of Cu (II) & Ni (II)- 3,4-MNAP

Sr. No.	Metal Ions	Salt	Interference	
			Cu (II)- 3,4-MNAP	**Ni (II)- 3,4-MNAP**
1)	Mg (II)	$MgSO_4$	46	93
2)	Ca(II)	$CaCl_2.2H_2O$	10	92
3)	Cd (II)	$CdCl_2$	93	05
4)	Mn (II)	$MnCl_2$	32	Interferes
5)	Co (II)	$CoSO_4$	52	67
6)	Ce (IV)	$Ce(SO_4)_2$	07	32
7)	Ba (II)	$BaCl_2$	Interferes	65
8)	Cr (III)	$K_2Cr_2O_7$	20	23
9)	Hg (II)	$HgCl_2$	94	65
10)	Ti (V)	K-titanyl oxalate	Interferes	Interferes
11)	Ni (II)	$NiCl_2$	Interferes	84
12)	Sn (II)	$SnCl_2$	27	Interferes
13)	Na (I)	NaCl	66	10
14)	Pb (II)	$PbSO_4$	Interferes	32
15)	V (V)	V_2O_5	22	91
16)	Zn (II)	$ZnSO_4$	39	87
17)	Al (III)	$AlCl_3$	21	06
18)	Pd (II)	$PdCl_2$	92	Interferes
19)	K(II)	KCl	10	65



Structure of Cu (II) 3,4-Methylenedioxy naphthaldehyde (3,4-MNAP)



Structure of Ni (II) 3,4-Methylenedioxy naphthaldehyde (3,4-MNAP)

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