

# SYNTHESIS AND BIOLOGICAL STUDIES OF SALICYLHYDRAZONE AND THEIR COMPLEXES WITH COPPER AND NICKEL

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## ABSTRACT

A pair of dihydrazone Schiff base ligands was prepared by refluxing salicyldehyde with malonyl dihydrazone or phthanoyl dihydrazone in methanolic medium in the molar ratio 2:1. When these ligands were allowed to reaction with Cu (II), Ni (II) salts, complex as of the type ML were obtained. Ligands and complexes were characterized on the basis of elemental analysis, spectral, conductance and magnetic studies.

**Key words:** - Copper (II) and nickel (II) complexes, salicylhydrazone.

The hydrazides and hydrazones metal complexes have important role in the field of coordination chemistry. Various hydrazides and their derivatives possess antibacterial activity against various micro-organism in addition they also possess an antifungal<sup>1,2</sup>, insecticidal<sup>3</sup> and anti-inflammatory<sup>4</sup> properties.

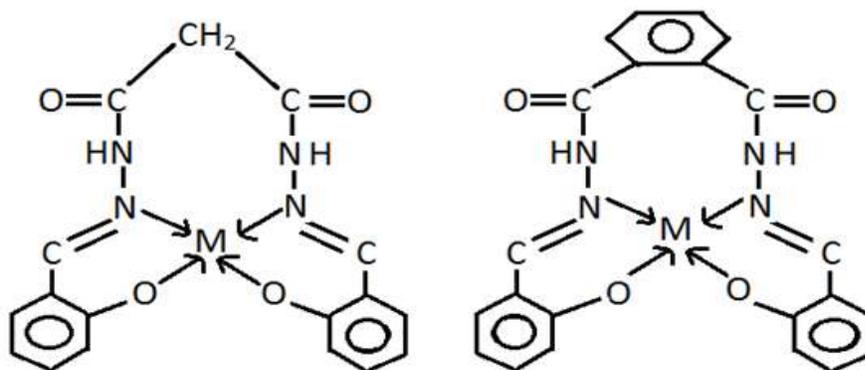
The present work deals with synthesis of some chemotherapeutically important salicylhydrazone complexes of copper (II) and nickel (II). The synthesized complexes are characterized and their biological activities have also been evaluated.

### Synthesis of salicyldehyde malonyl dihydrazone (SMDH):-

Malonyl dihydrazide (2.65 g, 2 mmol) was dissolved in 25 ml methanol and (4.88 g, 4 mmol) of salicyldehyde was added. The resultant mixture was refluxed for Ca.3h on a water bath. A grayish solid was re-crystallized from ethanol and dried over calcium chloride in vacuum dessicator under reduced pressure.

### Synthesis of salicyldehyde phthanoyl dihydrazone (SPDH):-

Phthanoyl dihydrazide (3.90 g, 2 mmol) was dissolved in 20 ml ethanol and salicyldehyde (3.66 g, 3 mmol) was added. The resultant mixture was refluxed for ca. 4h on a water bath. The yellow solid obtained which is filtered washed with ethanol and dried water reduced pressure.



(i) SMDH

(ii) SPDH

Structure of ligands

### Synthesis of copper (II) and nickel (II) complexes:-

*Synthesis of salicyldehyde malonyl dihydrazone copper (II) and nickel (II) complexes:-*

Salicyldehyde malonyl dihydrazone (10.14 g, 3 mmol) was dissolved in 10 ml, dimethyl formamide solution and copper (II) (3.75 g, 2 mmol) or nickel (II) nitrate (3.65 g, 2 mmol) was dissolved in 20 ml methanol. Both these solutions were mixed and the reaction mixture was refluxed for ca. 12 h on water bath. The above contents for cooled and kept overnight, on concentration the complex

was separated out in the form of Green crystals of Cu (II) and Yellow crystals of Ni (II). The crystals were filtered, washed with water, alcohol and finally with ether and done dried in vacuo.

### Synthesis of salicyldehyde phthanoyl dihydrazone copper (II) and nickel (II) complexes:-

Salicyldehyde phthanoyl dihydrazone (12.60 g, 3 mmol) was dissolved in 20 ml ethanolic solution of copper (II) (3.75 g, 2 mmol) or nickel (II) nitrate (3.65 g, 2 mmol). Both the solutions were mixed and the reaction mixture was refluxed on a water bath for ca. 16 h. A yellow crystalline product (Ni (II)) was obtained which was filtered, washed with DMF, ethanol and ether, Or, A Green crystalline product (Cu (II)) was obtained which was filtered, washed with DMF, ethanol and ether the crystals were finally dried in vacuo.

The physico-chemical properties of the synthesized ligands and copper (II) and nickel (II) complexes given in table-I.

**Table – I**

#### PROPERTIES OF LIGANDS AND ITS METAL COMPLEXES

	m.w/m.p. (°C)	Elemental analysis (%) Calculated (Found)			
		C	H	N	M
$C_{17}H_{16}N_4O_4$	338/ 290	(59.80) 60.35	(4.65) 4.73	(16.46) 16.56	
$C_{22}H_{18}N_4O_4$	402/ 305	(64.90) 65.67	(4.40) 4.47	(13.85) 13.93	
$Cu(C_{17}H_{14}N_4O_4)$	400/ 180 <sup>d</sup>	(50.65) 51.00	(4.40) 3.50	(13.85) 14.00	(15.81)15.92
$Cu(C_{22}H_{16}N_4O_4)$	464/ 185 <sup>d</sup>	(56.70) 57.01	(3.33) 3.45	(12.85) 12.90	(13.67)13.72
$Ni(C_{17}H_{14}N_4O_4)$	395/ 179 <sup>d</sup>	(51.40) 51.77	(3.48) 3.55	(14.13) 14.21	(14.80)14.90
$Ni(C_{22}H_{16}N_4O_4)$	459/ 182 <sup>d</sup>	(57.18) 57.39	(3.38) 3.47	(12.05) 12.17	(12.69)12.75

The bond between 3500-3060  $cm^{-1}$  and a strong band near 1630 indicates the formation of hydrazone due to the condensation of acid hydrazide with aldehyde and ketone. The N-H deformation occur<sup>5</sup> between 1300- 1260  $cm^{-1}$  and the bands of amide group in the region of 1630- 1600  $cm^{-1}$  in due to C=N stretching vibration in the ligands in the hydrazones on chelation with metal the normal frequency of amide I bond is shifted to lower frequency region 30-10 $cm^{-1}$  while the amide II the frequency increases<sup>6,7</sup> by 10-15  $cm^{-1}$ . The coordination of amide oxygen to the metal ion is also supported by the above changes in the amide group vibration.

The lowering in the frequency by 30-15  $cm^{-1}$  or more C=N stretching vibration (1630-1610  $cm^{-1}$ ) with a decreases in intensity of bond also suggested that nitrogen of azomethine group is co-ordinate to the metal ion<sup>8,9</sup>. Some new bands in the far IR region (620-510  $cm^{-1}$ ) and (470-440 $cm^{-1}$ ) indicates the formation of some new (Cu-O and Ni-O) and (Cu-N and Ni-N) and other bands in the metal chelates.

For biological studies the minimum concentration of the compound preventing the detectable growth is taken as a measure of biological activity. It is given in table –II.

**Table-II**

#### BIOLOGICAL ACTIVITIES OF SYNTHESIZED LIGANDS AND ITS COMPLEXES.

Name of the ligand/ complex	Zone of inhibition (MIC in $\mu g/ml$ )			
	S. aureus	E. coli	A. niger	C. Albicans
$C_{17}H_{16}N_4O_4$	100	100	100	100
$C_{22}H_{18}N_4O_4$	100	100	100	90
$Cu(C_{17}H_{14}N_4O_4)$	65	17.5	30	30
$Cu(C_{22}H_{16}N_4O_4)$	40	17.5	30	65
$Ni(C_{17}H_{14}N_4O_4)$	64	18	28	28
$Ni(C_{22}H_{18}N_4O_4)$	39	18	28	64

#### REFERENCES:-

- H. C. Rai and Kundan Kumar J. Phys. Sci., 3, 29(2011) .
- Magnus gustafsson, Andreas Fischer , Andrey Ilyukhins, Mikhail Malitrick and Pre Nordblad ; inorg chem ,49, 5339(2010).
- Yüksel Altun, Fitnat Köseoğlu, Havva Demirelli, İbrahim Yılmaz, Alaattin Çukurovalı and Nusret Kava. Braz. Chem. Soc. 20, 299, (2009).
- H. C. Rai, Priyanka and P.K. Ghosh, Asian J chem . 22 , 7799(2010).
- Umendra Kumar and Sulekh Chandra E-Journal of Chemistry, 7(4), 1238,(2010).
- N. Raman, S. R. Johnson, A. Sakthivel, J. Coord. Chem. 62,691(2009).
- D. P. Singh, R. Kumar, V. Malik, P. Tyagi, Transition Met. Chem.32, 1051,(2007)
- W. Ma, Y. Tian, S. Zhang, J. Wu, Transition Met. Chem.,31 97 (2006)
- D. P. Singh, Vandana Malik, Ramesh Kumar and Krishan Kumar J. Serb. Chem. Soc., 75(6) (2010) 763.