

## Potential of the fungicidal activity (2-hydroxynaphthalen-1-yl) (phenyl) methanone by metal chelation

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### Abstract

The reaction of  $\beta$ -naphthol with phenylcyanide in the presence of HCl have been studied and the product (2-hydroxynaphthalen-1-yl)(phenyl) methanone have been isolated. Divalent metal complexes of Co(II), Ni(II), Zn(II) and Pd(II) have been synthesized and tentative structures were proposed for these complexes based on elemental analysis, electrical conductivity, UV-Vis, IR, <sup>1</sup>HNMR, <sup>13</sup>CNMR. The spectra studies suggested bidentate co-ordination through the carbonyl and deprotonated hydroxyl group. The formula determination by method of continuous variation suggested a metal: ligand ratio of 1:2. A tetrahedral geometry has been suggested for the complexes. Preliminary in vitro tests fungicidal activity show that all prepared compounds display good activity to *Gibberella*, *Cercospora arachidicola*, *Physalospora piricola* and *Fusarium oxysporum*. Moreover, the palladium complex showed a higher inhibition percentage than other derivatives.

**Keywords:** Ligands; complexes; spectra; antibacterial studies; tetrahedral geometry.

### Introduction

Research interest in coordination chemistry derives its utility in several biological and industrial processes (Agarwal *et al.*, 2006). Recent advances in the pharmacological and clinical applications of metal complexes have stimulated their design and synthesis (Beraldo, 2004). The deep studies on new chemotherapeutic chelating agents are attracting the attention of chemist and biochemists (Boccarelli *et al.*, 2007). Chelating agents and their complexes have received most of the attention because of the semiconductive (Werkman *et al.*, 2008) spectroscopic (Muñoz *et al.*, 2009) and thermal (Al-Maydama *et al.*, 2009) properties as well as being used as anticonvulsant (Pandeya *et al.*, 2009), antibacterial, antifungi (Rodríguez-Argüelles *et al.*, 2009), antitumor (Ainscough *et al.*,

2008), transistors (Ando *et al.*, 2007), antiamebic (Husain *et al.*, 2008), anti-HIV (Sriram *et al.*, 2005), antimicrobial (John *et al.*, 2004) and antiviral (Chandra and Gupta, 2005) activities. The increase in the use of chelates and chelating agents has been accompanied by considerable progress in the understanding of their properties and in suggesting new and effective chelating agents for future application. This paper describes the potentiation of fungicidal activity(2-hydroxynaphthalen-1-yl) (phenyl)methanone by metal chelation

### Materials and methods

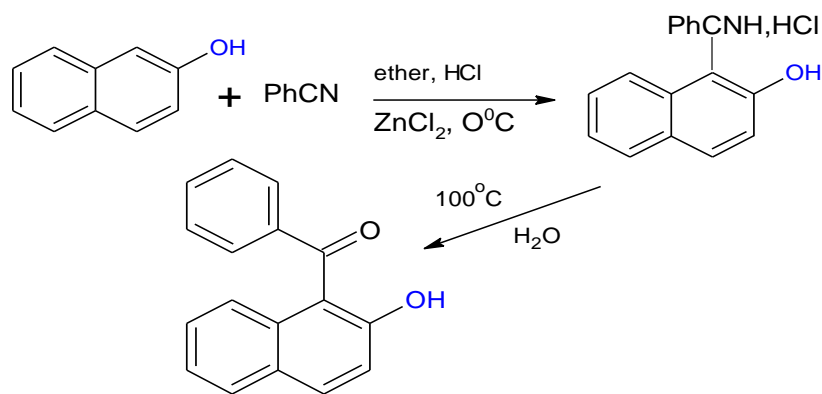
All reactions were carried out under strictly anhydrous conditions. The elemental analyses were determined on a Coleman C20 automatic analyzer. Conductivity was measured with a Digital conductivity meter D-511. The

electronic spectra were recorded on a Perkin-Elmer UV-Vis spectrophotometer. Infrared spectra were recorded on a Nicolet Raman 950 spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a QE-300 Perkin-Elmer spectrometer.

**Preparations of 2-hydroxynaphthalen-1-yl(phenyl)methanone**

β-naphthol (0.01mol) was dissolved in 100cm<sup>3</sup> sodium dried ether. Phenyl cyanide (0.01mol) was added. (0.001mol) of Zinc chloride was also added. HCl was generated and bubbled through the

reaction mixture for 4 hours maintaining the temperature at 0°C. The intermediate formed was left for 12 hours after which 100cm<sup>3</sup> of hot distilled water was added. This was accompanied by heating for 1 hour. The resulting solution was allowed to cool. A creamy precipitate was formed on cooling. The product was recrystallized in aqueous ethanol, air-dried and stored. Equation of reaction is shown in scheme 1.



Scheme 1: synthesis of (2-hydroxynaphthalen-1-yl)(phenyl)methanone

**Preparation of the metal complexes**

0.01mol of (2-hydroxynaphthalen-1-yl)(phenyl)methanone was dissolved in 10cm<sup>3</sup> ethanol and added to 0.005 mol of the metallic salt (cobalt acetate, nickel acetate, zinc acetate and palladium acetate). The solution was refluxed for 2 hours. The precipitate formed after cooling was recrystallized in methanol. The yield was recorded.

**Results and Discussion.**

Complexes are soluble in dimethylformamide, dimethylsulphoxide, nitrobenzene, tetrahydrofuran.

Conductivity data measurement in DMF

data fall within the range of 0.186 - 0.189 Ω<sup>-1</sup>cm<sup>-1</sup> indicating the complexes have considerable polarity.

**Electronic spectra**

The electronic spectra of the ligand and complexes were recorded at 300K. The solvent, absorption region and band assignments are shown in Table 2. The electronic spectra of the ligand /complexes shows a broad band at 38370, 36080, 36040, 36420 and 36540cm<sup>-1</sup>, which are assigned intraligand charge transfer (ILCT), due to weak transition of oxygen lone pair in ketones (n→π\*). The bands 31760, 31200 and 31750 and 31740cm<sup>-1</sup> are assigned ligand to metal charge transfer

(LMCT), these are absent in the electronic spectra of the ligand. The cobalt absorption bands at 16120, 22320 $\text{cm}^{-1}$  are assigned (d-d) transition  ${}^4T_2 \leftarrow {}^4A_2$  and  ${}^4T_{1(F)} \leftarrow {}^4A_2$ . The nickel absorption bands at 22220 and 16440 $\text{cm}^{-1}$  are assigned  ${}^3T_2 \leftarrow {}^3T_1$  and  ${}^3T_{1(F)} \leftarrow {}^3T_1$ , (d-d) transition. These bands are absent in the ligand, zinc and palladium complex. The vibrational frequencies have been obtained between 4000 -100  $\text{cm}^{-1}$  and possible assignments have been made. The following features of the IR spectra are of interest:

1. The weak broad band in the 3530 $\text{cm}^{-1}$  region which has been attributed to  $\nu(\text{OH})$  is present in the ligand but absent in the spectra of the complexes. This fact implies deprotonated OH in bonding.
2. The shift of the C=O stretching frequencies from 1725 $\text{cm}^{-1}$  in the ligand to 1695, 1690, 1690, 1690 $\text{cm}^{-1}$  lower frequencies in the complexes suggest that C=O is involved in chelation.
3. The bands 425, 405, 450 and 460 $\text{cm}^{-1}$  typically of the 1,3-diketones  $\nu(\text{M-O})$  are present in the complexes but absent in the ligand. This is usually interpreted as suggestive of bonding through oxygen atoms. IR spectral evidence therefore suggests that the ligand bond to the metal ion through the carbonyl and the deprotonated hydroxyl group.

Feature of interest in  ${}^1\text{H}$ NMR

spectra (Table 4): the chemical shift at 13.8 present in the ligand is assigned hydroxyl proton. This band is absent in the spectra of the complexes, suggesting deprotonation of the hydroxyl group during complexation.

Feature of interest in  ${}^{13}\text{C}$ NMR spectra data (Table 5): the chemical shift value at 208.8ppm in the ligand is assigned C=O. This band is shifted downfield (188.4, 182.6, 189.4, 185.7ppm) in the spectra of the complexes suggesting that carbonyl group takes part in complexation. The method of continuous variation was used to determine the metal:ligand ratio. The metal:ligand ratio of 1:2 was obtained for the complexes.

### **Biological Activity**

Preliminary in vitro tests for fungicidal activity of ligand and complexes have been carried out by the fungi growth inhibition method<sup>5</sup>. These compounds are dissolved in DMF at a concentration of 50 ppm. The data are summarized in Table 6, and show that all compounds display certain activity to *Physalospora piricola* at a low concentration. Moreover, the palladium complex are more active than the other derivatives. In addition, the palladium complex showed the highest inhibition percentage for *Physalospora piricola* (85.9%) in vitro.

**Table 1.** Physical and analytical data (2-hydroxynaphthalen-1-yl)(phenyl)methanone and its divalent metal complexes.

Compound	Reaction time	Colour	M.P (0°C)	Yield %	Elemental analysis Found(calcd.)%			
					C	H	O	M
[LH]	4	Creamy	86	49	82.21 (82.24)	4.86 (4.87)	12.87 (12.89)	- -
[Co(L) <sub>2</sub> ]	-	brown	180	57	65.83 (73.78)	3.52 (4.01)	15.92 (10.65)	14.68 (11.56)
[Ni(L) <sub>2</sub> ]	-	Orange	184	46	73.80 (73.81)	4.00 (4.01)	11.57 (11.57)	10.60 (10.61)
[Zn(L) <sub>2</sub> ]	-	Orange	188	44	72.92 (72.93)	3.97 (3.96)	11.40 (11.43)	11.66 (11.68)
[Pd(L) <sub>2</sub> ]	-	Orange	186	42	67.94 (67.95)	3.68 (3.69)	10.64 (10.65)	17.69 (17.71)

L = (2-hydroxynaphthalen-1-yl)(phenyl)methanone

**Table 2:** Electronic spectra

Compound	Solvent	Absorption, cm <sup>-1</sup>	Band assignment
[LH]	DMSO	38370	ILCT
[Co(L) <sub>2</sub> ]	DMSO	36080, 31760, 22320, 16120.	ILCT, LMCT, <sup>4</sup> T <sub>2</sub> ← <sup>4</sup> A <sub>2</sub> , <sup>4</sup> T <sub>1(F)</sub> ← <sup>4</sup> A <sub>2</sub>
[Ni(L) <sub>2</sub> ]	DMSO	36040, 31200, 21220, 16440	ILCT, LMCT, <sup>3</sup> T <sub>2</sub> ← <sup>3</sup> A <sub>1</sub> , <sup>3</sup> T <sub>1(F)</sub> ← <sup>3</sup> T <sub>1</sub>
[Zn(L) <sub>2</sub> ]	DMSO	36420, 31750,	ILCT, LMCT
[Pd(L) <sub>2</sub> ]	DMSO	36540, 31740.	ILCT, LMCT

L = (2-hydroxynaphthalen-1-yl)(phenyl)methanone

**Table 3.** IR spectra data (cm<sup>-1</sup>)

Compound	cm <sup>-1</sup>					
	ν(-C=C-) aromatic	ν(C-H) aromatic	ν(O-H)	ν(C=O)	ν(C-H) aliphatic	ν(M-O)
[LH]	1555(v)	3065(m)	3530 (b)	1725(s)	2960(s)	-
[Co(L) <sub>2</sub> ]	1565(v)	3022(m)	-	1695(s)	2850(s)	425(w)
[Ni(L) <sub>2</sub> ]	1550(v)	3082 (m)	-	1690(s)	2860(s)	405(w)
[Zn(L) <sub>2</sub> ]	1565(v)	3081(m)	-	1690(s)	2840(s)	450(w)
[Pd(L) <sub>2</sub> ]	1552(v)	3100 (m)	-	1690(s)	2860(s)	460(w)

v, variable; m, moderate; b, broad; s, strong; w, weak.

L = (2-hydroxynaphthalen-1-yl)(phenyl)methanone

**Table 4:** <sup>1</sup>HNMR data (δ, ppm)

Compound	Aromatic protons	Hydroxyl protons
[LH]	7.2-8.0(m)	13.8(s)
[Co(L) <sub>2</sub> ]	7.2-8.0(m)	-
[Ni(L) <sub>2</sub> ]	7.2-8.0(m)	-
[Zn(L) <sub>2</sub> ]	7.2-8.3(m)	-
[Pd(L) <sub>2</sub> ]	7.3-8.7(m)	-

L = (2-hydroxynaphthalen-1-yl)(phenyl)methanone m, multiplet; s, singlet;

**Table 5:** <sup>13</sup>CNMR spectra data (δ, ppm)

Compound	C domain	CH	C=O
(LH)	158-162	125-139	208.8
[Co(L) <sub>2</sub> ]	157-162	121-138	188.4

[Ni(L) <sub>2</sub> ]	162-164	121-138	182.6
[Zn(L) <sub>2</sub> ]	159-162	122-138	189.4
[Pd(L) <sub>2</sub> ]	158-162	121-138	185.7

L = (2-hydroxynaphthalen-1-yl)(phenyl)methanone

**Table 6:** Fungicidal activities of ligand and complexes.

Compound	Inhibition Ratio (%) (50ppm)				
	LH	[Co(L) <sub>2</sub> ]	[Ni(L) <sub>2</sub> ]	[Zn(L) <sub>2</sub> ]	[Pd(L) <sub>2</sub> ]
<i>Gibberela</i>	11.5	56.4	54.8	47.8	67.9
<i>Cercospora arachidicola</i>	31.4	60.6	67.4	49.2	75.3
<i>Physolospora piricola</i>	40.3	66.9	69.4	59.3	85.9
<i>Fusarium oxysporum</i>	18.4	45.7	47.2	37.2	78.4

L = (2-hydroxynaphthalen-1-yl)(phenyl)methanone

## Conclusion

The reaction of β-naphthol with phenyl cyanide in the presence of HCl have been studied and the product (2-hydroxynaphthalen-1-yl)(phenyl)methanone have been isolated. Divalent metal complexes of Co(II), Ni(II), Zn(II) and Pd(II) have been synthesized and tentative structures were proposed for these complexes based on elemental analysis, electrical conductivity, UV-Vis, IR, <sup>1</sup>HNMR, <sup>13</sup>CNMR. The spectra studies suggested bidentate coordination through the carbonyl and deprotonated hydroxyl group. The

formula determination by method of continuous variation suggested a metal:ligand ratio of 1:2. A tetrahedral geometry has been suggested for the complexes. The structures for the metal complexes are shown in Figure 1. Preliminary *in vitro* tests fungicidal activity showed that all prepared compounds display good activity to *Gibberela*, *Cercospora arachidicola*, *Physolospora piricola* and *Fusarium oxysporum*. Moreover, the palladium complex showed a higher inhibition percentage than other derivatives.

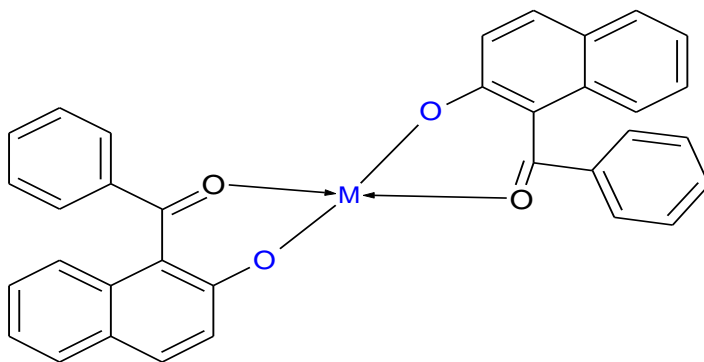


Figure 1: Suggested structures of metal complexes  
M= Co, Ni, Zn or Pd

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