

## Synthesis and antimicrobial activity of chalcone derivatives of ni (ii) and co (ii) complexes-an in vitro evaluation

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### ABSTRACT

A series of metal complexes of Ni (II) and Co (II) have been synthesized with biologically active ligands. These ligands were prepared by the condensation of substituted 2'-Hydroxyacetophenones and pyridine 2-carboxaldehyde and pyrrole 2-carboxaldehyde. The structures of the complexes have been proposed by analytical data, conductivity measurement, magnetic moment, IR, <sup>1</sup>H NMR spectra and thermal studies. Analytical data confirmed 1:2 (metal:ligand) stoichiometry and the spectral data suggest that all Ni(II) and Co(II) complexes have octahedral geometry.

*In vitro* antimicrobial activity of all synthesized compounds has been evaluated against four bacterial strains and four fungal strains. The compounds show net enhancement in activity on coordination of metals with ligand.

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### KEYWORDS

Chalcones;  
Transition metal complexes;  
Spectral study and anti-  
microbial activity.

### INTRODUCTION

Chalcones are open chain flavonoids in which two aromatic rings bound by an  $\alpha$ - $\beta$ -unsaturated carbonyl groups. The importance of chalcones lies in the wide range of pharmacological activities of the class such as antitumor<sup>[1,3]</sup>, antimalarial<sup>[2]</sup>, anti-inflammatory<sup>[4]</sup>, antilishmanial<sup>[5]</sup> and antimicrobial<sup>[6]</sup>. 2'-Hydroxychalcones known to be pharmacologically active, possess coordinating sites and are expected to form complexes with different metal ions. From the literature survey it is found that the chelating tendency of the compounds generally increases biological activity of these compounds than the free ligand.

We report here the synthesis of a series of Ni

(II) and Co (II) complexes obtained by the reaction of metal salts of Co(II) and Ni(II) with 1-(2'-Hydroxy-3'-bromo-5'-chlorophenyl)-3-pyridine-2-propen-1-one (L<sub>2</sub>) and 1-(2'-Hydroxy -5'-chlorophenyl)-3-pyrrole-2-propen-1-one (L<sub>4</sub>).

### EXPERIMENTAL

All the reagents are of A.R grade. All the melting points of compounds were determined in an open capillary tube and are uncorrected. Completion of the reaction was monitored by thin layer chromatography on pre coated sheets of silica gel-G.

General procedure for the synthesis of 2'-hydroxychalcone:

Equimolar quantities of substituted halohydroxy acetophenone and aromatic aldehyde in minimum quantity of alcohol was dissolved, 40% NaOH in water was added in portions, at room temperature. The reaction flask was loosely corked and kept at room temperature for about 20-21 hour. The contents of the flask were poured over crushed ice and then acidified by 10% HCl. The solid mass separated was filtered, washed with cold water and dried, then recrystallized from suitable solvent.

### Synthesis of metal complex

The ligand (0.02 mole) and the metal salt (0.01 mole) in 50 ml methanol was refluxed for 2 hours in a reaction flask. The solid mass separated was filtered through a sintered glass crucible (G4) and the residue was washed several times with hot methanol until the washings were free of the excess of ligand. Analytical and physical data is given in TABLE -1.

Molar conductance measurements were carried out in DMSO at  $10^{-4}$  M concentration using EQUIPTRONICS digital conductivity meter EQ-660 with range 20  $\mu$ &! to 20 m&! at room temperature. The magnetic susceptibility measurements of the complexes in the solid state were made on Guoy balance at room temperature using Hg [Co (NCS)<sub>4</sub>] as standard. Diamagnetic corrections were applied using pascals constant. The IR spectra of the metal complex and ligands in KBr pallets in the range of 4000-350  $\text{cm}^{-1}$  were recorded making use of FTIR-SCHIMADZU spectrometer.

UV-Visible spectra in DMF were recorded on a schimadzu multipurpose recording spectrophotometer model 1601 and TGA and DTA analysis of metal complexes were carried out in nitrogen atmosphere in the range 25-1000°C on Mettler system with a heating rate 10°C  $\text{min}^{-1}$  using alumina as a standard. The <sup>1</sup>H NMR spectra of compounds were recorded (in DMSO *d*<sub>6</sub>) on Avance-300 MHz spectrophotometer using TMS as an internal standard.

## RESULT AND DISCUSSION

All the complexes were stable at room temperature, insoluble in water and most of the common or-

ganic solvents but soluble in DMF, DMSO and  $\text{CHCl}_3$ . The analytical data of the complexes (TABLE-1) indicates that their stoichiometry may be represented as 1:2 metal to ligand ratio.

### IR Spectra

The ligand showed a weak broad band around 3028-3066  $\text{cm}^{-1}$ . In the IR spectra of Ni (II) complexes there is an intense broad band near 3359-3500  $\text{cm}^{-1}$  due to  $\nu$  OH of coordinated water molecule and at 3151-3468  $\text{cm}^{-1}$  due to  $\nu$  (OH) of coordinated water molecule in the IR spectra of Co (II). In the IR spectra of all the ligands an intense band appearing around 1658  $\text{cm}^{-1}$  is attributed to  $\nu$ (C=O)<sup>[7]</sup>. This band is shifted to lower wave number in the spectra of the complexes indicating coordination through oxygen of (C=O) group. The  $\nu$  (M-O) band for Ni (II) was observed in the complexes around 455-445  $\text{cm}^{-1}$  and for Co (II) complexes it is observed around 426-435  $\text{cm}^{-1}$ . The literature supports such interpretation<sup>[8]</sup>.

### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectra of Ni(II) and Co(II) complexes and ligands show well resolved signals, due to presence of metal ion there observed broad peaks indicating the formation of the complex. In the <sup>1</sup>H NMR spectrum of Ni (II) and Co (II) complex, the signal due to -OH proton (phenolic) is absent, suggesting the deprotonation of phenolic group attached to aromatic ring in the 2'-hydroxychalcone. The peak in the <sup>1</sup>H NMR spectra of ligands near at  $\delta$ 12.00 (s, 1H, OH) is disappear in the complex spectra confirming the coordination of the ligand to the metal ion through this phenolic oxygen atom. In the Ni (II) and Co (II) complex the broad signal at  $\delta$  3.30 is due to proton of coordinated water molecules.

### Magnetic moment

The magnetic moment values of the complexes are in the range of 2.78-3.13 B.M for Ni(II) complex and 4.82- 5.18 B.M for Co(II) complex, which are usually observed for the octahedral geometry of Ni(II) complex<sup>[9,10]</sup> and Co(II) complex<sup>[11]</sup>.

### Molar conductivity

The complexes were dissolved in DMSO and

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conductivity was measured. Conductivity of the DMSO was measured and solution of the complexes in DMSO with different concentrations was measured. The molar conductivity was calculated using the formula

$$\mu_v = \frac{K_v \times 1000}{M}$$

Where,  $\mu_v$  = molecular conductivity; K = conductivity of the solution of the complexes in DMSO; C = concentration of the complexes ( $10^{-4}$  M).

The molar conductance values of the complexes are in the range of 14.02-26.05 S cm<sup>2</sup> mol<sup>-1</sup> for Ni (II) complexes and 12.02-23.04 S cm<sup>2</sup> mol<sup>-1</sup> for Co (II) complexes suggesting their non electrolytic nature<sup>[12]</sup>.

### X-Ray diffraction study

The X-ray diffractogram of Ni (II) complex (Figure 1) shows good intense and sharp peaks, indicating high crystallinity of Ni (II) complex. The Ni (II) complex is successfully indexed to monoclinic crystal system. The observed density of Ni (II) complex is 1.9680 gm/cm<sup>3</sup>, while theoretical density from the X-ray data is 1.6256 gm/cm<sup>3</sup>. The closeness in the value of observed density and calculated density suggest that each reflex of X-ray diffraction pattern is indexed with perfectness. The X-ray data for Ni(II) complex having metal:ligand stoichiometry as 1:2 have formula factor Z=4. Monoclinic crystal system with Z=4 can be assigned space group P without condition on h, k, l values.

The X-ray diffractogram of [Co(L<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] shows good intense and sharp peaks, indicating high crystallinity of Co(II) complex. The standard deviation in lattice parameters for Co(II) complex is 0.032%. The lattice parameter for Co(II) complex

directed to Tetragonal is found to be as expected value of Z(Z=4) The observed density of Co(II) complex is 1.2378 gm/cm<sup>3</sup>, while theoretical density from the X-ray data is 1.1552 gm/cm<sup>3</sup>.

These values suggest that each reflex of X-ray diffraction pattern is indexed with perfectness.

### Thermogravimetric study

The thermogram of Ni(II) i.e. [Ni(L<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] and Co(II) i.e. [Co(L<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] show that the complexes were stable up to 135°C and 136°C where they loss surface water and consequently at 241°C they loses coordinated water<sup>[9]</sup> molecule presence of which is indicated by IR spectra. The dry complex than remains unchanged and it loses a large part of ligand at 455°C and at 347°C. There after the complex loses coordinated ligand in small fragments, to give metal oxide at around 989°C and at 983°C.

The percentage weight loss of organic part content from the Ni (II) complex is found to be 90.21% which is comparative to theoretical value 89.99%. The horizontal nature of the curve after temperature 989°C indicates the presence of thermally stable residual metal oxide (Ni-O). The percentage weight loss of the residual metal oxide is found to be 9.79%, which is very close to the theoretical value 10.01%. The percentage weight loss of organic part content from the Co (II) complexes are found matching with the theoretical values. After this the weight of the complex remains constant and the horizontal nature of the curve indicates the presence of thermally stable residual metal oxide (CoO).

Thermal analysis confirms the finding that, two moles of coordinated water per mole of metal complex is present in Ni (II) and Co (II) complexes.

On the basis of above discussion, the Ni (II) and

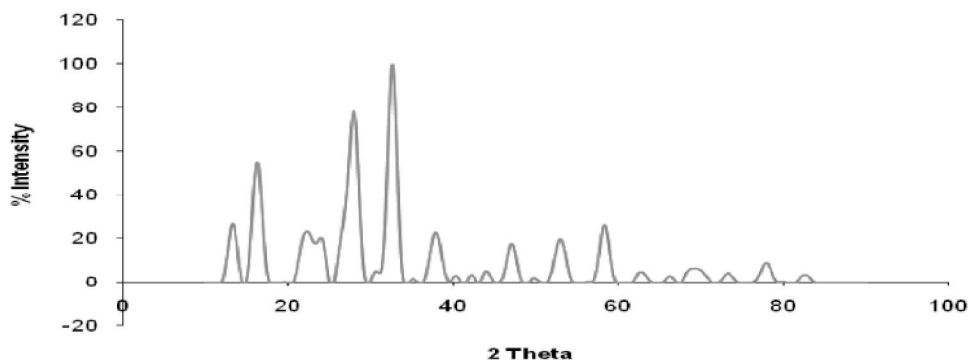


Figure 1

TABLE 1 : Magnetic moment, molar conductivity and analytical data of Ni (II) and Co (II) complexes

Sr.No.	Molecular Formula	Mol. Wt.	Colour	M. P./ D. P. °C	Elemental Analysis		Molar Conductivity Scm <sup>2</sup> mol <sup>-1</sup> × 10 <sup>-4</sup>	μ <sub>eff.</sub> B. M.
					Halogen Found (Calcd)	Metal Found (Calcd)		
1.	C <sub>28</sub> H <sub>20</sub> O <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> Br <sub>2</sub> Ni	770	Brown	252	29.41 (29.96)	7.36 (7.62)	15.03	2.78
2.	C <sub>26</sub> H <sub>20</sub> O <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> Ni	586	orange	288	12.56 (12.10)	10.38 (10.01)	21.04	2.92
3.	C <sub>28</sub> H <sub>16</sub> O <sub>4</sub> Cl <sub>2</sub> N <sub>2</sub> Br <sub>2</sub> Co	734	Brown	252	31.02 (31.43)	8.41 (8.02)	12.02	5.02
4.	C <sub>26</sub> H <sub>16</sub> O <sub>4</sub> Cl <sub>2</sub> N <sub>2</sub> Co	550	Brown	228	12.41 (12.89)	10.24 (10.71)	16.03	4.93

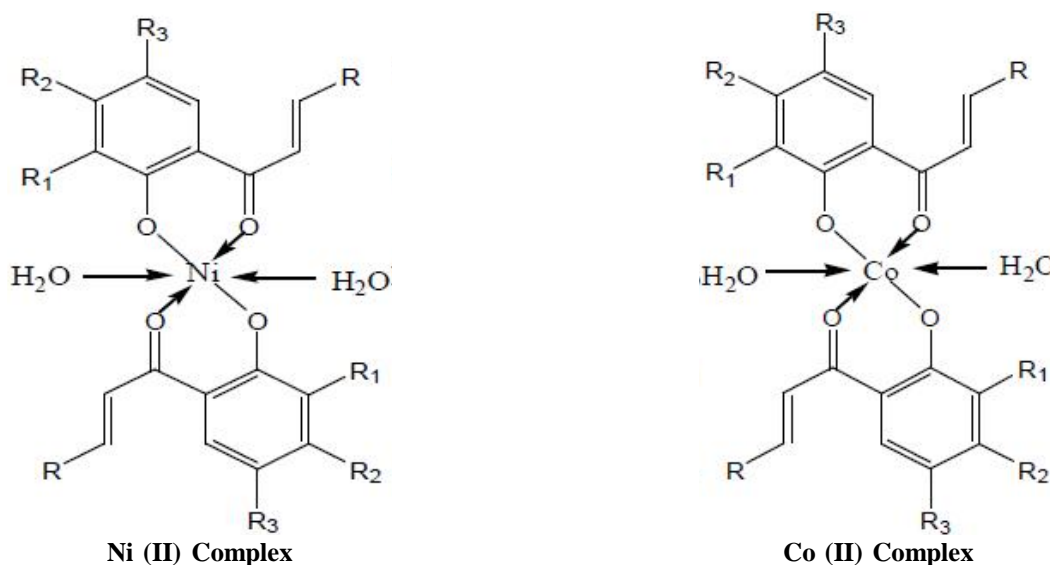


Figure 2

Sr.no.	Complex	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R
1.	[Ni(L <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Br	H	Cl	
2.	[Ni(L <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	H	H	Cl	
3.	[Co(L <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	Br	H	Cl	
4.	[Co(L <sub>4</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	H	H	Cl	

Co (II) complexes of L<sub>4</sub> and L<sub>2</sub> may be assigned following structure,

### ANTIMICROBIALACTIVITY

Antimicrobial activity was assayed by cup plate agar diffusion method<sup>[13]</sup> by measuring inhibition zones in mm. *In vitro* antimicrobial activity of all

synthesized compounds and standard have been evaluated against four strains of bacteria which include *Escherichia coli*, *Salmonella typhi*, *Staphylococcus aureus* and *Bacillus subtilis* and against four fungal strains like *Aspergillus niger*, *Aspergillus flavus*, *Fusarium moniliforme* and *Penicillium chrysogenum*. The standard used was penicillin and grysofulvin.

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TABLE 2 : Antimicrobial activity of synthesised Ni(II) and Co(II) complexes

Product	Comp. code	Bacteria					Fungi			
		Ec	St	Sa	Bs	An	Af	Fm	Pc	
C <sub>14</sub> H <sub>9</sub> O <sub>2</sub> NCIBr	L2	--	--	11	11	RG	RG	+ve	+ve	
C <sub>13</sub> H <sub>9</sub> O <sub>2</sub> NCl	L4	--	--	13	10	+ve	-ve	+ve	+ve	
C <sub>28</sub> H <sub>20</sub> O <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> Br <sub>2</sub> Ni	Vb	-ve	21	12	14	-ve	+ve	-ve	-ve	
C <sub>26</sub> H <sub>20</sub> O <sub>6</sub> Cl <sub>2</sub> N <sub>2</sub> Ni	VIIIb	16	-ve	23	10	-ve	-ve	+ve	-ve	
C <sub>28</sub> H <sub>16</sub> O <sub>4</sub> Cl <sub>2</sub> N <sub>2</sub> Br <sub>2</sub> Co	Vc	-ve	15	19	15	+ve	-ve	+ve	+ve	
C <sub>26</sub> H <sub>16</sub> O <sub>4</sub> Cl <sub>2</sub> N <sub>2</sub> Co	VIIIc	11	17	24	22	+ve	-ve	+ve	-ve	
Penicillin		18	20	32	28	NA	NA	NA	NA	
Grysofulvin		NA	NA	NA	NA	-ve	-ve	-ve	-ve	

Ec - *Escherichia coli*, St- *Salmonella typhi*, Sa- *Staphylococcus aureus*, Bs-*Bacillus subtilis*, An- *Aspergillus niger*, Af- *Aspergillus flavus*, Fm- *Fusarium moneliforme*, Pc- *Penicillium chrysogenum*, -ve- No growth, +ve- Growth, NA- Not Applicable Zone of inhibition is expressed in mm.

From the results of antimicrobial activity of ligand and complex it is clear that the complexes shows enhance activity than the ligands<sup>[14]</sup>. The increase in antimicrobial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to the combined activity of the metal and ligand<sup>[15]</sup>.

## CONCLUSION

The Ni (II) and Co (II) complexes are coloured, insoluble in most of the organic solvent but soluble in DMF, DMSO and CHCl<sub>3</sub>. The stoichiometry of the metal complexes obtained has been found to be 1:2. The infrared spectral data indicate that all ligands act as mononegative bidentate species towards Ni (II) and Co (II) complexes. Molar conductivity data shows the non electrolytic nature of the complexes. Thermal analysis of Co (II) and Ni (II) complexes confirms that there are two moles of coordinated water per mole of metal complex. The antimicrobial study shows that the complex shows enhance activity than their corresponding ligands. The electronic spectral data suggested that Ni (II) and Co (II) complexes have octahedral geometry.

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