

Syntheses, Characterization and Biological Activity of Nickel Chalcone Complexes

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Abstract: *The Nickel(II) chalcone complexes were prepared by refluxing Nickel sulphate heptahydrate with different substituted chalcones in methanoic medium. The chalcones were prepared with different aromatic aldehydes like Benzaldehyde, Hydroxy benzaldehyde, Nitro benzaldehyde and Chloro benzaldehyde. The synthesized Nickel complexes were characterized by different spectral techniques. The elemental analysis and IR spectral studies of the complexes revealed that the chalcone derivatives are bidentate ligand. The thermal study explained the stability of complex and its decomposition. Magnetic studies suggested the paramagnetic behavior of the complexes. UV spectral studies suggest that the complexes are in octahedral geometry. Conductance measurements suggest that all complexes are non-electrolyte in DMF. The synthesized ligand and metal complexes were screened for their antibacterial activity against E. coli and staphylococcus aureus bacterial strains and for antifungal activity against P. notatum and Candida.*

Keywords: Nickel sulphate, Chalcones, Complexes, Spectral Studies, TGA, Magnetic study, Antifungal and Antibacterial study

1. Introduction

Chalcones-one of the major classes of natural products with widespread distribution in vegetables, fruits, tea and spices have been great interest for their interesting pharmacological activities¹. Chemically, they consist of open chain flavonoids in which the two aromatic ring are joined by a three carbon α,β unsaturated carbonyl system². Synthetic chalcones are commonly synthesized with the reaction of acetophenone and benzaldehyde via Claisen-Schmidt condensation reaction. This reaction is catalysed by bases and acids under homogeneous conditions³. The IUPAC name of chalcones is 1,3-diphenyl-2-propene-1-one, in this it possess conjugate double bond and a delocalized π electron on both the benzene ring⁴. The importance of chalcones lies in the wide range of pharmacological activities such as antitubercular, anthelmintic⁵, fungicidal⁶, antitumor⁷ and antibacterial⁸ activity.

2. Preparation of complexes

To a hot solution of ligand (0.02M) in methanol, methanolic solution (0.01M) of the metal salt, Nickel sulphate heptahydrate ($\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$) was added drop wise with constant stirring and refluxed for 2-3 hrs. The resulting reaction mixture was cooled to room temperature and maintained pH up to 8.0 by adding ethanoic ammonia then again refluxed reaction mixture further for 30 min. The resultant product was filtered through Whatman filter paper no.1 and repeatedly washed with methanol until the washing were free from the excess of ligand. The products were finally dried over anhydrous calcium chloride in desiccator.

3. Instrumental Methods

The IR spectra of complexes were recorded on a Perkin-Elmer instrument in KBr pallets in the range of 4000-400 cm^{-1} . UV-Visible spectra were recorded using DMF as solvent on Shimadzu UV-VIS spectrophotometer in the range 200-1100nm. TGA analysis of metal complexes were carried out in nitrogen atmosphere in the range 25-900 $^{\circ}\text{C}$ on Rigaku Thermo Plus-8120 TG-DTA instrument with a heating rate 10 $^{\circ}\text{C min}^{-1}$ using Alumina as a standard. The conductance was measured in DMF solvent on Equiptronics Conductivity meter (EQ-664A).

4. Results and Discussion

All the complexes are coloured and stable to air and moisture. In order to check solubility of these Ni(II) complexes, different polar and non-polar solvents have been tried. It was observed that these complexes are insoluble in water and most common organic solvents but moderately soluble in DMSO, DMF. The elemental analysis shown in Table-1 indicates that, all metal complexes have 1:2 (metal:ligand) stoichiometry. Conductivity of metal complexes is an important technique to study the nature of complexes. The solution of an electrolyte conducts electric current by migration of ions under the influence of electric field. Hence the ability of any ion to transport charge depends on mobility of ions. Therefore by measuring the solution conductivity we can decide the electrolytic or non-electrolytic nature of the metal complexes, which helps us to ascertain its ionic and covalent nature. The molar conductance values obtained for these complexes at the 10⁻³M concentration in DMF are in the range of 18-28 $\text{mhos.cm}^2\text{mol}^{-1}$ suggesting⁹ their non-electrolytic nature. The observed conductivity values of Ni(II) complexes are presented in (Table-1).

Table 1: Physical and analytical data of metal complexes

Complex	Empirical Formula	MolWt.	Yield %	% Elemental analysis Found (calculated)						Molar conductance mhos.cm ² .mol ⁻¹
				M	C	H	N	Cl	O	
Ni L ₁	C ₃₄ H ₃₄ O ₆ Ni	596	72.28	9.67 (9.73)	68.49 (68.46)	5.65 (5.70)	-	-	16.20 (16.11)	18.23
Ni L ₂	C ₃₄ H ₃₄ O ₈ Ni	628	66.15	9.27 (9.23)	64.90 (64.97)	5.36 (5.41)	-	-	20.46 (20.38)	24.25
Ni L ₃	C ₃₄ H ₃₂ N ₂ O ₁₀ Ni	686	76.66	8.50 (8.45)	59.44 (59.48)	4.63 (4.66)	4.06 (4.08)	-	23.38 (23.32)	21.63
Ni L ₄	C ₃₄ H ₃₂ O ₆ Cl Ni	629	71.25	9.28 (9.22)	64.89 (64.86)	5.05 (5.09)	-	5.53 (5.56)	15.23 (15.26)	27.45

4.1 IR spectral values

The IR spectra are quite complex due to the presence of a large number of bands with varying intensities. Hence, assignment of all the bands without ambiguity is not possible. However, an attempt has been made to identify and

assign some of the structurally important bands on the basis of the reported infrared spectra of some chalcones¹⁰⁻¹¹. Some of these like ν CH(Aromatic), ν C=O, ν Ph-C=C, ν OH (Phenol) and ν C-O (Phenol) are in good agreement with the reported values¹²⁻¹³.

Table 2: Important IR spectral bands (cm⁻¹) of the complexes

Compound	C=CH(Aro)	C=O	C=C	OH group	C-O	M-O	-NO ₂	C-Cl
L ₁	2858	1640	1503	2921	1221	-	-	-
NiL ₁	2852	1611	1498	3368	1210	620	-	-
L ₂	2987	1639	1588	3242	1221	-	-	-
NiL ₂	2969	1623	1552	3443	1208	618	-	-
L ₃	2921	1635	1513	3390	1190	-	1520	-
NiL ₃	2853	1617	1495	3355	1204	623	1505	-
L ₄	2920	1635	1567	3527	1185	-	-	738
NiL ₄	2978	1613	1543	3386	1213	612	-	726

In the IR spectra of all the ligands an intense band appearing around 1642 cm⁻¹ is attributed to ν (C=O), this band is shifted to lower wave number 1611-1623 in the spectra of the complexes due to the coordination of the >C=O group to the metal ion through oxygen resulting in decrease of bond order of carbon to oxygen linkage. With respect to the ligands, the broad bands in the 2852-2978 cm⁻¹ region for all the ligands have been ascribed to ν CH(Aromatic) vibrations. The resonance effect is observed in adjacent group containing π electrons. In conjugated system ν (C=C), ν (C=O) their frequencies are shifted to lower frequencies to around 1500 and 1620 cm⁻¹ respectively. The conjugation of C=O group with C=C group results in delocalization of π electrons of both the unsaturated groups. Because of this there is decrease in the double bond character of both the C=O and C=C groups. This is as a result of the fact that the π electrons of the conjugated groups tend to delocalize over the entire molecule. The additional strong bands in the complexes in the region around 612-623cm⁻¹ are attributed to ν Ni-O vibrations and suggest bonding between metal and oxygen atoms.

4.2 Thermal measurements

TGA analysis is very important which carried out to confirm presence of water molecule in these complexes as well as to know their decomposition pattern. The analytical data suggest these complexes contain water molecules. We have to find out whether these water molecules are coordinated or present in lattice.

Table 3: Thermal data for Nickel metal complexes

Complex	Temperature Range (°C)	% Weight loss		Decomposition product
		Found	Calculated	
NiL ₁	140-210	5.96	5.88	2H ₂ O
	240-700	82.10	82.03	C ₃₄ H ₃₀ O ₄
	above720	11.95	12.09	NiO
NiL ₂	140-210	5.52	5.59	2H ₂ O
	240-700	82.96	82.91	C ₃₄ H ₃₀ O ₆
	above720	11.53	11.49	NiO
NiL ₃	140-210	5.19	5.13	2H ₂ O
	240-700	84.40	84.33	C ₃₄ H ₂₈ N ₂ O ₈
	above720	10.42	10.54	NiO
NiL ₄	140-210	5.65	5.58	2H ₂ O
	240-700	82.85	82.9	C ₃₄ H ₂₈ O ₄ Cl
	above720	11.43	11.47	NiO

The TG studies of the complexes were recorded in nitrogen atmosphere on Rigaku Thermo Plus-8120 TG-DTA instrument by increasing the temperature from room temperature up to 900°C at the heating rate of 10°C/min.

All the nickel chalcone complexes investigated shows similar behavior in their thermogram. The thermogram of all the complexes consists of three steps. The coordinated water is stable and volatilized above 140°C. In the first step the complex losses two water molecule in the temperature range between 140°C to 210°C indicates that the complex is thermally stable up to nearly 140°C above which it loses the water molecule. After 240°C, the anhydrous complex starts decomposing. Total mass loss up to 720°C was found to be in the range of 82.10-84.40%, which shows the formation of NiO. Finally, the residue left after 720°C is in the range of 10.42-11.95%, which resembles the theoretical values. Hence from TGA, it is clear that the complexes under study

contain two water molecules, which are coordinated to central metal ion¹⁴. On the basis of the above discussion, complexes [Ni (L)₂ (H₂O)₂] may be assigned Fig-2.

NiL₁: R₁=H & R₂=H; NiL₂: R₁=H & R₂=OH;
NiL₃: R₁=H & R₂=NO₂ and NiL₄: R₁=Cl & R₂=H

4.3 Magnetic susceptibility measurement

The magnetic susceptibility for all the Nickel(II) complexes at room temperature were recorded by the Gouy's method using Hg[Co(SCN)₄] as a calibrant and reported in Table-4. The effective magnetic moments were calculated¹⁵ after applying diamagnetic corrections for the ligand components using Pascal's constants. The room temperature μ_{eff} values for the Nickel(II) complexes¹⁶⁻¹⁷ were found in the range 2.88-3.15 B.M. The magnetic susceptibilities of the complexes are consistent with octahedral geometry around the central metal ion. The magnetic moments of the compounds investigated are in agreement with the findings of electronic absorption spectra.

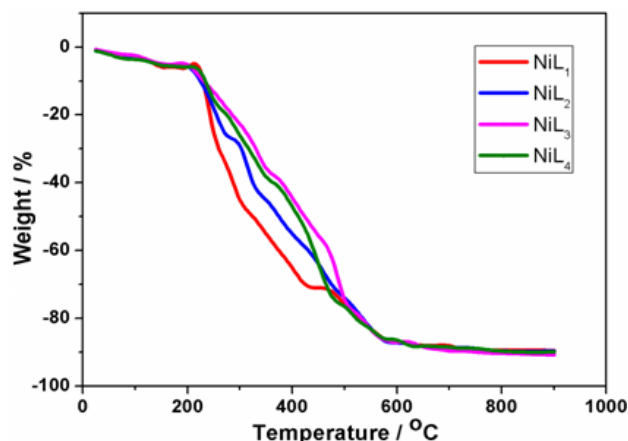


Figure 1: Thermogravimetry spectra of Ni(II) Complexes

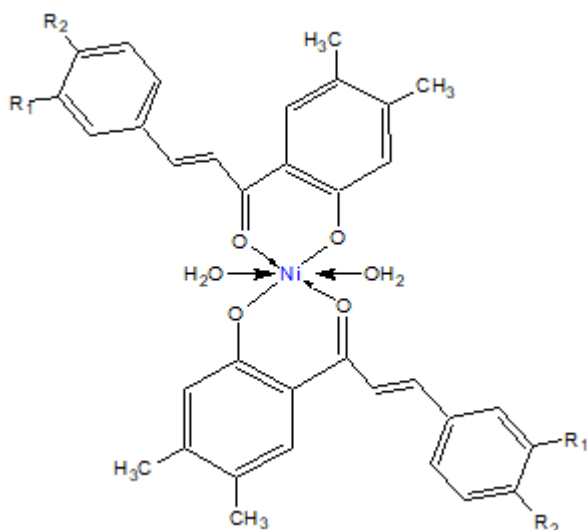


Figure 2: Structure of Nickel chalcone Complex

Table 4: Magnetic moment values of the Nickel (II) Chalcone complexes

Complexes	Magnetic moment(B.M.)
NiL ₁	2.96
NiL ₂	3.12
NiL ₃	2.88
NiL ₄	3.15

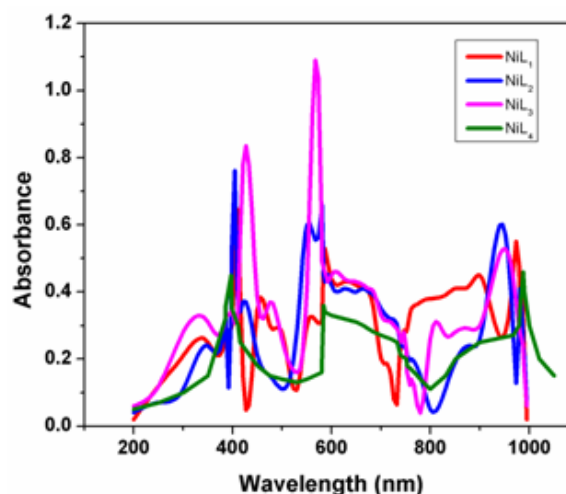
4.4 Electronic spectra

The electronic spectra of the metal complexes in DMF (10⁻³M) was recorded on Shimadzu UV-VIS spectrophotometer in the range 200-1100nm. The Ni(II) complexes are light blue in colour.

Table 5: Electronic spectral data for Nickel metal complexes

Complexes	(ν_1)	(ν_2)	(ν_3)	Dq (cm ⁻¹)	B'(cm ⁻¹)	β	$\beta\%$	CFSE (KJ/mol)
NiL ₁	10210	17045	24330	1021	716	0.69	31	146.57
NiL ₂	10185	17205	25107	1018	784	0.76	24	146.14
NiL ₃	10332	17225	24111	1033	689	0.67	33	148.29
NiL ₄	10116	17135	25205	1011	799	0.77	23	145.13

The electronic absorption spectra of Ni(II) complexes showed three bands at 10116-10332, 17045-17225 and 24111-25205cm⁻¹ with 10116-10332 cm⁻¹ representing 10Dq. These bands are assigned to the transitions $^3A_{2g} \rightarrow ^3T_{2g}(F)$, $^3A_{2g} \rightarrow ^3T_{1g}(F)$ and $^3A_{2g} \rightarrow ^3T_{1g}(P)$ transitions respectively. The value of ν_2/ν_1 is in the range 1.67-1.69 which lies in the usual range (1.60-1.82), reported for the majority of octahedral Ni (II) compounds¹⁸. Reduction of Racah parameter from 1030 cm⁻¹ (free ion value) to 689-799 cm⁻¹ and the $\beta\%$ value 23%-33% indicate the covalent nature of the compound. From these electronic absorption bands, elemental analysis data and observed magnetic moments it is concluded that the Ni(II) complexes in the present study has octahedral geometry.



5. Antibacterial and antifungal activities

It is known that killing of bacteria by chelated ligand is more powerful than non-chelated ligand, therefore chelated ligand acts as potent bactericidal agents. chelation increases the lipophilic character in complexes and results in an enhancement of activity.^{19,20}. By using disc diffusion method²¹ antimicrobial screening was done. Neomycin is used as standard references. All ligands and their metal complexes were screened against the bacteria (*Escherichia coli* and *Staph aureus*) and fungi (*P. notatum* and *Candida*).

Table 7: Antibacterial and antifungal activities (inhibition zone of bacterial growth, mm) of the ligand and metal complexes

Compound	Antibacterial activity		Antifungal activity	
	<i>E. coli</i> 1.0 mg ml ⁻¹	<i>S. aureus</i> 1.0 mg ml ⁻¹	<i>P. notatum</i> 250 µg disc ⁻¹	<i>Candida</i> 250 µg disc ⁻¹
L ₁	6	5	8	-
NiL ₁	9	-	11	-
L ₂	8	9	11	7
NiL ₂	11	13	12	9
L ₃	5	4	6	-
NiL ₃	-	7	9	-
L ₄	7	8	10	-
NiL ₄	10	10	-	-
Neomycin	26	27	-	-

The results obtained are tabulated in Table-7. From the table we can see Ni(II) complexes shows the moderate activity against *Escherichia coli* and *Staph aureus* bacteria. It was observed that metal complexes exhibited significant antifungal activity than chalcones at the same concentration against the fungi *P. notatum*. The order of inhibition with respect to metal complexes was NiL₂ > NiL₁ > NiL₃. Except L₂ and NiL₂ other Ni(II) complexes does not show activity against *Candida* fungi.

It was concluded from above data that electron withdrawing substituents like nitro, cyano at para position in ring A decreases the antibacterial and antifungal activity. Electron donating group like hydroxyl, methoxy at para position increases the activity. The increased activity of the chelates can be explained based on the overtone concept and the Tweedy chelation theory²². According to the overtone concept of cell permeability, the lipid membrane that surrounds the cell favors the passage of only lipid-soluble material.

6. Conclusion

All the transition metal complexes are coloured insoluble in most of the organic solvents but moderately soluble in DMSO and DMF. The stoichiometric ratio of metal to ligand is 1:2. The IR spectral data indicate that all ligands act as bidentate species towards all the complexes. Molar conductivity data shows the non electrolytic nature of the complexes. Thermal analysis of Ni(II) complexes confirms that there are two moles of coordinated water hence From the elemental analysis data, thermal studies, observed magnetic moments and electronic transitions, it is concluded that the Ni(II) complexes in the present study has octahedral geometry. In this study Ni (II) complexes shows the

moderate activity against *Escherichia coli*, *Staph aureus* bacteria and against *P. notatum*, *Candida* fungi.

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