

Synthesis Characterization and Antioxidant Activity of Ni (II) and Co (II) Quinoline Schiff Base

G.Sathya Priyadarshini¹, R. Namitha¹, D. Mageswari¹, G.Selvi^{2*}Research Scholar, PSGR Krishnammal College for Women, Peelamedu, Coimbatore, India¹Assistant Professor, PSGR Krishnammal College for Women, Peelamedu, Coimbatore, India²

ABSTRACT: Metal complexes $ML(H_2O)_2Cl$ where $M=Ni, Co$ & L is Schiff base formed by condensation of 2-thiosemicarbazino-4,8-dimethyl quinoline and salicylaldehyde has been prepared and characterised by magnetic measurements, IR, UV, NMR, SEM & EDAX analysis. IR and NMR spectra show that the nitrogen of the azomethine group, Oxygen of the phenolic ring and NH of thiosemicarbazone take part in coordination with the formation of chelated system. SEM and EDAX analysis shows the size and morphology of the complex. The antioxidant activity of newly synthesised compounds has been determined at a different concentration range by means of their interaction with the stable free radical 1,1-diphenyl-2-picryl hydrazyl (DPPH) on the basis of spectral and analytical data, it is evident that the Schiff base acts as tridentate ligand and complexes were Octahedral in nature.

KEYWORD: chelated system, azomethine, EDAX, antioxidant, morphology

1. INTRODUCTION

Transition metal complexes promotes synthesis is of outstanding importance in organic chemistry¹⁻⁵. Proper combination of the selected central metal and well designed ligands are the most important prerequisites for high efficiency. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. The quinoline scaffold is present in many classes of biologically-active compounds. Thiosemicarbazones are compounds that have been studied for a considerable period of time for their biological properties. Thiosemicarbazide may either behave as a monodentate ligand bonding only through the sulfur atom or as a bidentate ligand coordinating through the terminal nitrogen and the sulfur atoms. If the chelating ability of the thiosemicarbazide moiety is increased by inserting a suitable organic molecule possessing a further donor atom in the proximity of the N,S, thiosemicarbazide may act as a tridentate ligand forming a polymeric compound in some cases⁶. Thiosemicarbazones have a wide range of pharmacological activities such as antiviral, antibacterial, antioxidant activity and antitumour depending on the parent aldehyde, ketone and metal ion^{7, 8, 9}. The thiosemicarbazone side chain located at a position α to the heterocyclic nitrogen, through a conjugated N-N-S tridentate ligand system, is essential for anticancer activity¹⁰. In particular, the copper (II) complexes have been studied with regard to their antitumour potentials^{11, 12}. Interest in metal complexes with thiosemicarbazones has been stimulated because biological activity is often enhanced on complexation. Thiosemicarbazones usually react with metallic cation giving complexes in which the ligand behaves as chelating agent bonding through the sulphur and hydrazine nitrogen atoms. Ni (II) and Co (II) complexes of hydrazone derivatives are known for their versatile coordination. These complexes have tendency to yield stereochemistries of higher coordination number, to behave as neutral or deprotonated ligand and the flexibility in assuming different conformation¹³.

The present work deals with the synthesis of new Co and Ni complexes namely $[CoCl_2.6H_2O]$ with 4,8-dimethyl-2-(salicylidene-thiosemicarbazone)quinoline and $[NiCl_2.6H_2O]$ with 4,8-dimethyl-2-(salicylidene-thiosemicarbazone)quinoline.

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II. MATERIALS AND METHODS

Thin layer chromatography (TLC) was performed using glass plates coated with silica gel. Petroleum ether and ethyl acetate was used as eluent. Spots were visualized with iodine. Purification of crude sample was carried out using chromatographic column packed with silica gel. IR spectra were recorded in NICOLET IR 200 FT-IR spectrometer using KBr disc and the absorption frequencies quoted in reciprocal centimeters. UV spectra were recorded in UV-VIS spectrophotometer 3000⁺, LAB INDIA. ¹H NMR spectra were recorded in AMX-300(300MHz) spectrometer using tetra methyl silane (TMS) as internal reference. The chemical shift were expressed in parts per million (ppm). The chemical shift were expressed in parts per million (ppm). TGA-DSC curves were recorded on Shimadzu 60H model using 10°C/min. heating rate. X-RAY diffraction patterns were obtained by using Bruker D8 advanced diffractometer. Elemental analysis was carried out with Perkin Elmer 2400 series for C, H, O and N. The solvents and reagents used for synthesis were of reagents grade and purified by standard methods.

Synthesis of ligand: The Schiff base ligand, was obtained by treating 0.3g (0.0012 moles) of 2-thiosemicarbazone-4, 8-dimethyl quinoline with 0.1ml of salicylaldehyde. The reaction mixture was refluxed for 6 hours. Completion of the reaction was monitored with TLC. The product was filtered, washed thoroughly with ethanol and then dried in vacuum. The compound was crystallized from ethanol.

Synthesis of metal complex:

Cobalt complex: 0.135g (0.00056 moles) of Cobalt dichloride hexahydrate (CoCl₂·6H₂O) was completely dissolved in 20mL of ethanol and 0.2g (0.00057 moles) of 4,8-dimethyl-2-(salicylidene-thiosemicarbazone)quinoline was added to it. The reaction mixture was kept for continuous stirring for 6 hours and completion of the reaction was monitored with TLC. Dark green crystals obtained were separated, washed with ethanol and dried under vacuum.

Nickel complex:

0.135g (0.00056 moles) of Nickel dichloride hexahydrate (NiCl₂·6H₂O) was completely dissolved in 20mL of ethanol and 0.2g (0.00057 moles) of 4,8-dimethyl-2-(salicylidene-thiosemicarbazone)quinoline was added to it. The reaction mixture was kept for continuous stirring for 7 hours and completion of the reaction was monitored with TLC. Light brown crystals obtained were separated, washed with ethanol and dried under vacuum.

III. RESULTS AND DISCUSSION

The synthesized metal complexes are coloured solids and stable in air. Both the ligand and the metal complexes are characterised by UVIR NMR and TGA. In order to study the coordination mode of Schiff base to the metal complex, the characterization of the free ligand is compared with the characterization of the complexes.

UV Spectral studies:

The UV (nm) of the ligand spectrum showed three absorption bands at 261, 287 and 387nm. The first band would be assigned to π - π^* transition within the aromatic rings. The second band would be due to n - π^* transition within 'C=N' group. The absorption band at 387nm is due to charge transfer transition. The UV (nm) spectrum of the Nickel complex showed an absorption bands at 239nm corresponding to n - π^* transition, 402nm corresponding to π - π^* transition. The bands at 678 and 761nm corresponding to d-d transition. The UV (nm) spectrum of the Cobalt complex 238nm corresponds to π - π^* transition and 676nm corresponds to d-d transition

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U.V-Visible Spectra of free Ligand and their Complexes (10^{-3} M in DMF

Compounds	λ_{max} nm	Transitions
Ligand	261 287 387	$\pi-\pi^*$ $n-\pi^*$ charge transfer
Ni(II) Complex	239 402 678 761	$n-\pi^*$ $\pi-\pi^*$ d-d d-d
Co(II) Complex	238 676	$\pi-\pi^*$ d-d

The IR spectral studies:

The IR in cm^{-1} spectrum of the ligand shows vibrational bands at 3317.6 for $\nu(\text{O-H})$, 1203 for $\nu(\text{C-O})$, 3170 and 3263 for two $\nu(\text{N-H})$ and 1527 $\nu(\text{C=N})$. The IR spectrum of the metal complex, there is complete disappearance of $-\text{OH}$ stretching vibration which is present in the ligand, it indicates that 'OH' present in ligand is coordinated with metal as O-M. In addition, metal complexes exhibit broad bands in the range of 3379 cm^{-1} indicating the presence of coordinated water molecules in the metal complexes, the change in the intensity of $-\text{OH}$ of the IR region shows the disappearance of $-\text{OH}$ of hydroxyl and appearance of $-\text{OH}$ of H_2O . The frequency shift of the azomethine group from ligand to metal complex indicates that the C=N involved in the coordination.

Selected IR band assignments of Ligand and their Complexes in cm^{-1}

Assignments	Ligand	Ni(II) Complex
$\nu(\text{NH})$	3170	-
$\nu(\text{C=C})$	1604	1604
$\nu(\text{C=S})$	1489	1442
$\nu(\text{NH})$	3263	-
$\nu(\text{OH})$ Phenolic	3317	-
$\nu(\text{C=N})$	1527	1527
$\nu(\text{C-O})$ Phenolic	1203	-
Band due to coordinated water	-	3379

^1H NMR spectral Studies:

$^1\text{H-NMR}$ (DMSO) spectrum showed the peak at $\delta 11$ corresponds to $-\text{OH}$, $\delta 8.6$ signal corresponds to $-\text{NH}$, $\delta 9.2$ signal corresponds to another $-\text{NH}$, aromatic protons gives multiplet signal in the range of $\delta 7.7$ to 6.5, one singlet for $-\text{CH}_3$ protons at $\delta 3.2$ and $\delta 1.4$ and a singlet at $\delta 5.4$ infers the presence of N=CH . $^1\text{H-NMR}$ (DMSO) spectrum of the metal complex showed the peak at $\delta 8.6$ corresponds to NH , $\delta 10$ corresponds to NH and signal $\delta 5.4$ corresponds to C=N . On comparing with the ligand, $\delta 11$ corresponds to NH reduced to $\delta 10$ indicates the 'N' is coordinated to metal i.e., the electron density around the nitrogen atom is donated to central metal atom.

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¹H-NMR data of the ligand and their complexes in DMSO solution (ppm)

Assignments	Ligand	NQTS	CQTS
δ (NH)	9.2	9.9	9.8
δ (NH)	8.4	8.4	8.5
δ (CH ₃)	1.3	1.3	1.3
δ (CH ₃)	3.3	3.4	3.3
δ (OH)Phenolic	5.4	-	-
Aromatic protons	7.7-6.5	7.7-6.5	7.8-6.6

Thermal studies of the metal complex:

The thermogravimetric studies of the complex of the present investigation, was carried at the heating rate of 10 °C min⁻¹ under nitrogen atmosphere and weight loss as measured from the ambient temperature upto 1000 °C.

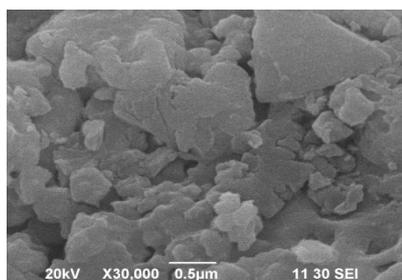
The TGA of the Nickel complex shows two stage decomposition.

1. The first stage decomposition is obtained in the temperature range 240 °C. The percentage weight loss (12.60 %) indicates the loss of two coordinated water molecules and one chlorine atom.
2. The two stage decomposition is obtained in the temperature range 400 °C-1000 °C. The percentage weight loss (1.09%) in this range corresponds to the ligand decomposition and leaving the metal residue.

The residue subsequently fragments through the several exothermic process and shown by the DSC curve.

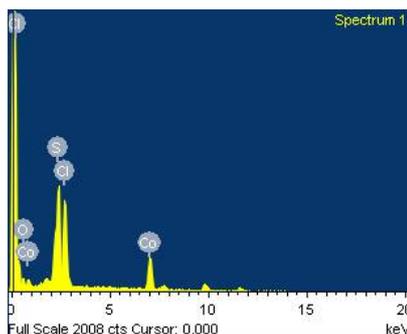
SEM analysis :

Scanning electron micrography issued to evaluate the morphology and size of the metal complex. The SEM micrographs of the complex image shown as figure. The size of the metal complex is found to be 0.5µm.



EDAX Analysis:

The vertical axis displays the number of X ray counts with the horizontal axis displays energy in kilovolt. The EDAX image is shown in figure . The results confirmed the presence of Co, O, S, Cl and Carbon elements in the complex and atomic weight percentage where 12.30%, 10.0%, 6.60 %, 7.50% and 47.5%

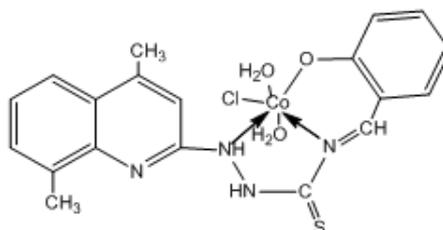


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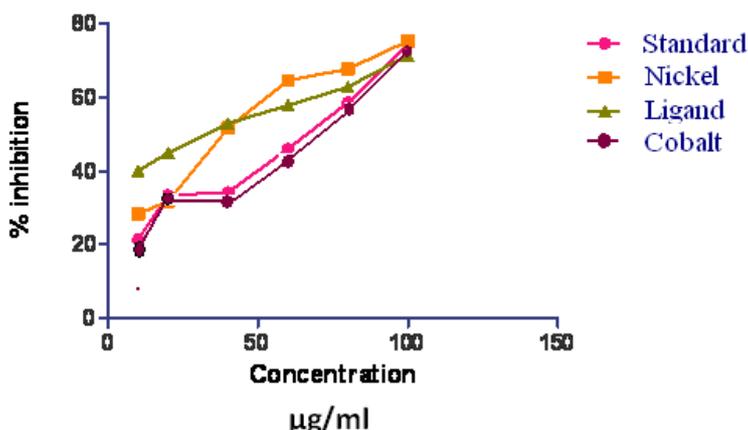
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From the spectral, SEM and EDAX analysis, the structure of the Cobalt complex is found to be



Antioxidant activity

DPPH Radical Scavenging Activity



DPPH radical scavenging Activity

The newly synthesized Schiff base and its metal complexes were screened for free radical scavenging activity by DPPH method. Antioxidant activity of these compounds was investigated by measuring radical scavenging effect of DPPH radicals. The results of the free radical scavenging activity of the compounds at different concentrations are shown in Figure-15. It is evident from the results that the free radical scavenging activity of these compounds was concentration dependent.

Among the examined metal complexes Ni (II) exhibited good scavenging activity where as Co (II) shown moderate activity than the ligand. The higher scavenging activity of Ni (II) complex on comparison to ligand, could be due to the coordination of metal with azomethine nitrogen and phenolic oxygen of the ligand.

The ligand shows an enhanced scavenging property than the Co (II) complex, for various concentrations at 100 µg/mL could be due to free electron mobility. At IC₅₀, Ni (II), Co (II) and ligand shows similar activity

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Concentration in µg/ml	Standard	Ni Complex	Co complex	Ligand
10.	21.42	28.34	20.78	40.13
20.	33.44	31.85	32.44	44.89
40.	34.24	51.70	33.21	52.94
60.	46.03	64.62	44.65	57.8
80.	58.61	67.68	56.85	62.81
100.	74.48	75.28	72.25	71.42
	IC ₅₀ = 49	IC ₅₀ = 46	IC ₅₀ = 45	IC ₅₀ = 43

IV. CONCLUSION

The present work was started with the aim of synthesis, characterization and anti oxidant activity of Ni(II) and Co(II) quinoline Schiff base complexes. The 4,8-dimethyl-2-(salicylidene-thiosemicarbazone) was prepared by reacting salicylaldehyde with 2-thiosemicarbazone-4,8-dimethyl quinoline which in turn was obtained from 2-chloro-4,8-dimethyl quinoline. The complexes were obtained by reacting Schiff base with [NiCl₂.6H₂O] and [CoCl₂.6H₂O]. New complexes were characterised by IR, UV, NMR spectra, SEM, EDAX and thermal analysis. In this complex quinoline Schiff base ligand coordinated in NNO donor fashion with the formation of chelated system.

Antioxidant activity of the Ni(II) and Co(II) complexes and ligand were done using DPPH assay. The result clearly indicates that Ni(II) complex exhibits higher scavenging activity among the test compounds as well as the standard.

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