

Synthesis and Characterisation of Nickel (II) Complexes with New Schiff Bases

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ABSTRACT: In present paper, synthesis of Nickel (II) complexes with DOSC and DOTSC ligands. The characterisation of ligands and complexes has been done on the basis of elemental analysis, magnetic moment data and spectral studies. The structures of complexes was also suggested.

KEYWORDS: DOSC, Magnetic Moment, Diphenyl, Semicarbazone.

I. INTRODUCTION

Schiff bases are an important class of ligands in different spheres [1-3]. Schiff bases as their coordination compounds have been reported [4-6] to possess different biological activities [7-10] because of the ready accessibility, diverse chemical activity broad spectrum of biological and pharmaceutical properties such as analgesic, antipyretic anti-inflammatory, anti-cancerous, bactericidal, Fungicidal has made the study of Schiff base as visible source of significance for the treatment of human life. As the microbial activity of an activity of an active ligand is altered many folds on coordination with a suitable metal ion. During present investigation, synthesis and characterisation of Nickel (II) complexes with a pair of semi and thiosemi carbazone ligands DOSC and DOTSC. The characterisation was done with help of elemental analysis, magnetic moment data, uv-visible spectra and IR spectral studies.

DOSC = 1,2-Diphenyl -4- Oxoquinazoline Semicarbazone

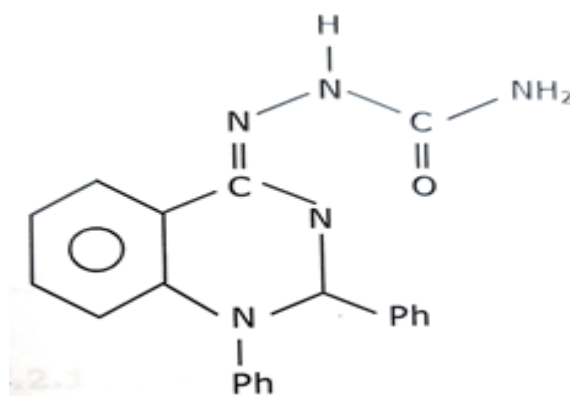


Fig-1

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DOTSC = 1,2-Diphenyl -4- Oxoquinazoline Thiosemicarbazone

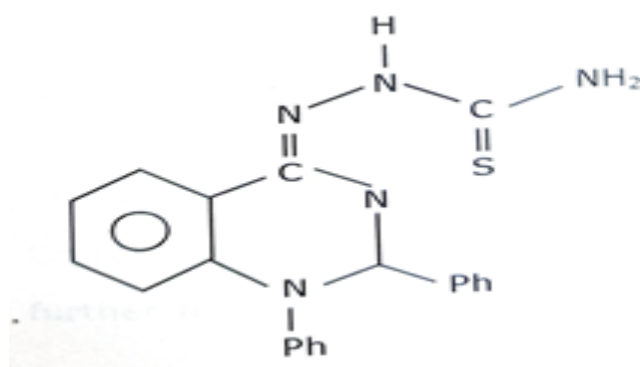


Fig-2

II. EXPERIMENTALS

Preparations of Ligands:

A suspension of 1,2-Diphenyl – 4 – oxoquinazoline (0.01 mole) in ethanol (20 ml) was treated with semicarbazide hydrochloride (0.01 mole) dissolved in 10% ethanolic solution of sodium acetate. The resulting reaction mixtures were heated on water bath for more than 3 hours when a crystalline cloudless solid began to separate. It was heated for further half an hour for complete precipitation. It was cooled, filtered, washed with aqueous ethanol dried and crystallized with metal Alcohol as colourless solid was obtained.

Preparation of Ni (II) Complexes with DOSC and DOTSC Ligands.

1,2-Diphenyl-4-oxoquinazoline semicarbazone (2.31g) and 1,2-Diphenyl-4- oxoquinazoline thiosemicarbazone (2.47g) in ethanol (20 ml) was dissolved in minimum volume of ethanol and treated an ethanolic solution of 1.18 g NiX₂ (X=Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻) separately. The reaction mixtures were heated on water bath for more than 3 hours when a crystallized precipitate was obtained. which was filtered and washed with cold water followed by methanol and ether and dried in oven. The complexes were insoluble in inorganic and organic solvents also.

III. RESULTS AND DISCUSSION

The physical characteristics of the ligands and complexes and elemental analysis of Ni, C, H, N, Cl, Br atoms were presented in table -1 & 2.

Table -1
Physical and Analytical Data of Ligands

Components	DOSC(Ligand)%	DOTSC (Ligand)%
Carbon	70.92 (70.98)	67.86 (67.92)
Hydrogen	4.74 (4.78)	4.52 (4.58)
Nitrogen	19.65 (19.71)	18.80 (18.86)
Sulphur	-----	8.98 (9.01)

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Table -2
Physical and Analytical data of Ni (II) Complexes (in %)

Complexes	Ni	C	H	N
[Ni (DOSC) ₂ Cl ₂]	9.98 (9.92)	44.69 (44.61)	4.35 (4.39)	23.60 (23.66)
[Ni (DOSC) ₂ Br ₂]	8.67 (8.62)	38.84 (38.79)	3.78 (3.82)	20.63 (20.57)
[Ni (DOSC) ₂ I ₂]	7.63 (7.58)	34.15 (34.08)	3.31 (3.35)	18.01 (18.07)
[Ni (DOSC) ₂ (NO ₃) ₂]	9.14 (9.10)	41.09 (40.04)	3.98 (4.03)	21.28 (21.71)
[Ni (DOSC) ₂ (ClO ₄) ₂]	6.07 (6.10)	52.08 (52.12)	3.35 (3.51)	14.42 (21.71)
[Ni (DOTSC) ₂ Cl ₂]	9.37 (9.14)	39.69 (39.60)	4.19 (4.16)	22.36 (22.44)
[Ni (DOTSC) ₂ Br ₂]	8.17 (8.23)	34.74 (34.66)	3.60 (3.64)	10.58 (19.64)
[Ni (DOTSC) ₂ I ₂]	7.32 (7.27)	30.72 (30.61)	3.26 (3.22)	17.42 (17.35)
[Ni (DOTSC) ₂ (NO ₃) ₂]	8.62 (8.67)	36.41 (36.50)	3.81 (3.84)	20.73 (20.68)
[Ni (DOTSC) ₂ (ClO ₄) ₂]	7.85 (7.80)	32.73 (32.84)	3.48 (3.45)	18.67 (18.61)

From elemental analysis of the ligands DOSC/DOTSC has been found to form complexes of type [Ni (DOSC)₂X₂] and [Ni (DOTSC)₂X₂].

Magnetic Moment of Complexes.

Magnetic moment data of all Ni (II) complexes has been found in range 3.25 to 3.60 B.M at 25⁰C. It means nickel present in +2 oxidation state and nickel complexes are octahedral coordinated. The magnetic moment data of all Ni complexes were tabulated in table-3.

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Table -3
Magnetic Moment of Ni(II) complexes

Complexes	Magnetic Moment (B.M)	Temperature (K)
[Ni (DOSC) ₂ Cl ₂]	3.05	295
[Ni (DOTSC) ₂ Cl ₂]	3.07	295
[Ni (DOSC) ₂ Br ₂]	3.11	295
[Ni (DOTSC) ₂ Br ₂]	3.09	295
[Ni (DOSC) ₂ I ₂]	3.14	295
[Ni (DOTSC) ₂ I ₂]	3.16	295
[Ni (DOSC) ₂ (NO ₃) ₂]	3.28	295
[Ni (DOTSC) ₂ (NO ₃) ₂]	3.26	295
[Ni (DOSC) ₂ (ClO ₄) ₂]	3.24	295
[Ni (DOTSC) ₂ (ClO ₄) ₂]	3.22	295

IR Spectra:

The ir Spectra of ligands and Ni (II) complexes have been recorded in Nujomul KBr/ cesium iodide disk during Perkin Elmer 577 modal and given in table-4 and table-5.

Table-4
Characteristics I.R spectra of the Ligand DOSC and its Ni (II) Complexes (in cm⁻¹)

Compounds	ν_{N-H}	$\nu_{C=O}$	$\nu_{C=N}$	ν_{M-O}	ν_{M-N}	ν_{M-X}
C₂₁H₁₇N₅O (DOSC)	3220 m,b	1660 s,b	1480 s,m	-----	-----	-----
[Ni (DOSC) ₂ Cl ₂]	3220 m,b	1705 m,b	1455 m,b	535 m	430 m	325 m
[Ni(DOSC) ₂ Br ₂]	3220 m,b	1700 m,b	1450 m,b	525 m	405 m	295 m
[Ni(DOSC) ₂ I ₂]	3220 m,b	1710 m,b	1460 m,b	565 m	420 m	265 m
[Ni(DOSC) ₂ (NO ₃) ₂]	3220 m,b	1700 m,b	1455 m,b	580 m	390 m	-----
[Ni(DOSC) ₂ (ClO ₄) ₂]	3220 m,b	1710 m,b	1450 m,b	555 m	400 m	-----

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Table-5
Characteristics I.R spectra of the Ligand DOTSC and its Ni (II) Complexes (in cm⁻¹)

Compounds	$\nu_{\text{N-H}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-X}}$
C ₂₁ H ₁₇ N ₅ S (DOTSC)	3460 m,b	1500 s,b	800 s,m	-----	-----	-----
[Ni (DOTSC) ₂ Cl ₂]	3460 m,b	1460 m,b	780 m,b	460 m	425 m	325 m
[Ni(DOTSC) ₂ Br ₂]	3460 m,b	1470 m,b	775 m,b	450 m	420 m	295 m
[Ni(DOTSC) ₂ I ₂]	3460 m,b	1475 m,b	770 m,b	465 m	410 m	275 m
[Ni(DOTSC) ₂ (NO ₃) ₂]	3460 m,b	1480 m,b	765 m,b	460 m	400 m	-----
[Ni(DOTSC) ₂ (ClO ₄) ₂]	3460 m,b	1465 m,b	760 m,b	470 m	395 m	-----

The ir Spectra of the ligand DOSC shows A medium and broad at 3220 cm⁻¹ and of ligand DOTSC shows a band at 3460 cm⁻¹ Which can also be assigned to the $\nu_{\text{N-H}}$ vibrations. The spectra of all the complexes shows this band without any change clearly indicated that primary amino group or secondary amino group has not taken part in the coordination with Ni (II) ion. The next ir spectra of structural significance in the spectrum of the DOSC appeared at 1660 cm⁻¹. This band was sharp and strong peak be assigned to $\nu_{\text{C=O}}$ of semicarbazone moiety of quinazoline. The position of this band in all Ni (II) complexes have been shifted to a higher frequency due to coordination to the oxygen atom of carbonyl group to the metal ion. The coordination by the appearance of a band in the far ir region at 580 – 520 cm⁻¹ in the complexes may be assignable to $\nu_{\text{M-O}}$. The ir spectra of both the ligands DOSC and DOTSC show broad band of medium intensity at around 1500 cm⁻¹ Which can be assigned to $\nu_{\text{C=N}}$. In the spectra of the complexes this band shows red shift in the region 1500-1400 cm⁻¹ clearly indicated the coordination of the N atom of azomethine group of semicarbazone or thiosemicarbazone moiety. The coordination through azomethine nitrogen is further confirmed by the appearance of a band in the far ir region at 425-395 cm⁻¹ in the Ni (II) complexes may be assignable to $\nu_{\text{M-N}}$. The ir spectra of the ligand DOTSC shows a sharp and strong peak in at 800 cm⁻¹ Which may be assigned to the $\nu_{\text{C=S}}$ of thiosemicarbazone moiety. In the spectra of the Ni (II) complexes this band shows red shift in the region 775-760 cm⁻¹ clearly indicated that thione sulphur of thiosemicarbazone moiety was coordinated with Ni (II) ion. The coordination through thione sulphur atom was further confirmed by the appearance of a band in the far ir region at 480-450 cm⁻¹ in the complexes may be assignable to $\nu_{\text{M-S}}$.

Electronic Spectra:

The electronic spectra of all Ni (II) complexes have been recorded using diffuse reflectance techniques taking Barnum sulphate as a standard in the region 11000-25000 cm⁻¹. The band position are tabulated in table-6.

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Table-6
Electronic Spectra of Ni (II) Complexes of the Ligands DOSC and DOTSC Ligands.

Complexes	Bond Position with assignment in cm ⁻¹		
	³ T _{1g} (F) → ⁴ T _{2g} (F)	⁴ T _{1g} (F) → ⁴ A _{2g} (F)	T _{1g} (F) → T _{2g} (F)
[Ni (DOSC) ₂ Cl ₂]	11400	15800	23100
[Ni (DOTSC) ₂ Cl ₂]	11500	15700	23200
[Ni (DOSC) ₂ Br ₂]	11800	15600	23000
[Ni (DOTSC) ₂ Br ₂]	11700	15500	23100
[Ni (DOSC) ₂ I ₂]	11300	15200	23600
[Ni (DOTSC) ₂ I ₂]	11200	15100	23500
[Ni (DOSC) ₂ (NO ₃) ₂]	11900	15300	23900
[Ni (DOTSC) ₂ (NO ₃) ₂]	12000	15400	23800
[Ni (DOSC) ₂ (ClO ₄) ₂]	12100	16200	24100
[Ni (DOTSC) ₂ (ClO ₄) ₂]	12200	16100	24200

Electronic Spectral of all Ni (II) complexes were indicated that three sharp and broad absorptions one in the region 12200 -11200 cm⁻¹, second in region 16200 – 15100 cm⁻¹ and third one in region above 23000 cm⁻¹. This indicated that stereochemistry of the Ni (II) complexes to be octahedral.

IV. CONCLUSION

Hence on the basis of elemental analysis, infraed spectra, electronic spectra, magnetic and moment data, the ligands DOSC and DOTSC acts in a neutral tridentate manner and coordination takes place through phenolic oxygen atom of Coumadin ring, imine N atom and thione S atom of the ligand and geometry of the complexes were proposed to be octahedral in nature as shown in fig -3 and fig- 4 .

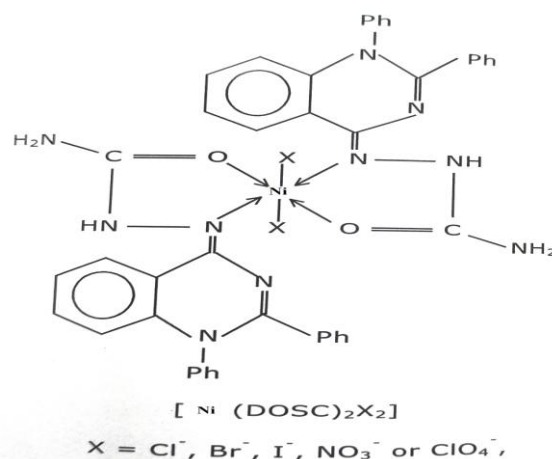


Fig -3

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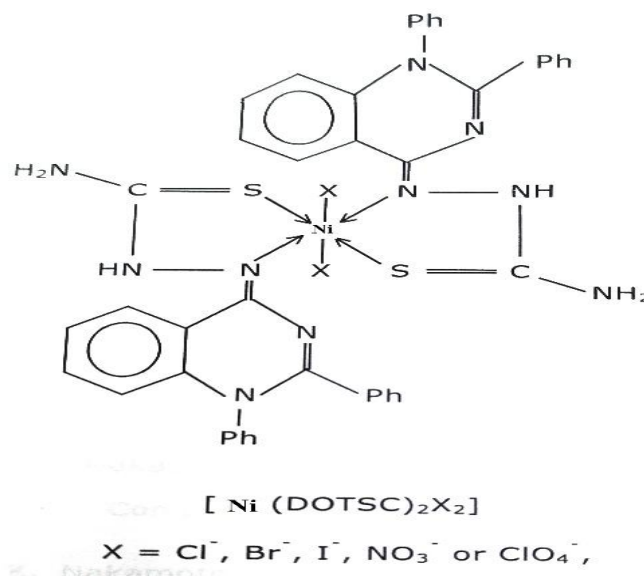


Fig -4

V. ACKNOWLEDGEMENT

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