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A SIMPLE APPROACH FOR PREPARATION OF BIS-(2-ARYL)-1-H-BENZIMIDAZOLE NICKEL (II) CHLORIDE COMPLEX

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Abstract: An ecofriendly method for synthesis of bis-(2-aryl)-1H benzimidazole metal salt complexes (5a-e) have been reported by interaction of alcoholic solution of metal salt and solution of 2-(aryl)-1H-benzimidazole (3a-e) in the ration 1:2 at room temperature and stirred continuously for 72 hrs. Initially 2-aryl-1H-benzimidazole (3a-e) as ligand were obtained by interaction of diphenylamine (1) and aryl acid (2a-e) without using solvent in presence of Fe_2O_3 as a catalyst. The data obtained from the Rast's camphor method, IR and colorimetric estimation fully supported the structure of above metal salt complexes.

Keywords: Benzimidazole, heterocycle-metal salt complex

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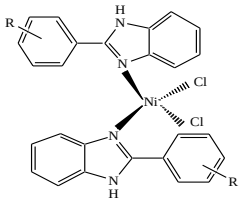
INTRODUCTION

The most prominent benzimidazole compound is N-ribosyl-dimethyl benzimidazole which acts as n-axial ligand for cobalt in vitamin B_{12}[1]. Benzimidazole, in an extension of the well-elaborated imidazole system, has been used to carbon skeletons for N-heterocyclic carbenes. The NHCs are usually used as ligands for transition metal complexes[1, 2]. Based on their broad biological function, they are used in clinical medicine as antiulcer activity[3], anti-tumor[4], anti-viral[5], anti-protozoal[6], anti-inflammatory[7] and anti-oxidant[8]. For effective antimicrobials indicates that the benzimidazole still remain as one of the most versatile class of compounds against microbes[9].

Many examples of metal containing drugs have been reported in the literature, gold containing complexes such as auranofin are commonly used to treat rheumatoid arthritis[10], radiopharmaceuticals based on metals such as technetium and rhenium are used in imaging and radiotherapy[11] and ruthenium complexes have had some success as anticancer drugs[12, 13]. Some of the reported earlier methods in which binuclear Cu (II) complex (Ni_2 (L) 3 bis-(2-hydroxy-5-bromosalicylideneamino)-propan-2-ol have been reported[14]. Bending interaction of water soluble Co (II) complex of Shiff base ligand (L), with calf thymus DNA (CT-DNA) has been reported. Synthesis of Cu (II), Co (II) and Hg (II) metal complex of unsymmetrical tetradentate Schiff base, o-hydroxy benzophenone-1, 2-diaminobenzene-pyrrole-2-carbaldehyde have also been reported [16-17] and Manganese (II) complex of the method of preparation was different that the deprotonated ligand coordinates to the Mn (II) ion with octahedrally hexacoordinate atom via the pyridine, nitrogen and sulphur atom was reported by C. L. Chen[18].
After extensive literature review, the attempt has been made to synthesis of bis-2-aryl-1 H-benzimidazole metal salt complex containing benzimidazoles heterocyclic as a ligand compound and Ni (II) as metal. The general structure shown below,



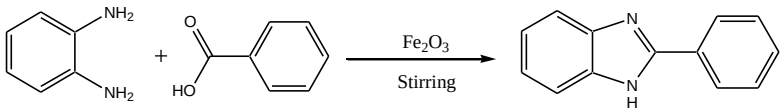
The above metal salt complexes containing aryl-benzimidazole ligands have characterized by Rast's camphor method, IR and colorimetric estimation.

EXPERIMENTAL

The melting point of synthesized compound were recorded using digital melting point apparatus (Veego -DMP) and uncorrected. Chemicals used were of A-R grade, IR spectra were recorded on Perkin Elmer spectrophotometer in the range 4000-400 cm in Nujol Mull as KBR pellet. Reactions were monitored by a TLC till single spot observed and colorimetric estimation was performed on Systronic Instrument for validation of Lambert Beer Law and Rast's Camphor method was used to determine the molecular weight of complex. All reactions were carried out by stirring on magnetic stirrer.

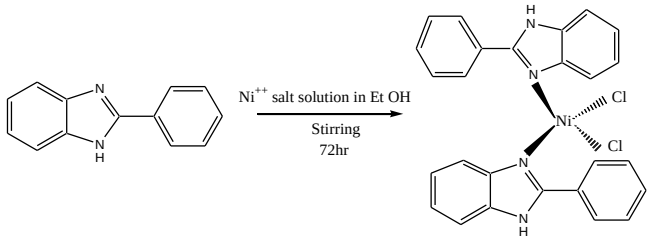
Preparation of bis(2-phenyl)-1-H-benzimidazole Nickel (II) chloride complex

Synthesis of 2-(phenyl)-1-H-benzimidazole 3a
An equimolar mixture of diphenylamine (1) and benzoic acid (2) was stirred together in presence of Fe_2O_3 as a catalyst for 30-45 min. A solid mass obtained and was identified as 2-(phenyl)-1-H-benzimidazole (3a) having melting point 290°C, % yield 60, molecular formula was found to be $C_{13}H_{10}N_2$.



1) Synthesis of bis (2-phenyl)-1 H benzimidazole Nickel (II) chloride complex

The alcoholic solution of Nickel salt was added drop wise to a completely dissolved and stirring solution of 2-(phenyl)-1-H-benzimidazole in 100 ml conical flask in mole ration 1:2 and stirred continuously for 72 hrs at room temperature. A solid mass obtained washed with methanol to get desire complex i.e. Bis-(2-phenyl)-1-H-benzimidazole Nickel (II) chloride complex (5a) having melting point 163°C, % yield 75, molecular formula was found to be $C_{26}H_{20}N_4NiCl_2$.



RESULT AND DISCUSSION

Synthesis of bis-(2-aryl)-1H benzimidazole metal salt complexes (5a-e) have been achieved by interaction of diphenylamine (1) and aryl acid (2a-e) in presence of Fe_2O_3 as a catalyst to form a 2-aryl-1H-benzimidazole (3a-e) as ligands. Further alcoholic solution of metal salt was added to solution of 2-aryl-1H-benzimidazole in the ration 1:2 and stirred continuously for 72 hrs, the product formed identified as bis-(2-aryl)-1H benzimidazoles metal (II) chloride complexes (5a-e). All complexes are soluble in solvent like acetonitrile, N, N-dimethyl formamide, dimethyl sulphoxide etc. Molecular weight determine by the Rast's Camphor method matching with the theorotical molecular weight of the complexes (5a-e).

Name of the compound	% yield	m. p.
1) Bis-[2-Phenyl]-1-H-benzimidazole Nickel (II) chloride complex (5a). $C_{26}H_{20}N_4NiCl_2$	75%	163°C
2) Bis-[2-hydroxy Phenyl]-1-H-benzimidazole Nickel (II) chloride complex (5b). $C_{24}H_{20}N_4NiCl_2$	60%	162°C
3) Bis-[2-(4-amino Phenyl)-1-H-benzimidazole] Nickel (II) chloride complex (5c). $C_{26}H_{22}N_6NiCl_2$	72%	161°C
4) Bis-[2-(4-chloro phenyl)-1-H-benzimidazole] Nickel (II) chloride complex (5d). $C_{24}H_{18}N_4NiCl_4$	74%	161°C
5) Bis-[2-(4-Nitro Phenyl)-1-H-benzimidazole] Nickel (II) chloride complex (5e). $C_{24}H_{18}N_6O_4NiCl_2$	72%	161°C

1) Rast's Camphor Method

Rast's Camphor method was employed to determine the molecular weight of bis-(2-aryl)-1-H-benzimidazoles Nickel (II) chloride complexes (5a-e). The 50 mg of the complex was weighted in a test tube and about 500 mg camphor was added. The test tube was sealed completely and heated on water bath until become a homogenous mixture. After cooling the melting point of the mixture was determined by using Beckman thermometer. The difference between the melting point of pure camphor and mixture was determined. The ratio of solute and solvent taken is 1:10 for determining the molecular weight of complexes by using formula.

$$M = \frac{1000 \text{ x } K \text{ x } w}{\Delta T \text{ x } W}$$

Where, M = molar mass of solute, w = mass of solute
W = mass of solvent (camphor), ΔT = depression in m. p.
K = molal depression constant (40)

Compound No.	Molecular weight of compound	Molecular weight of compound calculated by Rast's method
5a	518.03	571.42
5b	550.05	500
5c	548.09	444.44
5d	586.95	571.42
5e	608.05	666.66

2) IR spectra of complexes

All newly synthesized bis-(2-aryl)-1-H-benzimidazoles Nickel (II) chloride complexes (5a-e) were characterised by IR bands in solid state with KBr, the band appearing in the range 1612-1686 cm^{-1} reasonably assigned for Aro C=C stretching vibrations of the ligand. The characteristic stretching bands displays in the range 2900-3051 cm^{-1} and 3200-3400 cm^{-1} assigned for C-H and N-H stretching vibrations respectively. The far IR spectrum of the complexes shows bands in the range of 440-350 cm^{-1} have been attributed to M-N stretching vibrational frequency.

The IR spectral analysis of compound bis (2-phenyl)-1-H-benzimidazole Nickel (II) chloride complex (5a-e) showed the presence of following absorption bands.

Compound 5a: 3562, 2900, 1651, 435 cm^{-1}, N-H, C-H, Aro C=C, M-N Stretch
Compound 5b: 3383, 3041, 1686, 433 cm^{-1}, N-H, C-H, Aro C=C, M-N Stretch
Compound 5c: 3383, 3041, 1612, 430 cm^{-1}, N-H, C-H, Aro C=C, M-N Stretch
Compound 5d: 3394, 3051, 1651, 441 cm^{-1}, N-H, C-H, Aro C=C, M-N Stretch
Compound 5e: 3560, 2900, 1652, 432 cm^{-1}, N-H, C-H, Aro C=C, M-N Stretch

3) Calorimeter estimation

Colorimetric estimation involve measurement of absorbance of different concentration of bis-(2-aryl)-1-H-benzimidazoles Nickel (II) chloride complexes (5a-e) salt solution, when absorbance is plotted against concentration, calibration curve was obtained from which the concentration of metal can be find out using formulae

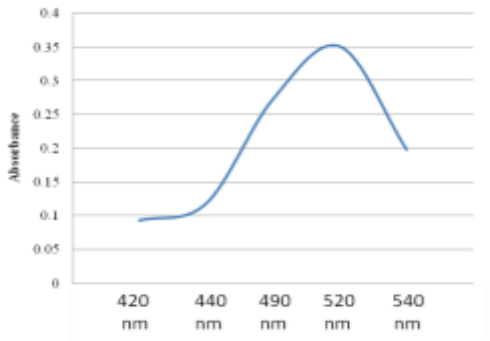
$$\log\frac{I_0}{I_t} = \varepsilon C x$$

Where, ε is molar extinction coefficient, C is concentration in mole/litre, x is thickness in cm.

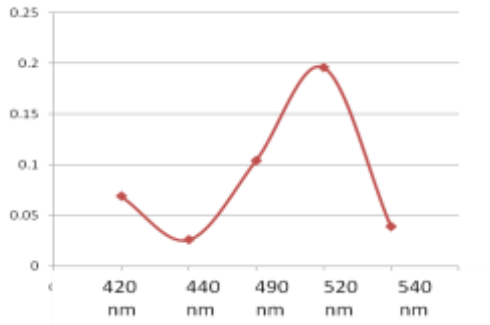
$\log\frac{I_0}{I_t}$ is called optical density (OD) or absorbance (

∴ OD or A = ε C x

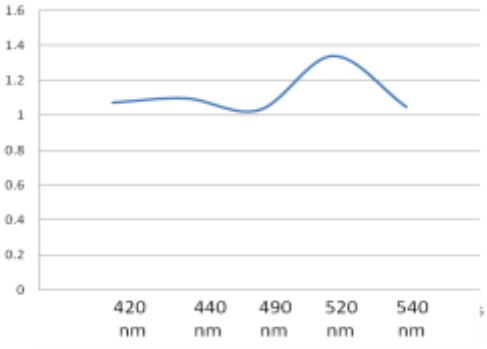
Colorimetric graph between absorbance and wavelength for compounds 5a-e



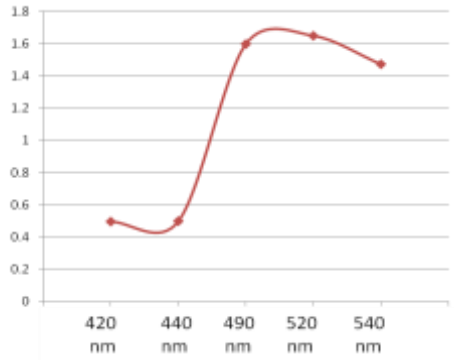
Bis-[2-Phenyl]-1 H-benzimidazole] Nickel (II) chloride complex (5a)



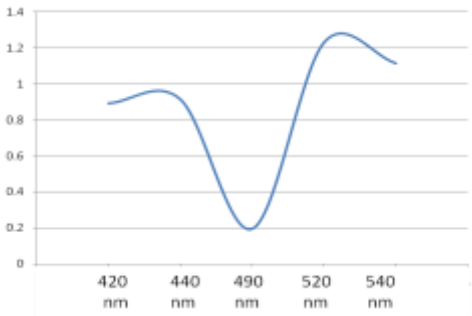
Bis [2-hydroxy Phenyl]-1H-benzimidazole] Nickel (II) chloride complex (5b)



Bis-[2-(4-amino Phenyl)-1H-benzimida -zole] Nickel (II) chloride complex (5c)



Bis-[2-(4-chloro phenyl)-1H-benzimidazole] Nickel (II) chloride complex (5d)



Bis-[2-(4-nitro-phenyl)-1H-benzimidazole] Nickel (II) chloride complex (5e)

All these newly synthesized bis-(2-aryl)-1H-benzimidazoles Nickel (II) chloride complexes (5a-e) salt complexes were shown characteristic maximum absorption wavelength at about 520 nm indicate formation of heterocyclic ligands and their metal complexes.

CONCLUSION

An ecofriendly method for synthesis of bis-(2-aryl)-1H benzimidazole metal salt complexes (5a-e) have been reported with some merits such as simple, clean, efficient and easy work up procedure. The representative complex salts have been achieved by interaction of alcoholic solution of metal salt and solution of 2-(aryl)-1H-benzimidazole (3a-e) in the ration 1:2 at room temperature and stirred continuously for 72 hrs. The data obtained

from the Rast's camphor method, IR and colorimetric estimation fully supported the structure of above metal salt complexes.

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