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Microwave assisted synthesis, spectral and antibacterial investigations on complexes of Ni (ii) with amide group containing ligands

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Abstract: The Present research work describes the synthesis, spectral and antibacterial studies on the complexes of few complexes of Nickel (II) with amide group containing ligands. The characterizations of the compounds have been carried out on the basis of elemental analysis, infrared, electronic spectra and magnetic susceptibility studies. Antibacterial activities of these ligands and complexes have also been reported on S.aureus and E.coli microorganisms. The diffuse reflectance spectrums of the complexes show bands in the region 9165 cm^{-1} to 27027 cm^{-1} assignable to $^3A_{2g}$ (F) $\rightarrow ^3T_{2g}$ (F),$^3A_{2g}$ (F) $\rightarrow ^3T_{1g}$(F), $^3A_{2g}$ (F)$\rightarrow ^3T_{1g}$ (P)transitions. The magnetic moment (2.87 BM) of the complex indicates high octahedral environment. The microwave method of synthesis of complexes have been found easier, convenient and ecofriendly.

Keywords: Microwave, amide, Nickel (II).

1. INTRODUCTION

Amides play vital roles in nature. All proteins are polyamides and make up a large part of the animals body [1]. They are found in all living cells and are principle materials of skin, muscles, nerves, blood, enzymes, antibodies and many hormones. Metal or metalloid amide are compounds which contain one or more $–CONH_2$ ligand groups or a simple derivative [such as –CONHR, $-CONR_2$, where R = methyl, phenyl, $SiMe_3$ etc.) attached to metal. Amides of sodium and potassium are the first examples of metal amides. Metal or metalloid amides may be mono, di- or poly nuclear and nitrogen is in a three coordinated environment. Metal amides include many important natural products such as heamin (a porphyrin), chlorophyll (a dihydroporphyrin), vitamin B_{12} etc. Importance of amide group containing compounds have also been recognized in various fields of chemistry and biology [2-4].

Manganese is essential to organisms and activates numerous enzymes and for certain enzymes there appears to be a high specificity for manganese (II). Deficiency in soils has led to the infertility in mammals bone malformation in growing chicks [5]. Recently complexes of Mn(II) with high antimicrobial property have been reported and their characterization have been made on the basis of spectral investigations[6-7]

The present research work describes the synthesis, spectral and antibacterial studies on the complexes of Ni (II) with amide group containing ligands. The complexes have been characterized on the basis of elemental analysis, infrared, electronic spectra and magnetic susceptibility studies.

The PVC plasticized based sensor incorporates Mn^{II} [2-formylquinoline thiosemicarbazone] complex in the presence of tri dodecyl methyl ammonium chloride (TDMAC) as a lipophilic cationic additive [8].

2. EXPERIMETAL

2.1 Apparatus

(i) EC Double Beam UV-VIS Spectrophotometer (UV 5704SS), with quartz cell of 10 mm light path was used for Electronic spectral measurement at GCRC (Green Chemistry Research Center) Govt. Dungar College (NAAC A-Grade) Bikaner, (Raj.).

(ii) IR spectra were recorded on Bruker Optic Model Alpha (FT-IR) (Zn-Se Optics, ATR) (4000-500 cm-1) using KBr disc at SIL, P.G. Dept. of chemistry, Govt. Dungar College (NAAC-A- Grade) Bikaner, Rajasthan.

(iii) Microwave synthesis was carried out in domestic microwave oven Model KENSTAR-OM20ACF, 2450MHz, 800W and GMBR (Green Microwave Biochemical Reactor) at GCRC, P.G. Dept. of Chemistry, Govt. Dungar College (NAAC-A- Grade) Bikaner, Rajasthan.

(iv). All biological activities have been carried out with horizontal laminar, BIFR, Bikaner.

2.2 Materials and method

Synthesis of Nickel (II) complexes with amide group containing ligand

For the synthesis of Nickel (II) complexes with amide group containing ligands, a solution of Nickel Chloride (0.001 mole in 30 ml ethanol) has been taken in a 250 ml round bottom flask, in this solution respective amide ligand (i.e. N2PB, N2PA, N46DM2PB, N46DM2PA, N6H2MC4PB, N6H2MC4PA, N26DH4PB, N26DH4PA) (0.003 mole) was added slowly with constant stirring. The reaction mixture was placed on a magnetic stirrer with constant stirring for 6-7 hours at room temperature.

In the alternative green synthesis, the reaction mixture was irradiated in a microwave reactor at 600 W for 2-10 minutes.

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The solid precipitate obtained in both the methods was separated and crystallized. Crystals were purified and recrystalized with alcohol and dried under vacuum.

3. RESULT AND DISCUSSION

The complexes of Ni (II) with amide group containing ligands are stable at room temperatures over a long period of time. The nickel complexes were, soluble appreciably in DMF, methyl alcohol, ethyl alcohol but partial soluble in water.

The elemental and metal estimations gave satisfactory results as expected. The physical and analytical data of complexes are given in Table 1.

3.1. Electronic Spectra

The nickel (II) ion has $3d^8$ outer electronic configuration which gives rise to the triplet d singlet terms (in order of increasing energy) ^3F, ^1D, ^1P, ^1G, ^1S. Six coordinate octahedral nickel (II) complexes exhibit a simple spectrum involving three spin allowed transitions since, in an octahedral field ^3F ground term splits into triplet terms, so these three transitions are,

$$^3A_{2g}\,(F) \rightarrow {}^3T_{2g}\,(F)\ (\nu_1)$$
$$^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(F)\ (\nu_2)$$
$$^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(P)\ (\nu_3)$$

These three transitions are observed in the regions of 7000-13000 cm^{-1}, 11000-20000 cm^{-1} and 20000-28000 cm^{-1}. These bands are show in Table 1.

These observations reveal that Ni (II) complexes have octahedral environment.

3.2. Vibrational Spectra

Vibrational spectra were recorded in KBr pellets and polyethylene film in mid and far IR regions and some diagnostic bands are presented in Table 3. An examination of the vibrational spectra of all complexes reveal the same coordination sites offered by amide group containing ligands for complexation as in the case of copper and cobalt complexes.

The IR bands due to amide ν (N-H) mode observed at 3163-3382 cm^{-1} for the free amide group containing ligands are shifted to higher frequencies indicating non-participation of nitrogen atom of amide group in coordination.

Amide -I band due to ν(C=O) shift negatively opposite to that of ν (N-H) in the complexes suggesting carbonyl oxygen coordination [9].

In complexes pyrimidinyl nitrogen participates in bonding, which has been confirmed by the 20-82 cm^{-1} negative shifting of pyrimidinyl ring peak in complexes to the comparison of ligands.

These observations have ambiguous and support the final structural conclusions of the complexes and the mode of bonding in them.

3.3. Magnetic Susceptibility Measurements

The magnetic behaviour of bivalent nickel complexes depends upon the nature of the ligand and geometry of the complexes.

Octahedral Ni (II) complexes involve sp^3d^2 hybridization. Ni (II) complexes exhibit paramagnetic behaviour due to the presence of two unpaired electrons [8]. The magnetic moment values are given in Table 2.

Table- 1: Physico-chemical Data of Ni (II) Metal Complexes(C.M.= Conventional method, M.M.= Microwave method)

S. No.	Complexes	Colour	Reaction period		Yield %		Elemental analysis Calculated(Found)%		
			C.M. hrs.	M.M. min.	C.M.	M.M.	C	H	N
1	$[Ni\text{-}(N2PB)_3]Cl_2$	Pale Yellow	6	2.30	40	50	54.47 (54.40)	3.71 (3.65)	17.33 (17.25)
2	$[Ni\text{-}(N2PA)_3]Cl_2$	Colourless	6	2.30	35	50	39.92 (39.85)	3.88 (3.84)	23.29 (23.20)
3	$[Ni\text{-}(N46DM2PB)_3]Cl_2$	Light yellow	6	2.40	30	45	57.77 (57.70)	4.81 (4.75)	15.55 (15.45)
4	$[Ni\text{-}(N46DM2PA)_3]Cl_2$	Orange	6	2.40	40	45	46.08 (46.00)	5.28 (5.15)	20.16 (20.10)

Table-2 : Magnetic moments and electronic Spectral data of ligand and Ni(II)metal complex

SN	Ligand and Complex	R_f value	μ_{eff} (BM)	Electronic Spectral Bands λ_{max} (cm^{-1})	Tentative assignments	Expected Geometry
1	$[Ni\text{-}(N2PB)_3]Cl_2$	$(.0931)^a$		9551,11376,12484,13550, 15384,18587,20491,22050 ,24630,27173	$^3A_{2g}\,(F) \rightarrow {}^3T_{2g}\,(F), {}^3A_{2g}\,(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(P)$	Distorted Octahedral
2	$[Ni\text{-}(N2PA)_3]Cl_2$	$(0.944)^a$		9153,13850,14836,16129, 17006,18315,26631	$^3A_{2g}\,(F) \rightarrow {}^3T_{2g}\,(F), {}^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(F)$ $^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(P)$	Distorted Octahedral
3	$[Ni\text{-}(N46DM2PB)_3]Cl$	$(0.900)^a$		9165,14084,14598,16103, 17241,26990,	$^3A_{2g}\,(F) \rightarrow {}^3T_{2g}\,(F), {}^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(F)$ $^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(P)$	Distorted Octahedral
4	$[Ni\text{-}(N46DM2PA)_3]Cl_2$	$(o.869)^b$		9610,14771,16863,18867, 22624,24630,	$^3A_{2g}\,(F) \rightarrow {}^3T_{2g}\,(F), {}^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(F)$ $^3A_{2g}\,(F) \rightarrow {}^3T_{1g}\,(P)$	Distorted Octahedral

a= acetone: carbon tetrachloride (6:4), *b*= acetone: carbon tetrachloride (7:3)

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Table- 3: IR Vibrational frequencies of Ni (II) transition metal complexes

S. No	Complexes	ν_{N-H} (amide)	$(\nu_{C=O})^a$	$(\nu_{C-N+\delta N-H})^b$	$(\nu_{N-H+\delta C-N})^c$	Pyrimidinyl	ν_{M-N}	ν_{M-O}	ν_{M-cl}
1	N2PB	3382	1674	1410	1288	1621			
	$[Ni-(N2PB)_3]Cl_2$	3464	1645	1500	1360	1580	483	492	----
2	N2PA	3339	1735	1408	1288	1618			
	$[Ni-(N2PA)_3]Cl_2$	3461	1681	1475	1397	1578	482	518	----
3	N46DM2PB	3319	1673	1449	1319	1643			
	$[Ni-(N46DM2PB)_3]Cl$	3383	1671	1475	1334	1613	485	491	----
4	N46DM2PA	3318	1739	1447	1369	1642			
	$[Ni-(N46DM2PA)_3]Cl$	3384	1670	1508	1384	1560	471	545	----

a: - amide - I band, b: - amide - II band, c: - amide – III band

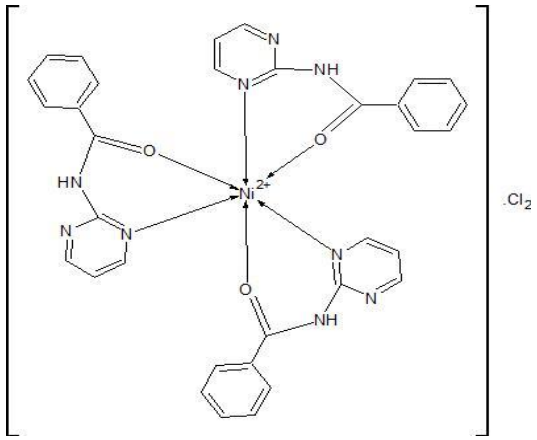

Fig. 1. Tentative Structure of Complex $[Ni-(N2PB)_3]Cl_2$

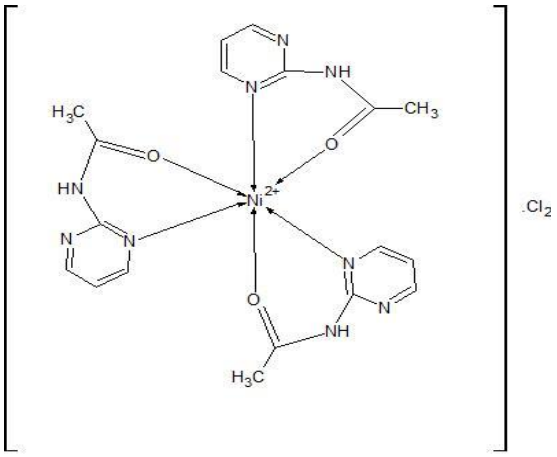

Fig.2. Tentative Structure of Complex $[Ni-(N2PA)_3]Cl_2$

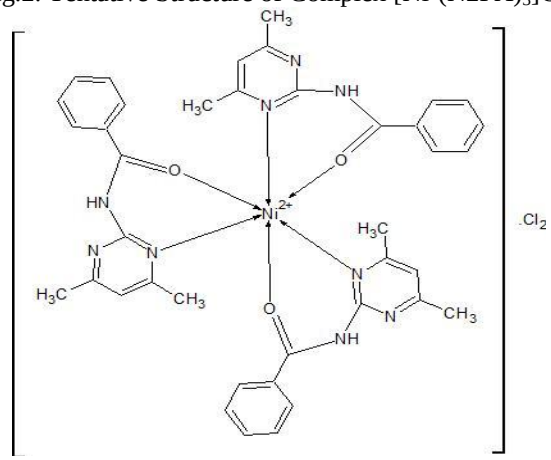

Fig.3. Tentative Structure of Complex $[Ni-(N46DM2PB)_3]Cl_2$

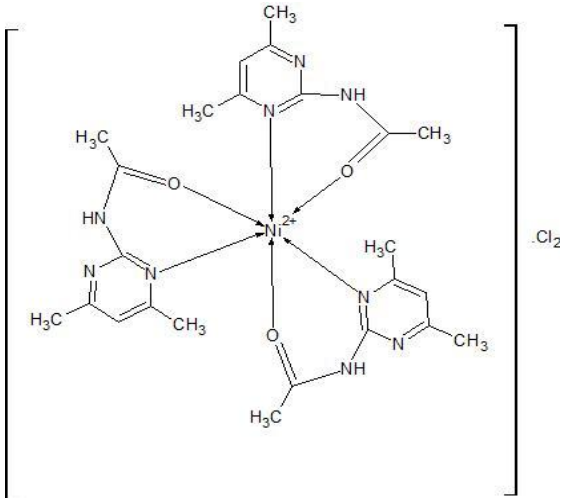

Fig.4. Tentative Structure of Complex $[Ni-(N46DM2PA)_3]Cl_2$

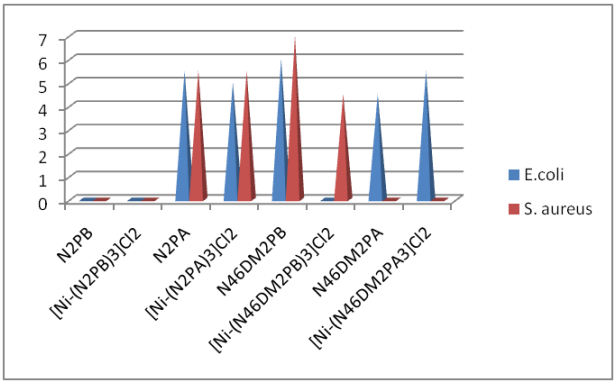

Fig.5. Biological activity of amide Ligands and their metal complexes.

4. CONCLUSION

On the basis of vibrational spectra, it is concluded that amide ligands show tetradentate behaviour in their Ni (II) complexes by coordinating through carbonyl oxygens of amide groups. The electronic spectral assignments are characteristic to the geometries adopted by metal ions in complexes. Thus, Ni (II) adopts octahedral geometry in the complexes of amide ligand. The magnetic moments tally with the electronic spectral data.

On the basis of these studies the tentative structures have been proposed for the complexes and which are given in Fig. 1 to 4 for Ni (II) complexes [10].

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Ligand are more antibacterial activity compare to their metal complexes exept $[Ni\text{-}(N46DM2PA)_3]Cl_2$. Fig. 5

On the basis of vibrational spectra, it is concluded that amide ligands show tetradentate behaviour in their Ni (II) complexes by coordinating through carbonyl oxygen of amide groups. The electronic spectral assignments are characteristic to the geometries adopted by metal ions in complexes. Thus, Ni (II) adopts octahedral geometry in the complexes of amide ligand. The magnetic moments tally with the electronic spectral data. On the basis of these studies the tentative structures have been proposed for the complexes and which are given in Fig.1 to 4 for Ni (II) complexes.

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