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Synthesis & Characterisation of Ni (Ii) Chelates of Diethylmesoxalate Phenylhydrazone and Their Electron Releasing As Well As Electron Withdrawing Substituent in Ammoniacal Medium

Nimisha Kiran[1]* Dr. Sheo Satya Prakash[2]

[1] PhD Scholar of Chemistry, Magadh University, Bodhgaya, Bihar

[2] Professor of Chemistry, A. N. College, Patna Magadh University

Abstract – The presents work describes the synthesis and characterization of complexes of Ni (II) with unsubstituted and with substituted (electron releasing as well as electron withdrawing substituent in phenyl nucleus) ligand obtained by coupling of aryldiazonium salt with diethylmalonate. Due to insoluble nature of complexes,[1] H NMR and conductivity data could not be obtained as existence. Since all complexes decomposes before ionization as its melting point are very conclusive evidence could not be obtained by mass spectra. In absence of conductivity data, 1HNMR and mass spectra all the complexes are characterized mainly on the basis of elemental analysis, magnetic moment values, uv-visible spectra and IR Spectra.

Keywords: NI (II) Chelates / Diethylmesoxalate phenylhydrazones/ electronic spectral studies/ IR Spectral studies / Magnetic studies.

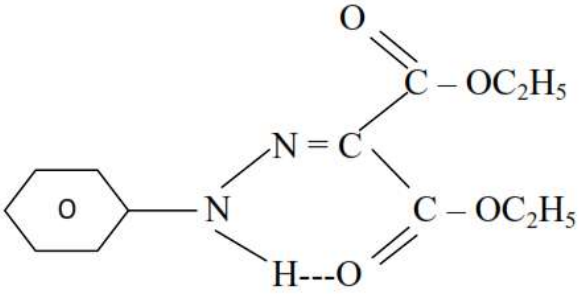
- x -

INTRODUCATION

The structure of product formed by coupling of active methylene compounds with arylhydrazonium salts or by condensation of arylhydrazines with carbonyl compounds has generated in fact, so much arguments and speculation as hardly any other topic in the whole realm of organic chemistry so far. Since the normal hydrazone is capable of tautomerising to the azo and enehydrazine forms unambiguous assignment of structure to the coupling product has eluded final solution till recent past.[1]

In the light of above controversies regarding the structure of coupling products, the structure of various coupling products have been investigated by several workers and they are proved to be hydrazones[2] on the basis of more recent and advanced techniques such as[13] CNMR, Mass spectra and X-ray studies. For correctness of hydrazono structure of coupling product of benzenediazonium chloride with active methylene compound, sysnthesis and charactrisation of their derivatives have been carried out by Sahay and co-worker.[3-8]

These hydrazones can behave as polydentate ligned due to presence of several donor sites. Coordination compounds of such arylhydrazones have been reviewed by Prasad, Sahay and Srivastava.[9] This prompted us to study the present work and in continuation of our previous work[10], our finding in the synthesis and characterization of Ni (II) complexes with unsubstitued and substituted (electron releasing as well as withdrawing) ligand (HL) obtained by coupling of aryldiazonium chloride with diethylmalonate are reported here.



Where

$HL_1 \Rightarrow X = H$
$HL_2 \Rightarrow X = O\text{-}NO_2$
$HL_3 \Rightarrow X = m\text{-}NO_2$
$HL_4 \Rightarrow X = p\text{-}NO_2$
$HL_5 \Rightarrow X = O\text{-}CH_3$
$HL_6 \Rightarrow X = p\text{-}CH_3$

MATERIALS AND METHODS

Diethylmesoxalate phenylhydrazone and their electron releasing & electron withdrawing substituent in phenylnucleus were synthesized by coupling benzendiazonium chloride with diethylmalonate in sodium acetate medium.[11-12] Nickel Sulphate hexahydrate (1.314 gm, 0.005 mol) was dissolved in water and ammonium hydroxide was added drop wise till a clear solution was obtained and to this an ethanolic solution of ligand (0.005 mole) or a solution of ligand (0.005 mole) in N, N-Dimethyl formamide was added. The pH of the reaction mixture was checked and found to be 9-10. The resulting of mixture was refluxed on small flame or water bath for about six hours. The pH of the reaction mixture was checked time to time and maintain by adding few drop of ammonium hydroxide. Coloured ppt. of complexes were obtained. Complexes were filtered in hot and washed several times with water and then with benzene for complete removal of unreacted metal salt and ligand. All complexes were carefully crystallized with nitrobenzene and dried over fused $Cacl_2$. Absence of free ligand was ascertained by T.L.C. All complexes were found to be insoluble in water and organic solvents.

DISCUSSION

The elemental data (Table) show that the isolated Ni^{+2} complexes have the general composition $[NiL(OH)(NH_3)_2(CH_2O)]$ for all ligands. In this present investigation magnetic moment of Ni^{+2} complexes fall within the range 2.93 to 3.16 B.M. These values are in the range expected for Ni^{+2} octahedral complexes.[13-14] In the absence of magnetic susceptibility at different temperature, the observed data at room temp. is sufficient enough to rule out any antiferromagnetic coupling between adjacent Ni^{+2} ion. This also indicates that though H-bonding exist between H atom of coordinated H_2O or OH or NH_3 group and the O atom of ester group the neighbouring Ni^{+2} ions are apart from each other.

The diffuse reflectance spectra of Ni^{+2} complex with ligand HL_1displays broad bands (ignoring the peak due to ligand part) in vicinity of 10416 cm^{-1} (960nm), 15748 cm^{-1} (635nm) and 22883 cm^{-1} (437nm) similar to octahedral complexes[15]. The three bands may be assigned due to transition respectively and are labeled as $Ʊ_1$, $Ʊ_2$ and $Ʊ_3$ respectively.

$^3A_{2g}(F) \quad ^3T_{2g}\,(F)$ ------------- $(Ʊ_1)$

$^3A_{2g}(F) \quad ^3T_{1g}\,(F)$ ------------- $(Ʊ_2)$

and $^3A_{2g}(F) \quad ^3T_{1g}\,(F)$ ------------- $(Ʊ_3)$

The ratio $Ʊ_2/Ʊ_1$ of the frequencies of the first and second band maxima is 1:51, which is characteristic of Ni^{+2} complex having octahedral environments.

In IR spectra, the band around 3100-3150 cm^{-1} which has been assigned to $Ʊ_{N\text{-}H}$ vibration in ligand appears around 3020-3080 cm^{-1}. Two possibilities many occur

- Due to involvement of lone pair of nitrogen in coordination with metal, a lowering may be observed.
- The deprotonation of imino hydrogen and appearance of new peak due to coordinated NH3 molecule.

In first case, a neutral ligand is taking part which seems improbable. The peak at around 1270-1300 cm^{-1} and 1210-1250 cm^{-1} may be assigned as $\int N-H$ mode of vibration due to coordinated NH_3 molecule.[16] However these assignment are not conclusive due to presence of several peaks in this region. The $Ʊ_{C=O}$of ester part (which is not H-bonded) observed at around 1700 cm^{-1} in ligand is shifted to lower frequency by 10-40 cm^{-1} and attributed to H-bonding between the O atom of ester O and H atom of coordinated H_2O or OH or NH_3 groups. The $Ʊ_{C=O}$ [H-bonded in ligand] are localized around 1620-1640 cm^{-1} is further shifted to lower frequency and usually couple with $Ʊ_{C=N}$ vibration and observed around 1620 cm^{-1} (sh). The red shift of $Ʊ_{C=O}$ indicate the coordination of ester O to metal ions. The aquo complexes display a broadband at 3300-3400 cm^{-1} (s), which may be attributed to $Ʊ_{O\text{-}H}$ of water molecule.[17-18] In the region 3320-3380 cm^{-1} (m) the complexes displays a sharp and medium band which is due to $Ʊ_{O\text{-}H}$ of coordinated hydroxy group in the complexes.[19] The presence of H_2O molecule and / or OH group might have been confirmed by comparison of IR spectra in low region frequency region of the sample and its dentrated sample. Due to our limited resources this study could not be undertaken. However in the absence of above study we can assign the O-H stretching unambiguously. The O-H stretching mode observed at around 3200-3600 cm^{-1} is sharp and usually can be seen even in the presence of water absorption.[20-21] In far IR region the complexes displays 2-3 new band located around 500-580 cm^{-1} and 410-430 cm^{-1} attributed to $\upsilon_{Nickel-O}$ and $\upsilon_{Nickel-N}$ respectively.[20-21]

All complexes are stable at room temperature and do not loss weight below 140^0c indicating that H_2O, NH_3 and hydroxy groups are present in coordination sphere.[22] After heating over 140^0c loss of weight was observed gradually with change in colour indicating loss of coordinated molecule from complex.

In this way the Ni^{+2} can be assigned the following structure:-

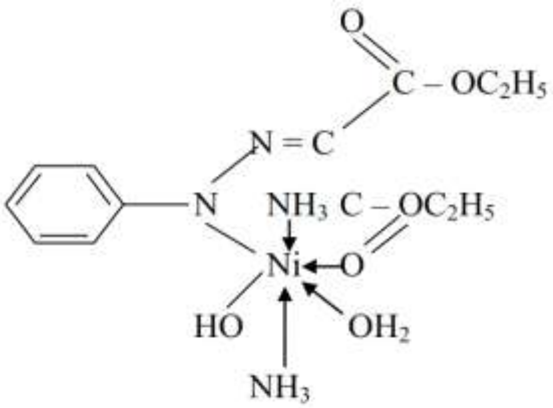


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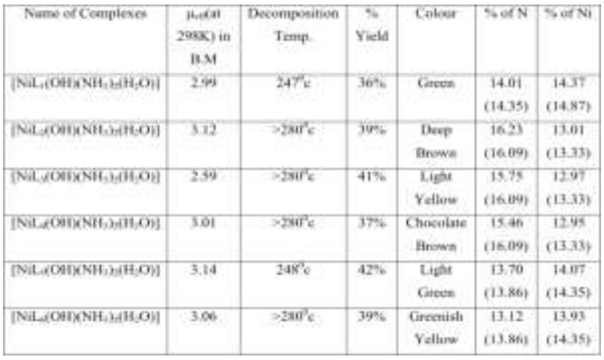
Table-5

Physical Constants, Magnetic Moment and Analytical data of Ni^{+2} complexes



Name of Complexes	μ_{eff}(at 298K) in B.M	Decomposition Temp.	% Yield	Colour	% of N	% of Ni
$[NiL_1(OH)(NH_3)_2(H_2O)]$	2.99	247^0c	36%	Green	14.01 (14.35)	14.37 (14.87)
$[NiL_2(OH)(NH_3)_2(H_2O)]$	3.12	$>280^0c$	39%	Deep Brown	16.23 (16.09)	13.01 (13.33)
$[NiL_3(OH)(NH_3)_2(H_2O)]$	2.59	$>280^0c$	41%	Light Yellow	15.75 (16.09)	12.97 (13.33)
$[NiL_4(OH)(NH_3)_2(H_2O)]$	3.01	$>280^0c$	37%	Chocolate Brown	15.46 (16.09)	12.95 (13.33)
$[NiL_5(OH)(NH_3)_2(H_2O)]$	3.14	248^0c	42%	Light Green	13.70 (13.86)	14.07 (14.35)
$[NiL_6(OH)(NH_3)_2(H_2O)]$	3.06	$>280^0c$	39%	Greenish Yellow	13.12 (13.86)	13.93 (14.35)

Corresponding Author

Nimisha Kiran*

PhD Scholar of Chemistry, Magadh University, Bodhgaya, Bihar