

Four and six coordinate complexes of divalent nickel

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ABSTRACT

Some complexes of Ni(II) with 2-3 dihydrazino quinoxaline have been synthesized and characterized by analytical, conductance, spectral and magnetic data. The ligand behave as bis donor in all the complexes through the ring azomethine nitrogen and phenolic oxygen.

Key words: Four and six coordinate complexes, divalent nickel.

INTRODUCTION

In continuation of our earlier work we have isolated the complexes of bivalent nickel with naphthoyl hydrazones of 2:5- Di-hydroxy-actophenone ($C_{19}H_{16}N_2O_3$).

Six- coordinate Nickel complexes having general formula $[Ni(L)_2]$ & four-co-ordinate dimeric complex of the composition $[Ni(L)]_2$ have been isolated and identified.

These complexes have been characterized by elemental analysis and by conductance, magnetic, electronic & infrared spectral measurements.

EXPERIMENTAL

General methods of preparation & isolation of bivalent Nickel complexes.

Two types of nickel complexes were isolated.

Type 1

Warm aqueous ethanolic solution of the nickel chloride was treated with ethanolic solution of the Schiff base in 1:1 molar ratios. The precipitate

formed, after refluxation for three hours was allowed to settle. The precipitate was washed with water, ethanol and ether and finally dried in vacuo. The yield of complex 70-80% Analysis correspond to molecular formula $[Ni(L)_2]$.

The complexes were stable upto 260°C. Highly soluble in nitromethane DMSO. DMF and CH_3CN partially soluble in acetone and ethanol and insoluble in other common organic solvents.

Type II

A solution of ligand (0.50 m mol) in ethanol (50 ml) was treated with a solution of nickel acetate (0.50 m mol) (50 ml ethanol). The pH of the mixture was adjusted to 5.5 by addition of 3N-HCl and then the solution was refluxed for two hours. The pertinent orange-yellow was obtained after evaporation of the solvent and drying in vacuo over P_4O_{10} (Yield 50-65%). Analysis correspond to $[Ni(L)]_2$ molecular formula.

The complexes did not melt or decompose upto ~280°C. Highly soluble in dimethylformamide nitromethane, CH_3CN and DMSO and less soluble in alcohol and acetone and insoluble in other common organic solvents.

RESULTS AND DISCUSSION

Analytical data shows that nickel form two types of complexes in which this ratio is 1:2 and 1:1. The complexes have the composition.

$[\text{Ni}(\text{L})_2]$, (Type I), $[\text{Ni}(\text{L})_2(\text{Type II})]$ Molar conductance of 10^{-3} M solutions of the complexes in dimethyl sulphoxide are found in the range 17-22 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ showing them to be non electrolyte¹.

In the green nickel complexes of type I, $[\text{Ni}(\text{L})_2]$, the ligands are present in ketonic form while in orange type II, $[\text{Ni}(\text{L})_2]$ they are bonded in enolic form as revealed by the I.R. spectra of the complexes. The tendency of such ligands to act in enolic form largely depends upon the aromaticity of

the nucleus of the hydrazine residue, and pH of the reaction medium⁽²⁾ which facilitate the removal of proton from phenolic group and bind the metal through oxygen in providing the dimeric structure.

Infrared Spectral Studies

On comparing the infrared spectra of the free ligands and the Ni(II), complexes the various points of attachment of the ligand with metal ions have been identified and discussed in detail.

Amide Group Vibrations

None of the spectra of the complexes exhibit absorption bands at 1700 and 3200-3400 cm^{-1} which could be assigned to unreacted keto or primary amine group³⁻⁴. The ligands under investigation shows tautomerism, as such can exist

Analytical Data of Six Coordinated Nickel (II) Complexes

Complex	Found %				(Calculated %)			
	(Ni)	C	H	N	(Ni)	C	H	N
$[\text{Ni}(\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_3)_2]$	8.25	65.30	4.16	7.90	(8.42)	(65.45)	(4.30)	(8.03)

Analytical, Magnetic and Electronic Spectral Data (cm^{-1}) of four Coordinate Nickel(II) Complex(cm^{-1})

Complex	Analytical Data								μ_{eff}	$^1\text{A}_{1g}$
	Found%				Calculated%					
	(Ni)	C	H	N	(Ni)	C	H	N	300°K	
$[\text{Ni}(\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_3)_2]$	15.40	60.38	3.60	7.30	(15.58)	(60.52)	(3.71)	(7.43)	0.30	15312 18893

in ketoD enolic form. Characteristic bands due to amide group appear in the region 1600-1680, 1510, 1250, 650-665 and 490-510 cm^{-1} in the free ligand, which are assigned to ν (C=O) (amide-I); ν (CN+ δ NH) (amide-II), ν (CN) amide-III, (C=O, out of plane deformation) amide-IV and (C=O in plane deformation) amide VI, respectively, showing that the ligand exist in keto form. The band appearing at 3060 cm^{-1} is assigned to ν (NH)⁵.

In the IR-spectra of nickel (Type-I) the position of band appearing at 3060 cm^{-1} due to –NH remain unaffected after complexation, indicating the non involvement of this group in coordination. However the ligand exhibits a band at 1625 cm^{-1} assignable⁶ to ν (C=O) (amide oxygen). The frequency of this band in all the complexes shifted to lower side suggesting involvement of amide oxygen in chelation⁷. Also in the spectra of complexes, amide-I and is shifted to lower frequency

(1620-1650 cm^{-1}) while an increase in frequency is notice in amide-II (1530-1550 cm^{-1}) and amide-III get split into two components between 1200-1220 and 1360-1380 cm^{-1} , No visible change is observed in the position of amide (IV) band (640-660 cm^{-1}) while the band corresponding to amide VI shows a small upward shift (500-515 cm^{-1}). Due to changes in amide group frequency, electron density on oxygen atom of $>\text{C}=\text{O}$ decreases, due to its coordination with metal ions. A new band in the far IR-region due to ν (C-O), ν (M-N) appeared in all the complexes further support terdentate coordination to the metal ion⁸.

Strong band at 1082 cm^{-1} due to ν (C=O) in the case of said ligands, disappear in Ni-Type (II) complexes suggesting enolisation of the ligands and their chelation through the enolic oxygen. The lack of absorption due to ν (N-H) and amide group vibration, and the appearance of strong absorption band, around 1595-1598 cm^{-1} due to $>\text{C}=\text{N}-\text{N}=\text{C}<$ residue confirm deprotonation of the imino proton. The aforesaid coordination pattern of the metal derivatives is further strengthened by the appearance of non-ligand bands in the spectra of metal complexes in the region 490-450, 420-370 cm^{-1} due to ν (M-O) and ν (M-N) vibrations.

Azomethine Group Vibrations

IR-peak for C=N group is observed at 1620 cm^{-1} in the free ligand, where as in the present

context, the complex showed in IR-frequencies in the range 1600 cm^{-1} Shift to frequencies of the metal ligand complex from that of the free ligand reveals the coordination through hetero 'N' atom at 'C=N' group in the complex.

Phenolic Group Vibrations

The IR-frequencies of the phenolic -OH group of the ligand is generally observed around 3265 cm^{-1} which disappear on complexation indicating that bonding through phenolic oxygen atom to metal ion after deprotonation of the phenolic -OH group of the ligand. It is further supported by down ward shifting of ν (C-O) phenolic observed at 1350 cm^{-1} which get shifted to \sim 1330 cm^{-1} . All these observations suggest a distorted octahedral geometry around central metal atom⁹.

In case of Ni (II) Type-II complexes the two bands observed around 1520 and 1280 cm^{-1} in the azomethines are usually associated with the phenolic (C-O) stretching and bending vibrations, respectively¹⁰ shifts to the higher frequency (\sim 1300 cm^{-1}) in the corresponding complexes showing thereby the bonding of the Ni atoms through phenolic oxygen and enolisation of these ligands as well as bonding through oxygen. The splitting of $>\text{C}=\text{N}$ to the formation of $>\text{C}-\text{N}-\text{N}=\text{C}$ group in the complex, further substantiate the bonding through (M \bullet O-C) and involvement of phenolic oxygen in bridging, to form bi-or poly nuclear structure¹¹⁻¹².

Assignments of the Important Frequencies in the Infra-red Spectra of Six-Coordinate Nickel (II) Complex (cm^{-1})

$[\text{Ni}(\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_2)_3]_2$	Assignments
3015mb	ν (N-H) assym and sym
1630s	ν (C=O) of amide I
1600s	ν (C=N) of azomethine
1595m	Phenyl ring vibrations
1545s	(ν CN+ δ NH) of amide II
1525s	Phenolic ν (CO)
1370m1200m	Split of amide III
1270m	Phenolic CO bending
650m	(C=O) out of plane deformation (amide IV)
510m	(C=O) in - plane deformation (amide VI)
480-490wb	ν (Ni-N)+ ν (Ni-O) phenolic
415w	ν (Ni-O) ketone

Assignments of the Important frequencies in the infrared spectra of Four-Coordinate Nickel (II) Complex (cm^{-1})

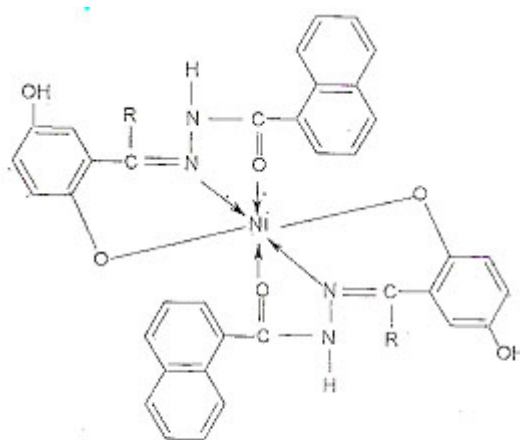
$[\text{Ni}(\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_3)_2]$	Assignments
1600s	ν (C=N) of azomethine
1590s	$>\text{C}=\text{N}-\text{N}=\text{C}<^*$
1555s	Phenolic ν CO
1310m	Phenolic CO bending
480m470m450w460w	ν (Ni-N) + ν (Ni-O)phenolic bridging
400w	ν (Ni-O) enolic

* Coupled with phenyl ring vibrations.

Nicke (II) has 3d electronic configuration and should exhibit a moment value higher than expected for two unpaired electrons in octahedral (2.8-3.2 B.M.) and tetrahedral (3.4-4.2 B.M.) complexes, where as square planar complexes would be diamagnetic. Inereare in moment value from that of spin only value may be due to some mixing in of upper states via spin orbit coupling.

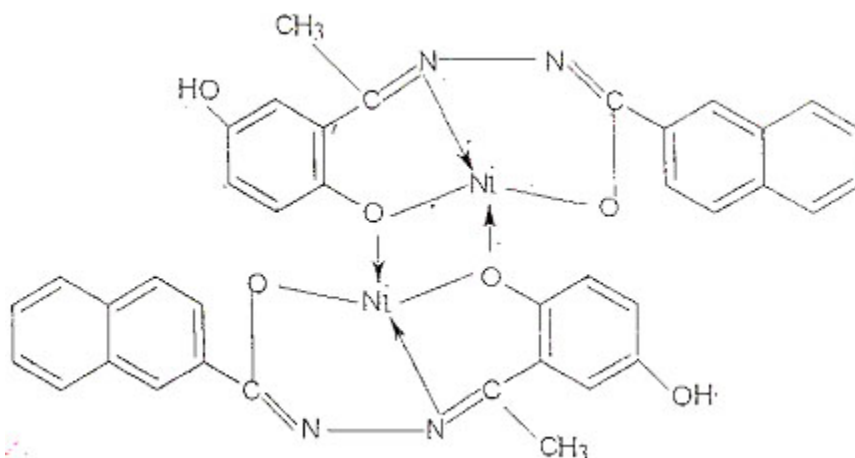
The measured magnetic moment of 3.0-3.20 B.M. for the complexes is in the reported for the spin free octa hedral nickel (II) complexes¹³.

Therefore three spin allowed transitions are observed in octahedral nickel (II) complexes. The energies of these transitions are readily



Six-Coordinate Octahedral Ni(II)

R = CH₃-



Four-Coordinate Square Planar Ni (II)

expressed as functions of $10Dq$ and B . For terms of maximum multiplicity, the energy difference is dependent upon B - and in case of nickel (II), $E(^3F-^3P) = 15B$. The value of B of these complexes calculated from diagonal sum rule $15B = \nu_2 + \nu - 3\nu_1$ (B-free ion 1080 cm^{-1}). Using the value of first spin allowed band (ν_1) and $10Dq$, the energies of ν_2 - and ν_3 -bands were calculated from the equation.⁽¹⁴⁾

$$\nu_{2+3} = \frac{1}{2} (15B+30Dq) + \frac{1}{2} [225B^2 + (10Dq)^2 - 180 B \cdot Dq]^{1/2}$$

The value of ν_2/ν_1 for the present complexes lie in the range 1.65-1.68 conform octahedral geometry around Ni (II) ion.

The ligand show bands at $\sim 215 \text{ nm}$ and $\sim 250 \text{ nm}$ attributable to $\delta-\delta^*$ electronic transitions

Magnetic and Electronic Spectral Data (cm^{-1}) of Six-Coordinate Nickel (II) Complex

Complex	μ_{eff} B.M.	$^3A_{2g}(F) \rightarrow$			Calculated band positions		[($\nu_3-\nu_2$ / ν_1 B β) ν_2] cale. ν_2 - obs.]			
		$^3T_{2g}(F)$ (ν_1)=10 Dq	$^3T_{1g}(F)$ (ν_2)	$^3T_{1g}(P)$ (ν_3)	(ν_3)	(ν_2)	(ν_2)	(ν_1)	B	β
[Ni(C ₁₉ H ₁₄ N ₂ O ₃) ₂]	3.12	10180	17110	25720	16900	25920	410	1.68	763	0.70

within the benzenoid ring and the auxochrome (-OH group) and chromophore (>C=N-group) attached to the benzene ring are responsible for the shift of these bands to the lower energy region. These bands shift to 245 nm and 260 nm in the corresponding compounds due to an increase of electron density on the auxochromic oxygen and chromophoric nitrogen. The ligands further show two maxima at ~ 310 and $\sim 410 \text{ nm}$, which have been assigned to the $\pi-\pi^*$ and $n-\pi^*$ transitions of the >C=N- chromophore and which shift to the lower frequency side in the metal complexes.

Nickel Complexes of Type-II

The spectrum of nickel complexes display a relatively weak band at 560 nm with a shoulder at 500m. This low intensity band is ascribed to (d-d) transition in square planar complexes and assigned to $^1A_{1g} \rightarrow ^1B_g$ based on D_{2h} micro-symmetry⁽¹⁵⁾. The absence of bands around 2000. 1000 and 400 nm rules out the tetrahedral or octahedral geometry of the complexes. This is consistent with the diamagnetic behaviour of the complex.

On the basis of above facts low magnetic moments and different physico chemical studies suggest the following oxygen bridged binuclear structure to the present complexes.

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