



Adducts of Nickel(II) complexes of cyclo(1,2)-dibiguanidinyl bis[2-hydroxy-w-(Benzoyl/4-chlorobenzoyl/3-nitroBenzoyl/3,5-dinitroBenzoyl) acetophenone] with pyridine, 2-methylpyridine and 4-methyl pyridine

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ABSTRACT

NickleNi(II) forms a large number of coordination compounds with different stereochemistry's e.g. tetrahedral, octahedral and square planar. The relative ease of formation and abundance of octahedral complexes may be explained on the basis of crystal field stabilization energy of the d^8 configuration because the stabilization energy produced by an octahedral field on a d^8 ion is higher than that produced by a tetrahedral field.

The Jahn-Teller effect leading to distortion of symmetry is practically inoperative in geometry and favors octahedral geometry. On the other hand, square planar configuration is favored in strong ligand fields leading to the pairing of all the eight 3d electrons. The octahedral complexes involve $sp^3dz^2dx^2-y^2$ (outer orbital) hybridization and the tetrahedral complexes have sp^3 hybridization. Both the types show magnetic moment values corresponding to the presence of two unpaired electrons.

INTRODUCTION

The micro analytical data and the molar conductance values ($142-160 \text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) indicated the formation of ionic, 1:1 Nickel(II) complexes. The spectral and magnetic data have been used to elucidate and explain the stereochemistry.

The stretching vibrations due to (N-H) and ($>C=N$) mode of ($>C=N-H$) in the spectra of the ligands remained unchanged suggesting the non-involvement of nitrogen of (N-H) groups in coordination. The band observed in the spectra of the ligands at $1645-1615\text{ cm}^{-1}$ diagnostic of ($>C=N-C$) mode showed appreciable lowering $25-30\text{ cm}^{-1}$ in the spectra of complexes indicating the involvement of nitrogen atom of this group in complexation.

Another absorption band characteristic of ($C=N$) group underwent a negative spectral shift from $1350-1320$ and $1290-1260\text{ cm}^{-1}$ in the free ligands to $1330-1305$ and $1265-1245\text{ cm}^{-1}$ in the complexes establishing thereby the involvement of imine nitrogen in coordination. In the spectra of the complexes a new band at $1245-1220\text{ cm}^{-1}$ due to stretching frequency of chelate ring indicated the complex formation (Syamal, 1978).

The appearance of a broad band at $3450-3400\text{ cm}^{-1}$ due to (O-H) mode in the spectra of the complexes suggested the presence of coordinated water (Rana and Shah, 1986). The involvement of oxygen and nitrogen in coordination was further confirmed by the appearance of new absorption bands in the far infrared region at $505-485$ and $450-435\text{ cm}^{-1}$ which were assigned to (M-O) and (M-N) stretching vibrations, respectively (Ferraro, 1971 and Nakamoto, 1978).

The square planar complexes involve dx^2-y^2 $S_p x P_y$ hybridization and are invariably diamagnetic. For octahedral Nickel(II) complexes the magnetic moments range from 2.9 to 3.3 BM depending on the magnitude of orbital contribution (Greenwood, 1990).

The effective magnetic moment values of nickel(II) complexes of L_I-L_{IV} at 25°C were found to be 3.18 - 3.28 B.M. indicating the presence of two unpaired electrons.

Six coordinated nickel(II) complexes exhibit a simple spectrum involving three spin allowed transitions to

the $3p$ (F) $5 3p$ (F) and 3 (P) levels. In addition, two spin forbidden bands to $1E_g$ and $1T_{2g}$ are frequently observed (Lever, 1968). The Tanabe-Sugano diagram representing the splitting patterns for the ground term $3p$ and the excited state 3 , in an octahedral field is shown in Fig.

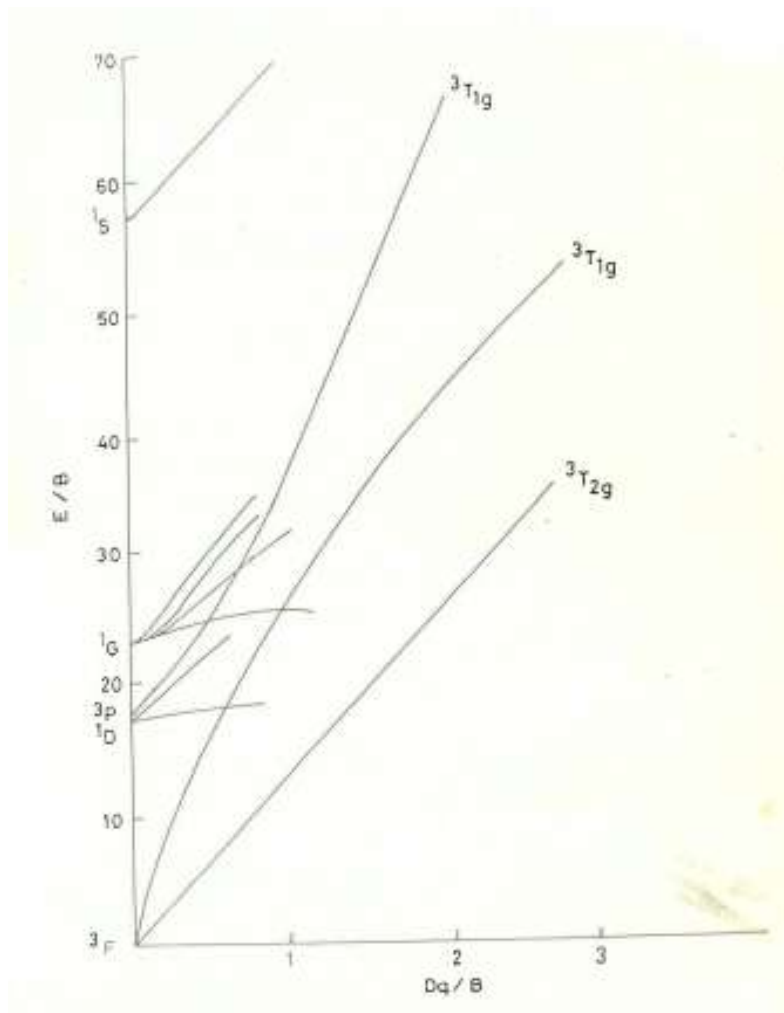


Fig: Tanabe-Sugand Diagram for Ni(II) in an octahedral field

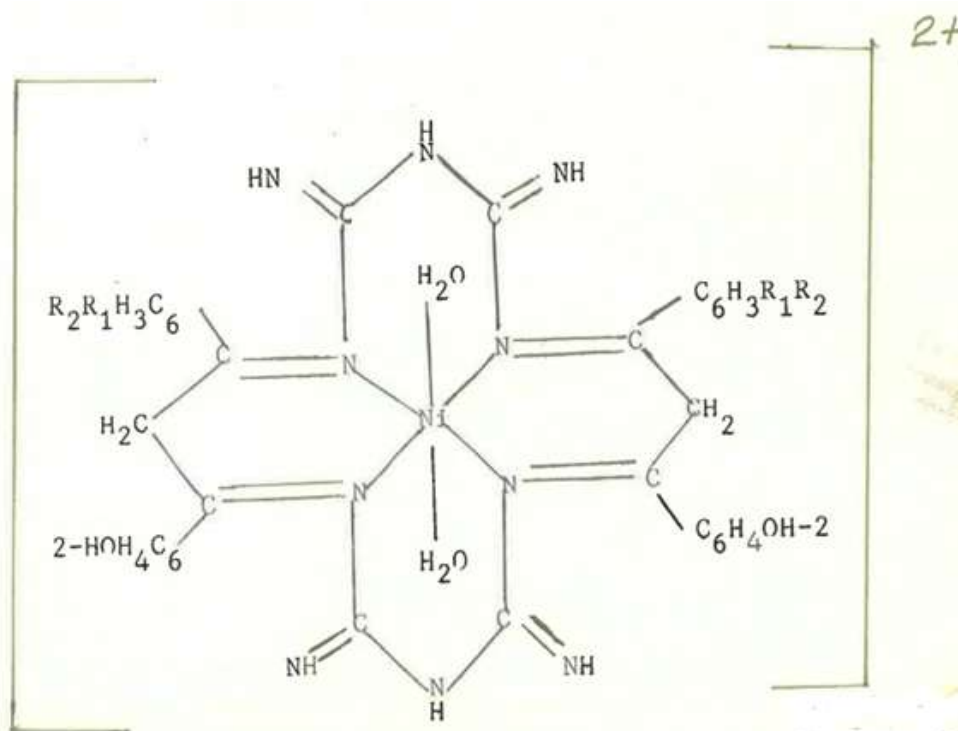
The calculated values for energy ratio (1.62-1.71), $10 Dq$. ($10300-10830 \text{ cm}^{-1}$), interelectronic Racah Parameter ($695-770 \text{ cm}^{-1}$) and the nephelauxetic ratio (.667-.739) were consistent with those for octahedral complexes (Lever, 1984).

The values of B and B were less than the free ion value (1041 cm^{-1}) because the electron repulsion was weaker in the complexes than in the free ion, This weakening was to be expected, because the occupied molecular orbitals are delocalized over the ligands and away from the metal.

The delocalization increased the average separation of the electrons and hence reduced their repulsion (Shriver et al. 1990).

The ligand field stabilization energy for the complexes ($147.74\text{-}155.45\text{ KJ mol}^{-1}$) was in good agreement with the reported values for octahedral complexes (Lever et al., 1965; Ellis et al., 1975 and Sacconi, 1968).

On the basis of above discussion, the Ni(II) complexes were assigned octahedral geometry with 1:1 stoichiometric ratio, in which the ligand acted as tetradentate coordinating through imine group nitrogen.



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The stoichiometry of the adducts was confirmed by their elemental analysis and molecular weight determination. The conductance values ($120\text{-}153\text{ ohm}^{-1}\text{cm}^{-1}\text{ mol}^{-1}$) suggested ionic nature of these adducts. The structure elucidation was done on the basis of spectral and magnetic studies.

(i) Infrared spectra

A comparison of the spectra of the adducts and the free ligands has been utilized to identify the coordination sites. A negative spectral shift of the order of $25\text{-}15\text{ cm}^{-1}$ in (C-N) mode suggested the involvement of imine nitrogen in coordination (Das et al. 1990).

The stretching vibrations due to (C=N) mode of (>C=N-C) group also underwent hypsochromic shifting in the spectra of the adducts which further supported coordination through nitrogen of this group: The band due to (O-H) was absent in the spectra of the adducts indicating the absence of coordinated water which was further confirmed by the disappearance of D (M-O) band at 485-505 cm^{-1} in the spectra of the adducts. A perusal of the IR spectra of the Ligand and the adducts revealed that the (N-H) absorption frequencies at 3280-3340 and 3190-3260 cm^{-1} in the spectra of the ligands were present at the same position in the spectra of the adducts suggesting the non-involvement of nitrogen atom of (N-H) group in coordination.

The new band at 1240-1220 cm^{-1} in the spectra of the adducts assigned to chelate ring suggested the formation of the complex (Syamal, 1978).

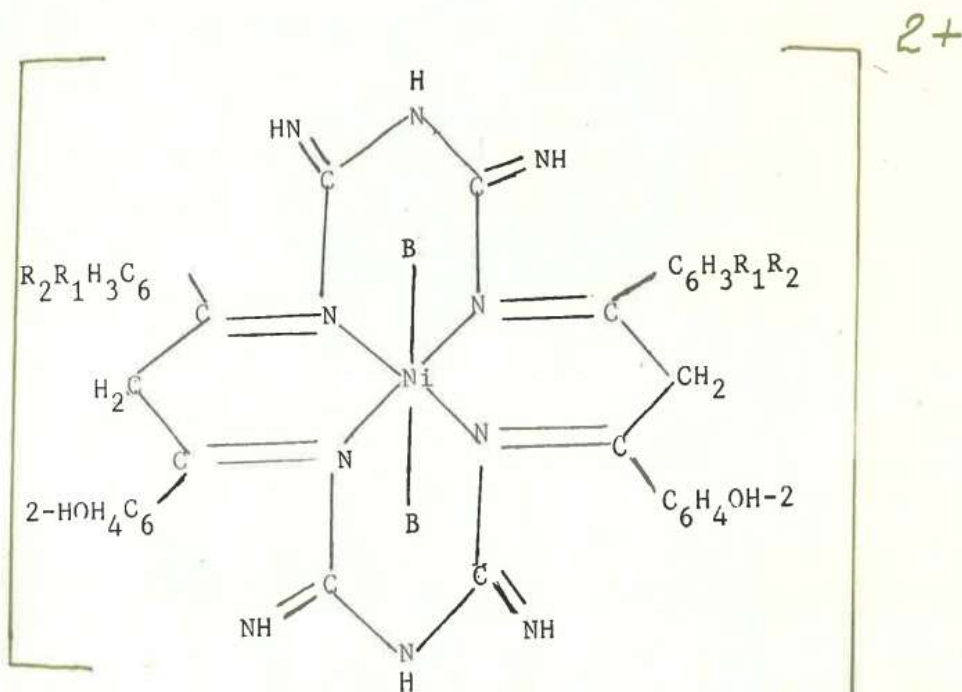
(ii) Magnetic moment and electronic spectra

The observed magnetic moments for the adducts of Ni(II) complexes (3.15 – 3.23 B.M.) correspond to the presence of two unpaired electrons (Greenwood and Barnshaw, 1990). The electronic spectra of the adducts exhibited three bands in the region 10400-11300, 17300-18400 and 24000-25740 cm^{-1} which were assigned to corresponding transitions confirming the octahedral geometry for the adducts (Sacconi, 1968).

Various ligand field parameters, for example, energy ratio in the range 1.60-1.64 and ligand field stabilization energy in the range 149.26 – 162.20 KJ mol^{-1} were characteristics of octahedral geometry around nickel(II) (Lever, 1984; Sacconi, 1968).

The B value for these adducts (633-770 cm^{-1}) were considerably lower than the free ion value (1041 cm^{-1}) suggesting thereby considerable orbital overlap and delocalization of the orbitals because of decreased inter-electronic repulsion from electron delocalization resulting in appreciable amount of covalent character of metal ligand bond (Shriver, 1990).

Based on the elemental analysis, molar conductance magnetic and spectral data the adducts were assigned octahedral configuration with the ligands behaving as tetradentate.



RESULTS

Table 1: Physical and analytical data of nickel(II) complexes of cyclo(1,2)-dibenzimidazolyl bis(2-hydroxy-2-(benzoyl/4-chlorobenzoyl)acetophenone (L_I and L_{II}) and their adducts.

Compound	Molecular formula	Yield (%)	Analytical data %					Molecular weight
			calculated		observed			
			C	H	N	Cl	N	
$[Ni(L_I)(H_2O)_2]Cl_2$	$C_{34}H_{34}Cl_2N_{10}O_4Ni$	78	52.13 (52.65)	4.21 (4.38)	18.03 (18.06)	9.00 (9.16)	7.51 (7.60)	768.0 (774.7)
$[Ni(L_I)(Py)_2]Cl_2$	$C_{44}H_{40}Cl_2N_{12}O_2Ni$	73	58.70 (58.86)	4.13 (4.45)	18.67 (18.73)	7.81 (7.91)	6.43 (6.56)	881.0 (896.7)
$[Ni(L_I)(2-Me-Py)_2]Cl_2$	$C_{46}H_{44}Cl_2N_{12}O_2Ni$	70	59.44 (59.68)	4.03 (4.75)	18.13 (18.16)	7.53 (7.67)	6.32 (6.36)	912.0 (924.7)
$[Ni(L_I)(4-Me-Py)_2]Cl_2$	$C_{46}H_{44}Cl_2N_{12}O_2Ni$	72	59.18 (59.68)	4.69 (4.75)	18.11 (18.16)	7.49 (7.67)	6.30 (6.36)	915.0 (924.7)
$[Ni(L_{II})(H_2O)_2]Cl_2$	$C_{34}H_{32}Cl_2N_{10}O_4Ni$	82	48.31 (48.40)	3.61 (3.79)	16.15 (16.60)	16.80 (16.85)	6.58 (6.98)	840.0 (842.7)
$[Ni(L_{II})(Py)_2]Cl_2$	$C_{44}H_{38}Cl_2N_{10}O_2Ni$	78	54.64 (54.72)	3.33 (3.93)	17.21 (17.41)	14.19 (14.71)	6.09 (6.10)	958.0 (964.7)
$[Ni(L_{II})(2-Me-Py)_2]Cl_2$	$C_{46}H_{40}Cl_2N_{10}O_2Ni$	78	55.33 (55.59)	4.13 (4.23)	16.81 (16.92)	14.06 (14.30)	5.50 (5.93)	967.0 (992.7)
$[Ni(L_{II})(4-Me-Py)_2]Cl_2$	$C_{46}H_{42}Cl_2N_{10}O_2Ni$	65	53.27 (55.59)	4.03 (4.23)	16.63 (16.92)	14.11 (14.30)	5.41 (5.93)	961.0 (992.7)

Table : Physical and analytical data of nickel(II) complexes of cyclo(1,2)-dibiguanidinyl bis[2-hydroxy- α -(3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] (L_{III} and L_{IV}) and their adducts

Compound	Molecular formula	Yield (%)	Analytical data % observed (calculated)					Molecular weight
			C	H	N	Cl	H	
$[Ni(L_{III})(H_2O)_2]Cl_2$	$C_{34}H_{32}Cl_2N_{12}O_8Ni$	79	47.00 (47.12)	3.42 (3.69)	19.09 (19.40)	8.14 (8.22)	6.71 (6.80)	862.0 (865.7)
$[Ni(L_{III})(Py)_2]Cl_2$	$C_{44}H_{38}Cl_2N_{14}O_6Ni$	79	53.21 (53.40)	3.61 (3.84)	19.43 (19.82)	7.09 (7.18)	5.82 (5.95)	981.0 (988.7)
$[Ni(L_{III})(2-Me-Py)_2]Cl_2$	$C_{46}H_{42}Cl_2N_{14}O_6Ni$	78	54.23 (54.29)	4.11 (4.13)	19.18 (19.27)	6.81 (6.98)	5.76 (5.79)	1011.0 (1016.7)
$[Ni(L_{III})(4-Me-Py)_2]Cl_2$	$C_{46}H_{42}Cl_2N_{14}O_6Ni$	84	54.14 (54.29)	4.01 (4.13)	19.16 (19.27)	6.92 (6.98)	5.53 (5.79)	1006.0 (1011.7)
$[Ni(L_{IV})(H_2O)_2]Cl_2$	$C_{34}H_{30}Cl_2N_{14}O_{12}Ni$	71	42.17 (42.68)	3.19 (3.13)	20.14 (20.50)	7.41 (7.53)	6.11 (6.16)	942.0 (955.7)
$[Ni(L_{IV})(Py)_2]Cl_2$	$C_{44}H_{36}Cl_2N_{16}O_{10}Ni$	64	48.81 (48.98)	3.03 (3.33)	20.11 (20.78)	6.53 (6.58)	5.38 (5.46)	1070.0 (1087.7)
$[Ni(L_{IV})(2-Me-Py)_2]Cl_2$	$C_{46}H_{40}Cl_2N_{16}O_{10}Ni$	68.5	49.21 (49.91)	3.41 (3.61)	20.21 (20.25)	6.35 (6.42)	5.16 (5.32)	1093.0 (1105.7)
$[Ni(L_{IV})(4-Me-Py)_2]Cl_2$	$C_{46}H_{40}Cl_2N_{16}O_{10}Ni$	67.5	49.34 (49.91)	3.01 (3.61)	20.13 (20.25)	6.27 (6.42)	5.11 (5.32)	1100.0 (1105.7)

Table : Infrared spectral characteristics of nickel(II) complexes of cyclo(1,2)-dibiguanidinyl bis[2-hydroxy- α -(benzoyl/4-chlorobenzoyl) acetophenone] (L_I and L_{II}) and their adducts.

Compound	Assignments (cm^{-1})						
	$\nu(N-H)$	$\nu(C=N)$ of ($>C=N-H$)	$\nu(C=N)$ of ($>C=N-C$)	$\nu(C-N)$	Chelate ring vibration	$\nu(M-O)$	$\nu(M-N)$
$[Ni(L_I)(H_2O)_2]Cl_2$	3320,3190	1680	1620	1310,1260	1245	505	450
$[Ni(L_I)(Py)_2]Cl_2$	3320,3190	1680	1595	1320,1255	1220	-	445
$[Ni(L_I)(2-Me-Py)_2]Cl_2$	3320,3190	1680	1610	1315,1260	1225	-	455
$[Ni(L_I)(4-Me-Py)_2]Cl_2$	3320,3190	1680	1595	1320,1255	1240	-	450
$[Ni(L_{II})(H_2O)_2]Cl_2$	3340,3260	1665	1590	1330,1260	1220	500	435
$[Ni(L_{II})(Py)_2]Cl_2$	3340,3260	1665	1600	1325,1260	1235	-	440
$[Ni(L_{II})(2-Me-Py)_2]Cl_2$	3340,3260	1665	1595	1300,1265	1230	-	445
$[Ni(L_{II})(4-Me-Py)_2]Cl_2$	3340,3260	1665	1595	1310,1260	1230	-	440

Table : Infrared spectral characteristics of nickel(II) complexes of cyclo(1,2)-dibiguanidiny] bis[2-hydroxy- β -(3-nitrobenzoyl/3,5-dinitrobenzoyl) acetophenone] (L_{III} and L_{IV}) and their adducts.

Compound	Assignments (cm^{-1})						
	$\nu(\text{N-H})$	$\nu(\text{C=N})$ of ($>\text{C=N-H}$)	$\nu(\text{C=N})$ of ($>\text{C=N-C}$)	$\nu(\text{C-N})$	Chelate ring vibration	$\nu(\text{M-O})$	$\nu(\text{M-N})$
$[\text{Ni}(L_{III})(\text{H}_2\text{O})_2]\text{Cl}_2$	3300,3210	1665	1610	1305,1245	1230	495	440
$[\text{Ni}(L_{III})(\text{Py})_2]\text{Cl}_2$	3300,3210	1665	1605	1305,1235	1220	-	435
$[\text{Ni}(L_{III})(2\text{-Me-Py})_2]\text{Cl}_2$	3300,3210	1665	1605	1300,1240	1225	-	435
$[\text{Ni}(L_{III})(4\text{-Me-Py})_2]\text{Cl}_2$	3300,3210	1665	1600	1305,1235	1220	-	430
$[\text{Ni}(L_{IV})(\text{H}_2\text{O})_2]\text{Cl}_2$	3280,3190	1670	1625	1325,1265	1220	485	445
$[\text{Ni}(L_{IV})(\text{Py})_2]\text{Cl}_2$	3280,3190	1670	1625	1315,1265	1225	-	430
$[\text{Ni}(L_{IV})(2\text{-Me-Py})_2]\text{Cl}_2$	3280,3190	1670	1620	1320,1275	1232	-	435
$[\text{Ni}(L_{IV})(4\text{-Me-Py})_2]\text{Cl}_2$	3280,3190	1670	1620	1320,1275	1230	-	435

Table : Magnetic moment and electronic spectral data of nickel(II) complexes of cyclo(1,2)-dibiguanidiny] bis[2-hydroxy- β -(benzoyl) acetophenone] (L_I) and their adducts.

Compound	$3 \xrightarrow{A} 3 (F)$ $2g \text{ (cm}^{-1}\text{)}$	$3 \xrightarrow{A} 3 (F)$ $2g \text{ (cm}^{-1}\text{)}$	$3 \xrightarrow{A} 3 (F)$ $2g \text{ (cm}^{-1}\text{)}$	$3 \xrightarrow{A} 3 (P)$ $2g \text{ (cm}^{-1}\text{)}$	μ_{eff} (B.M.)
	$3 \xrightarrow{T} 2g$	$3 \xrightarrow{T} 1g$	$3 \xrightarrow{T} 1g$	$3 \xrightarrow{T} 1g$	
$[\text{Ni}(L_I)(\text{H}_2\text{O})_2]\text{Cl}_2$	10830	17890	25300	3.21	
$[\text{Ni}(L_I)(\text{Py})_2]\text{Cl}_2$	10920	18300	25700	3.21	
$[\text{Ni}(L_I)(2\text{-Me-Py})_2]\text{Cl}_2$	11300	18150	25740	3.23	
$[\text{Ni}(L_I)(4\text{-Me-Py})_2]\text{Cl}_2$	10770	18110	25500	3.19	

Table : Ligand field parameters and molar conductance data of nickel(II) complexes of cyclo (1,2)-dibiguanidiny] bis[2-hydroxy- α -(benzoyl) acetophenone] (L_I) and their adducts.

Compound	10Dq (cm^{-1})	B (cm^{-1})	β	LFSE (KJ mol^{-1})	$\Delta \nu_{2/1}$	Molar conductance ($\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)
$[\text{Ni}(L_I)(\text{H}_2\text{O})_2]\text{Cl}_2$	10830	713	.684	155.45	1.65	160
$[\text{Ni}(L_I)(\text{Py})_2]\text{Cl}_2$	10920	749	.719	156.74	1.67	140
$[\text{Ni}(L_I)(2\text{-Me-Py})_2]\text{Cl}_2$	11300	666	.639	162.20	1.60	124
$[\text{Ni}(L_I)(4\text{-Me-Py})_2]\text{Cl}_2$	10770	753	.723	154.59	1.68	120

CONCLUSION

In the present investigation, the Nickel(II) complexes of the ligands L_I - L_{IV} displayed three absorption bands in the region 10300-10830, 17600-17890 and 24100-25300 cm^{-1} which were assigned to transitions. The values were in good agreement with the octahedral geometry.

The various ligand field parameters like ligand field splitting energy, energy ratio, Racah inter-electronic parameter, nephelauxetic ratio and ligand field stabilization energy (LFSE) were calculated from electronic absorption spectral data.

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