STUDY OF INTERELECTRONIC REPULSION PARAMETERS OF NI(II) OCTAHEDRAL COMPLEXES

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Abstract: Spectroscopy has emerged as vast and versatile field of research in Physics as it form a very effective tool for calculating the various crystal-field parameters in metal complexes. Transition metal complexes of Ni(II)-ion has been synthesised from N-(2'-benzoic acid)-2-hydroxy-3-methoxy benzalidine , pyridine and α - picoline, with the general composition NiL_2X_2 (where X= Pyridine & α - picoline). The crystal-field parameter i.e. D_q, B, β are calculated with the help of IR and electronic spectra of the complexes.

Keywords: racah parameter; D_q; β

1. Introduction:

The interelectronic repulsion perturbation operating on given configuration produces various terms having different energies. Energy states (spectral terms) in metal atoms of ions in complexes arise from coupling of the angular momentum $(\vec{l})$ of individual electrons, in conformity with the Pauli Exclusion Principle, given rise to the total angular momentum $(\vec{L})$. Development of different energy levels is attributed to difference in electron repulsion. The electronic configuration of a free metal-ion generates various terms due to interelectronic repulsive perturbation. The energy-gap between two terms of the same spin-multiplicity is called Racah parameter. When the free metal-ion is placed in the environment of a crystal-field, this interelectronic repulsion parameter gets reduced due to spreading of electronic cloud of the free metal-ion to the ligands. The different ligands produce crystal field of different strength, the reduction in interelectronic repulsion parameter of the free metal-ions is different [1]. The ligand environment variations give information about many thermodynamic, spectral and magnetic properties [2]. In this paper, we report the calculation of various crystal-field parameters of Ni(II) metal-ion octahedral complexes with the help of IR and electronic spectra.

2. Experimental:

For the present paper, ligand BHMB has been prepared by the reported method [3, 4]. BHMB = N-(2'-benzoic acid)-2-hydroxy-3-methoxy benzalidine. By using above ligand, complexes of the general formula NiL_2X_2 have been synthesised, where L = BHMB, X = pyridine & α - picoline.

Elemental analyses were carried out using Elemental analyser of Dept. of Chemistry, IIT-Patna. Metal contents were determined gravimetrically. Consolidated account and % composition are given in Table – 1.

Table 1: Consolidated account of Ligand & Complexes. % composition found/(calculated).

S. No.	Complex	Colour	Melting Point(^{O}C)	Metal (in %)	C (in %)	H (in %)	N (in %)
1.	Ligand-Schiff Base (BHMB)	Light Yellow	192		66.68 (66.42)	4.43 (4.40)	5.00 (5.17)
2.	$[Ni(BHMB)_2(Py)_2]$	Bright Green	324	7.49 (7.77)	63.38 (63.24)	4.47 (4.74)	7.18 (7.38)
3.	$[Ni(BHMB)_2(\alpha$-	Green	330	7.32	64.36	4.92	6.61

	pico)$_2$]			(7.50)	(64.06)	(5.08)	(6.73)

Magnetic susceptibility measurements were made on a Cahn 2000 Faraday Balance using $Hg[Co(CNS)_4]$ ($\chi_g = 16.44\times10^{-6}$ g/cm^{-3} at 28 ^{o}C)as the calibrating agent. Molar conductance measurements of newly synthesized compounds have been done using Conductivity meter (CG 857 Schott Grate GmbH) with DMSO solution of 10^{-3} M concentration with dip-type cell having platinum electrode. FTIR spectra were recorded on PerkinElmer Spectrum Version 10.03.05 using KBr Disc Method. The electronic spectra of the complexes were recorded on a Lambda 950-PerkinElmer-UK.

FTIR Spectra:

The FTIR spectra of free ligand and complexes are shown in Fig.1 to Fig.3. Mode of linkage of ligand with metal ion has been traced out and studied by the comparison of the FTIR spectra of free ligand and that of complexes. The free ligand absorbs strongly at 3540 cm^{-1}. This band is assigned to phenolic-OH group of free ligand [5].

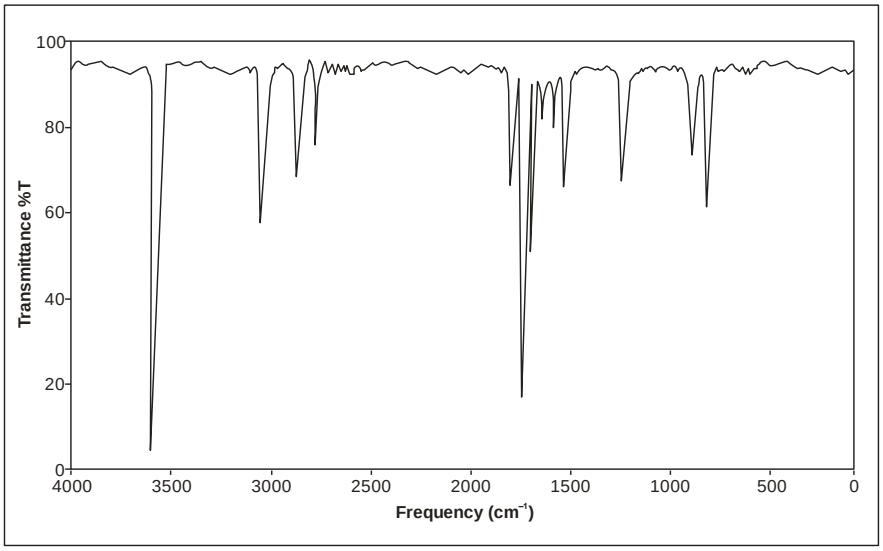

Figure 1: IR spectra of free ligand (BHMB).

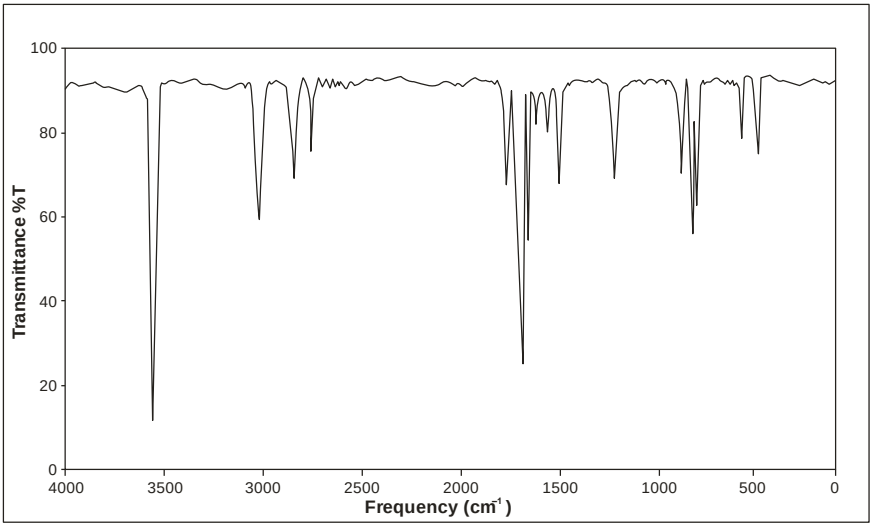

Figure 2: IR spectra of the complex $[Ni(BHMB)_2(Py)_2]$.

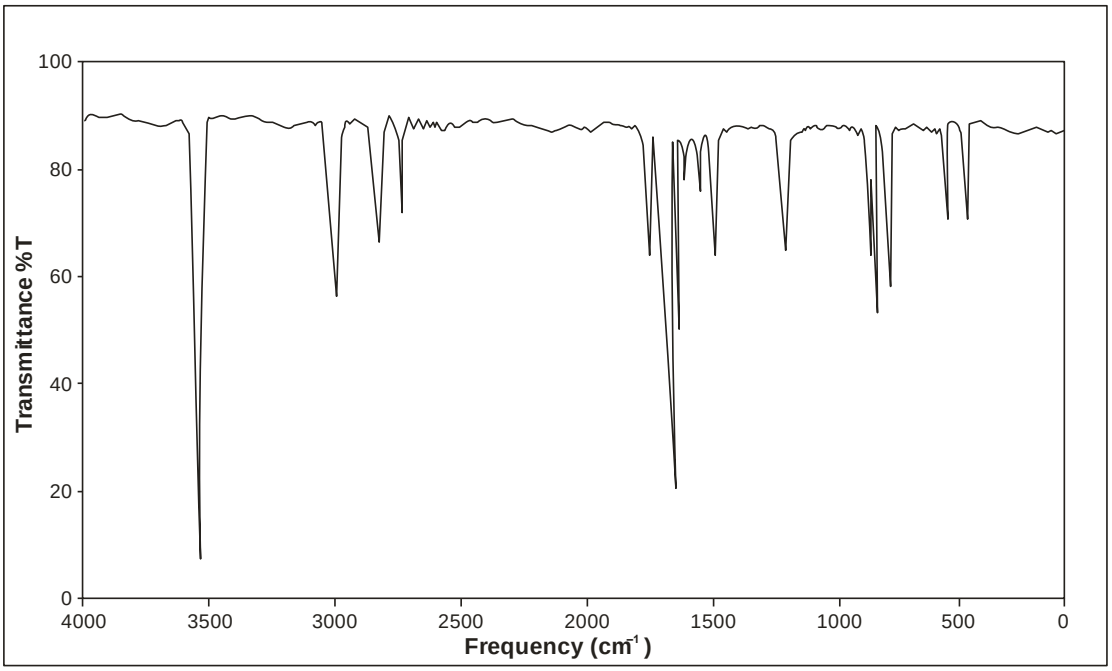

Figure 3: IR spectra of the complex $[Ni(BHMB)_2(\alpha\text{-pico})_2]$.

This band does not undergo any appreciable shift in the spectra of complexes which indicates that phenolic oxygen is not taking part in coordination to the metal-ion in complexes. The appearance of band at 1160 cm^{-1} shows the presence of methoxy-group in the ligand. This band remains intact in all the complexes. This indicates non-participation of methoxy-group in coordination to the metal-ion. The sharp band appearing at 1640 cm^{-1} is safely assigned to the azomethyne group vibration [6]. This band undergoes shift by 30-35 cm^{-1} to lower frequency in almost all the complexes which is indicative of coordination through azomethine nitrogen to the metal-ion. A band at 1720 cm^{-1} shows the presence of aro-COOH group in the free ligand [7]. The absence of a band near 1690 cm^{-1} clearly shows that the acid is in monomer form. In complexes this band shifts to 1560-1570 cm^{-1} and 1400-1410 cm^{-1} due to anti symmetric and symmetric stretching of ν_{C-O} of carboxylate-ion respectively. It shows that during complexation the deprotonation of acid group has occurred followed by coordination through it. The difference between $\left(\nu_{asym(COOH^-)} - \nu_{sym(COOH^-)}\right)$ is found as greater than 160 cm^{-1} which is indicative of monodentated coordination [8]. The change in IR- frequencies of free ligand in complexes has been given in the Table-2.

Table 2: Change in IR- frequencies of free ligand in complexes.

Functional Group	Free Ligand (in cm^{-1})	Complex of Ni (in cm^{-1})
Phenolic-OH	3540	3540
ν_{C-H} (in plane of aromatic)	3000	3000
ν_{C-H} of $-CH_3$ group	2820	2820
$\nu_{CH=}$ of aromatic group	2730	2730
$\nu_{aro-COOH}$ monomer	1720	1580 1415
$\nu_{CH=N}$ vibration	1640	1600
$\nu_{benzine}$ ring vibration	1610 1570 1510 1450	1610 1570 1510 1450
$\nu_{aro-O-CH_3}$	1160	1160

Out of plane bending C-H vibration of tri-substituted benzene ring	815	815
Out of plane bending C-H vibration of di-substituted benzene ring	740	740
ν_{M-N}		500
ν_{M-O}		415

Electronic Spectra:

Electronic spectra of complexes were in DMSO solution.

Electronic spectra of Ni(II) complexes:

Under octahedral Symmetry the splitting of terms and energy-states are shown in the Fig.4.

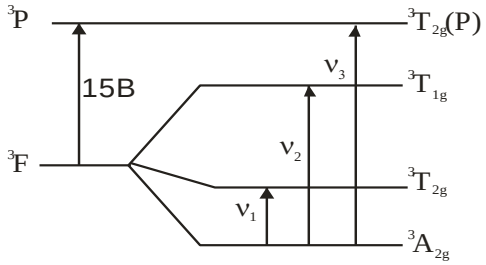

Figure 4: Splitting of terms and energy-states under octahedral symmetry.

Electronic spectra of Ni(II) complexes show electronic transition bands at 8900-9200 cm^{-1} , 14950-15270 cm^{-1} & 25900-26950 cm^{-1} shown in Table-3. These bands may be assigned to ${}^3T_{2g} \leftarrow {}^3A_{2g}$; ν_1 ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$; ν_2 and ${}^3T_{1g}(P) \leftarrow {}^3A_{2g}$; ν_3 transitions respectively. The position of bands indicates that these complexes have distorted octahedral geometry [9].

Electronic spectral bands (cm^{-1}), conductivity ($Ohm^{-1}cm^2mol^{-1}$) and magnetic moment (μ in B.M.) of the complexes formed are shown in Table-3.

Table 3: Electronic spectral bands, conductivity and magnetic moment of the complexes.

S. No.	Complex	Electronic spectral bands (cm^{-1})			Conductivity ($Ohm^{-1}cm^2mol^{-1}$)	Magnetic Moment (μ in BM)
		ν_1	ν_2	ν_3		
1.	$[Ni(BHMB)_2(Py)_2]$	8900	14950	25990	14.78	3.17
2.	$[Ni(BHMB)_2(\alpha\text{-pico})_2]$	9200	15270	26950	12.32	3.19

Calculation of different crystal-field parameters:

The data obtained were used to calculate the values of different crystal-field parameters using Tanabe- Sugano diagram for d^8-systems (shown in Fig.5).

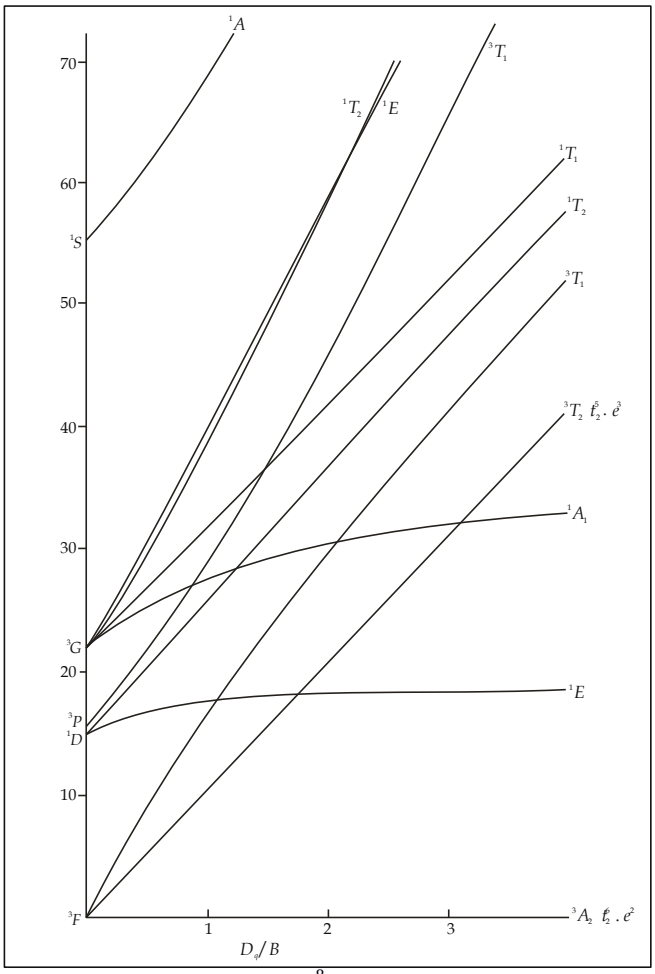

Figure 5: Energy level diagram (Tanabe-Sugano) for d^8 ions in an octahedral field (C=4.709B).

For complex $[Ni(BHMB)_2(Py)_2]$:

ν_1 = 8900 cm^{-1} ; ν_2 = 14950 cm^{-1} ; ν_3 = 25990 cm^{-1} So, $\nu_2/\nu_1 = 14950/8900 = 1.679 \approx 1.68$, $\nu_3/\nu_1 = 25990/8900 = 2.92$ and $\nu_3/\nu_2 = 25990/14950 = 1.738 \approx 1.74$

The ratio ν_2/ν_1 was used to find out the value of *E/B* from Tanabe-Sugano diagram. The ratio ν_2/ν_1 =1.68 fits well at D_q/B at 0.97. Since $\nu_1 = 10D_q$ = 8900 and D_q/B =0.97, $\Rightarrow B = 890/0.97 = 917.52\ cm^{-1}$. As for Ni^{+2} – ion, B_o = 1041 cm^{-1} so, reduction in Racah parameter of free metal ion Ni (II) after complexation is

$$= B_O - B = 1041 - 917.5 = 123.48\ cm^{-1}$$

where B_O is the value of Racah parameter of free Ni (II) ion = 1041 cm^{-1}. And, % reduction in Racah parameter of free metal ion Ni (II) after complexation is

$$= \left(\frac{B_O - B}{B}\right) \times 100 = \left(\frac{1041 - 917.52}{1041}\right) \times 100 = 11.86\%$$

The Nephelauxetic effect is $\beta = \frac{B}{B_o}$ where, *B* is Racah parameter of Ni (II) in complex while B_O is Racah parameter of Ni (II) in Free State. So, $\beta = \frac{B}{B_O} = \frac{917.52}{1041} = 0.88138 \approx 0.882$. So, the reduction in Racah parameter of Ni (II) for free metal- ion is nearly (100 – 11.86) = 88.14 %.

For complex $[Ni(BHMB)_2(\alpha\text{-pico})_2]$:

ν_1 = 9200 cm^{-1} ; ν_2 = 15270 cm^{-1} ; ν_3 = 26950 cm^{-1} So, $\nu_2/\nu_1 = 15250/9200 = 1.657 \approx 1.66$, $\nu_3/\nu_1 = 26950/9200 = 2.929 \approx 2.93$ and $\nu_3/\nu_2 = 26950/15270 = 1.764 \approx 1.76$

The ratio ν_2/ν_1 =1.66 fits well at D_q/B =0.99 on Tanabe-Sugano diagram. Since $\nu_1 = 10D_q$ = 9200 and D_q/B =0.99, $\Rightarrow B = 920/0.99 = 929.29\ cm^{-1}$. Reduction in Racah parameter of free metal ion Ni (II) after complexation is

$$= B_O - B = 1041 - 929.29 = 111.71\ cm^{-1}$$

where B_O is the value of Racah parameter of free Ni (II) ion = 1041 cm^{-1}. And, % reduction in Racah parameter of free metal ion Ni (II) after complexation is

$$= \left(\frac{B_O - B}{B}\right) \times 100 = \left(\frac{1041 - 929.29}{1041}\right) \times 100 = 10.73\%$$

Nephelauxetic effect, $\beta = \frac{B}{B_O} = \frac{929.29}{1041} = 0.8926 \approx 0.892$. So, the reduction in Racah parameter of Ni (II) for free metal- ion is nearly (100 – 10.76) = 89.27 %. Values of crystal-field parameters of Ni(II) complexes formed are given in Table-4.

Table 4: Values of crystal-field parameters of metal complexes.

S. No.	Complex	$\frac{\nu_2}{\nu_1}$	$\frac{\nu_3}{\nu_1}$	$10D_q$ (in cm^{-1})	B (in cm^{-1})	Reduction in Racah parameter of Ni (II) after complexation (In %)	Reduction in Racah parameter of Ni (II) for free metal- ion (In %)
1.	$[Ni(BHMB)_2(Py)_2]$	1.68	2.92	8900	917.52	11.86	(100 – 10.76) = 89.27
2.	$[Ni(BHMB)_2(\alpha\text{-pico})_2]$	1.66	2.93	9200	929.29	10.73	(100 – 11.86) = 88.14

A.B. P. Lever reported in his article [10] related to the various transitions for Ni (II) d^8 system under octahedral symmetry, he derived different equations involving D_q and B for different transitions which are given below.

1. $T_{2g} \leftarrow A_{2g}$; $\nu_1 = 10D_q$

2. $T_{1g}(F) \leftarrow A_{2g}$; $\nu_2 = \left[15D_q + \frac{15}{2}B - \frac{1}{2}\sqrt{225B^2 + 100D_q{}^2 - 180D_qB}\right]$

3. $T_{1g}(P) \leftarrow A_{2g}$; $\nu_3 = \left[15D_q + \frac{15}{2}B + \frac{1}{2}\sqrt{225B^2 + 100D_q{}^2 - 180D_qB}\right]$

4. $(\nu_3 + \nu_2 - 3\nu_1) = 15B$

Using these equations D_q and B values of Ni(II) complexes have also been derived as below.

For complex $[Ni(BHMB)_2(Py)_2]$:

$^3T_{2g} \leftarrow {}^3A_{2g}$; $\nu_1 = 8900\,cm^{-1}$; $^3T_{1g}(F) \leftarrow {}^3A_{2g}$; $\nu_2 = 14950\,cm^{-1}$ and $^3T_{1g}(P) \leftarrow {}^3A_{2g}$; $\nu_3 = 25990\,cm^{-1}$. As $(\nu_3 + \nu_2 - 3\nu_1) = 15B$ $\Rightarrow B$ = 949.33 cm^{-1}

(i) As $\nu_1 = 10D_q$, hence $8900 = 10D_q$ $\Rightarrow D_q$ = 890 cm^{-1}

(ii) As $\nu_2 = \left[15D_q + \frac{15}{2}B - \frac{1}{2}\sqrt{225B^2 + 100D_q{}^2 - 180D_qB}\right]$, hence

$14950 = [15D_q + (7.5 \times 949.33) - \frac{1}{2}\sqrt{225 \times (949.33)^2 + 100D_q{}^2 - (180 \times 949.33)D_q}$ $\Rightarrow D_q$ = 902.065 cm^{-1}

(iii) As $\nu_3 = \left[15D_q + \frac{15}{2}B + \frac{1}{2}\sqrt{225B^2 + 100D_q{}^2 - 180D_qB}\right]$, hence

$25990 = [15D_q + (7.5 \times 949.33) + \frac{1}{2}\sqrt{225 \times (949.33)^2 + 100D_q{}^2 - (180 \times 949.33)D_q}$ $\Rightarrow D_q$ = 878.186 cm^{-1}

Hence, average of D_q = $\frac{890.000 + 902.065 + 878.186}{3}$ = 890.083 cm $^{-1}$ $\Rightarrow$ D_q = 890.083 cm^{-1}

$\therefore 10D_q = 8900.83$ cm $^{-1}$. And, reduction in Racah parameter of free metal ion Ni (II) after complexation $= B_O - B = 1041 - 949.33 = 91.67\,\text{cm}^{-1}$. And, % reduction in in Racah parameter of free metal ion Ni (II) after complexation

$$= \left(\frac{B_O - B}{B}\right) \times 100 = \left(\frac{1041 - 949.33}{1041}\right) \times 100 \approx 8.81\%$$

and, Nephelauxetic effect, $\beta = \frac{B}{B_O} = \frac{949.33}{1041} = 0.9119 \approx 0.912$. So, the reduction in Racah parameter of Ni (II) for free metal- ion is nearly (100 – 8.81) = 91.19 %.

For Complex [Ni(BHMB)$_2$(α-pico)$_2$]:

$^3T_{2g} \leftarrow {}^3A_{2g}$; $\nu_1 = 9200\,\text{cm}^{-1}$; $^3T_{1g}(F) \leftarrow {}^3A_{2g}$; $\nu_2 = 15270\,\text{cm}^{-1}$ And $^3T_{1g}(P) \leftarrow {}^3A_{2g}$; $\nu_3 = 26950\,\text{cm}^{-1}$

As $(\nu_3 + \nu_2 - 3\nu_1) = 15B$ $\Rightarrow$ B = 974.66 cm^{-1}

(i) As $\nu_1 = 10D_q$, hence $9200 = 10D_q$ $\Rightarrow$ D_q = 920 cm^{-1}

(ii) As $\nu_2 = \left[15D_q + \frac{15}{2}B - \frac{1}{2}\sqrt{225B^2 + 100D_q{}^2 - 180D_qB}\right]$, hence

$15270 = [15D_q + (7.5 \times 974.66) - \frac{1}{2}\sqrt{225 \times (974.66)^2 + 100D_q{}^2 - (180 \times 974.66)D_q}$ $\Rightarrow D_q$ = 920.805 cm^{-1}

(iii) As $\nu_3 = \left[15D_q + \frac{15}{2}B + \frac{1}{2}\sqrt{225B^2 + 100D_q{}^2 - 180D_qB}\right]$, hence

$26950 = [15D_q + (7.5 \times 974.66) + \frac{1}{2}\sqrt{225 \times (974.66)^2 + 100D_q{}^2 - (180 \times 974.66)D_q}$ $\Rightarrow D_q$ = 919.221 cm^{-1}

Hence, average of D_q = $\frac{920 + 920.805 + 919.221}{3}$ = 920.01 cm $^{-1}$ $\Rightarrow$ D_q = 920.01 cm^{-1}

$\therefore 10D_q = 9200.01$ cm $^{-1}$. And, reduction in in Racah parameter of free metal ion Ni (II) after complexation $= B_O - B = 1041 - 974.66 = 66.34\,\text{cm}^{-1}$. And, % reduction in in Racah parameter of free metal ion Ni (II) after complexation

$$= \left(\frac{B_O - B}{B}\right) \times 100 = \left(\frac{1041 - 974.66}{1041}\right) \times 100 \approx 6.37\%$$

And, Nephelauxetic effect, $\beta = \frac{B}{B_O} = \frac{974.66}{1041} = 0.936$. So, the reduction in Racah parameter of Ni (II) for free metal- ion is nearly (100 – 6.37) = 93.63 %.

The values of different parameters of Ni(II) complexes derived by taking account of different equations given by A. B. P. Lever have been given in Table 5.

Table 5: Values of different crystal field parameters of metal complexes.

S. No.	Complex	D_q (in cm^{-1})	$10D_q$ (in cm^{-1})	B (in cm^{-1})	Reduction in B =($B_O - B$) (in %)	Nephelauxetic Effect $\beta = \frac{B}{B_O}$
1.	$[Ni(BHMB)_2(Py)_2]$	890.083	8900.83	949.33	8.81	0.912
2.	$[Ni(BHMB)_2(\alpha-picoline)_2]$	920.01	9200.10	974.66	6.37	0.936

The values of *Dq* and *B* are very close to the values derived from fitting the spectral bands into the Tanabe-Sugano diagram. The slight difference in values may be attributed to the fact that the published version of Tanabe-Sugano diagram are generally so condensed that the derivation of $\frac{D_q}{B}$ and $\frac{E}{B}$ is only approximation [11, 12]. We can see that these values of crystal-field parameters are in good agreement with the reported values for Ni(II) octahedral complexes [13, 14] .Finally, it should be emphasized that the main factors responsible for Nephelauxetic effect are found to be covalency, coordination number for host and valence & spin state of the centre metal ion. Racah parameter (B) of Ni (II) free ion undergoes distinct decrease in all the complexes. It shows the spreading of electron cloud of Ni (II) ion to the ligands causing a certain extent of covalency in these complexes of Ni(II).

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