Chapter V

ELECTRONIC SPECTRAL STUDIES OF COBALT(II) AND NICKEL(II) COMPLEXES

5.1 General

Most of the transition metal complexes absorb radiations in the visible and ultraviolet regions of the electromagnetic spectrum and give rise to their electronic absorption spectra. The study of electronic absorption spectra of transition metal complexes has constituted one of the major efforts in recent years to characterise and understand the nature of electronic structure and bonding in these compounds. Electronic transitions occur when electrons within the molecule or ion move from one energy level to another. Four general types of electronic transitions may be observed with transition metal complexes. 1) Transitions may occur between the split d- levels of the central atom, giving rise to the so-called d-d or ligand field spectra. 2). Transitions may occur from molecular orbital located primarily on the ligands, to non-bonding or anti bonding molecular orbitals located primarily on the metal atom. Such transitions are termed ligand to metal charge transfer transitions. 3). The transitions which involve electrons being excited from non bonding or anti bonding orbitals located primarily on the metal atom to anti bonding orbitals located primarily on the ligands are termed metal to ligand charge
transfer transitions. The electronic transitions which involve electrons being excited from one ligand orbital into another ligand orbital.

The electronic spectrum can be recorded by irradiating the solution of a compound and by measuring the absorbance versus wave length or wave number. The absorbance can also be called as 'optical density' and defined by

\[ A = \log \frac{I_0}{I} \]

where \( I_0 \) and \( I \), the intensities of incident and transmitted radiation respectively.

5.2 Nature of electronic spectral bands

Important characteristics of electronic spectral bands of transition metal complexes are the intensities and band widths.

5.2.1 Band intensities

A transition between two energy states can occur only if the transition moment integral is non zero. In the case of transition metal complexes the energy states correspond to d- orbital wave functions which have gerade symmetry. According to La Porte rule transitions are allowed only between gerade and ungerade states, ie, \( g \leftrightarrow u \). The transitions \( g \leftrightarrow g \) and \( u \leftrightarrow u \) are forbidden. Since d-d transitions are forbidden in a transition metal complex with octahedral symmetry, electronic spectral bands of such complexes have weak intensities. There are certain mechanisms by which the La Porte rule can be violated. If the d-orbital wave function is mixed with some p-character which has an ungerade symmetry, the transition moment integral
does not vanish and the transitions occur. The extent of d-p mixing influences the band intensity. When the d and p wave functions are mixed, the inversion centre about the central atom is removed.

There are two important mechanisms by which the centre of inversion can be removed. 1. The central metal ion is placed in a statically distorted field. 2. The vibrations of the ligand can create a distorted field for a brief duration of time which is enough for electronic transition to occur. The most important statically distorted field is exemplified by the tetrahedral complex. The other mechanism by which an electronic d-d transition may gain some intensity is known as vibronic coupling, i.e. coupling of vibration and electronic wave functions.

Electronic transitions are governed by spin selection rule also. Transition for which $\Delta S \neq 0$ are spin or multiplicity forbidden. But this rule is not completely valid when spin-orbit coupling is possible in the metal complex. Therefore spin forbidden transitions appear in the spectra of many transition metal complexes, but they are generally weak.

The intensities of electric-dipole transitions are in the range of $\varepsilon \sim 10^4 - 10^6$, if allowed fully. But when they are both spin forbidden and La Porte forbidden the band intensities are expected to be extremely weak. Thus the intensities of the band would be in tune with the extent to which the transition is allowed or forbidden. Inferences drawn from the study of a large number of cubic field metal complexes are given below.
1. Most of the hexa co-ordinate complexes give similar electronic spectra with comparable band intensities and band position indicating that $O_h$ is the effective symmetry.

2. The ligand field spectra of metal complexes containing organic ligands often give more intense bands than those containing inorganic ligands.

3. The spectra of complexes containing metal ions of higher oxidation state are more intense than those of complexes of metal ion in the lower oxidation states.

4. The intensity of the spectral bands sometimes reflects upon the nature of the metal-ligand bond, larger the covalency greater will be the intensity of the bands.

5. The band intensities are more for acentric metal complexes than for centro symmetric complexes.

5.2.2 Band width

If the electronic transitions take place from an orbitally non-degenerate energy level to another of the same type, a narrow band may result in the absorption spectrum. But the electronic spectra generally give rise to broad bands. This implies that the transitions are spread over a range of energies. There are several factors that may serve to remove the degeneracy of the terms and thereby produce broad bands. These include symmetry lowering by 1) molecular vibrations 2) spin-orbit coupling and
3) Jahn-Teller effect.\(^{291, 292}\) All these factors lead to asymmetrically shaped bands. Band broadening by the vibrational mechanism is very common. As the metal-ligand bond vibrates, the bond length fluctuates continuously so that the value of $D_q$ lies over a small range of energies. The magnitude of ligand field parameter $D_q$ depends on the metal-ligand bond length. The band widths are proportional to the slopes given by $\Delta E/\Delta D_q$ for the excited states. Larger the slopes, greater would be the band widths. Both spin-orbit coupling and the Jahn-Teller effect may serve to broaden bands by lifting the degeneracy of otherwise degenerate, for example $E$ and $T$, ground terms. It might be noted that if the degeneracy has already been lifted by a low-symmetry static ligand field or by spin-orbit coupling, the Jahn-Teller effect is not necessary or operative.

5.3 **Electronic spectra of cobalt(II) and nickel(II) complexes**

5.3.1 **Electronic spectra of cobalt(II) complexes**

The common oxidation states of cobalt are +2 and +3. The complexes are either octahedral or tetrahedral. Since the difference in ligand field stabilization energy between octahedral and tetrahedral complex is very small, Co(II) forms more tetrahedral complexes than any other transition metal ions. Several cases are reported in which equilibrium exists between octahedral and tetrahedral structures.\(^{293}\)

The electronic spectra of cobalt(II) complexes have been largely studied by Liehr.\(^{294}\) The six-coordinate high spin cobalt (II) is a commonly
encountered 3d⁷ system and in a high spin octahedral environment, the likely transitions are

\[ {^4T_{1g}(F)} \rightarrow {^4T_{2g}} \quad v_1 \quad E \sim 8Dq \]
\[ {^4T_{1g}(F)} \rightarrow {^4A_{2g}} \quad v_2 \quad E \sim 18Dq \]
\[ {^4T_{1g}(F)} \rightarrow {^4T_{1g}(P)} \quad v_3 \quad E \sim 6Dq + 15 B^I \]

(Dq and B^I are ligand field parameters).

It can be seen that the energy difference \( v_2 - v_1 \) is exactly equal to 10Dq. Unfortunately the \( v_2 \) transition is usually very weak and rarely observed.

In general in six-coordinate cobalt (II) complexes (high spin) two principal regions of absorption are observed. A band near 8000-10000 cm\(^{-1}\) can be assigned to the \( ^4T_{1g}(F) \rightarrow ^4T_{2g} \) transition. In addition a multiple structured band, assigned to \( ^4T_{1g}(F) \rightarrow ^4T_{1g}(P) \) is seen in the visible region near 20000 cm\(^{-1}\). The transition to \( ^4A_{2g} \) is very weak often appearing as a shoulder near 12000 cm\(^{-1}\).

\[ {^4T_{1g}(F)} \rightarrow {^4T_{2g}} \quad v_1 \quad \sim \quad 8000-10000 \text{ cm}^{-1} \]
\[ {^4T_{1g}(F)} \rightarrow {^4A_{2g}} \quad v_2 \quad \sim \quad 12000 \text{ cm}^{-1} \]
\[ {^4T_{1g}(F)} \rightarrow {^4T_{1g}(P)} \quad v_3 \quad \sim \quad 20000 \text{ cm}^{-1} \]

The allowed transitions in tetrahedral fields for Co (II) complexes are

\[ {^4A_2} \rightarrow {^4T_2(F)} \quad v_1 \quad E \sim 10Dq \]
\[ {^4A_2} \rightarrow {^4T_1(F)} \quad v_2 \quad E \sim 18Dq \]
\[ {^4A_2} \rightarrow {^4T_1(P)} \quad v_3 \quad E \sim 12Dq + 15 B^I \]
5.3.2 **Electronic spectra of nickel(II) complexes**

The six coordinated nickel(II) belongs to the $3d^8$ system. The electronic spectrum of an octahedral nickel(II) complex is expected to show three spin allowed transitions,

$$
\begin{align*}
^3A_2g \to ^3T_2g(F) & \quad \nu_1 \quad E \sim 10Dq \\
^3A_2g \to ^3T_1g(F) & \quad \nu_2 \quad E \sim 18Dq \\
^3A_2g \to ^3T_1g(P) & \quad \nu_3 \quad E \sim 12Dq + 15B^1
\end{align*}
$$

These transitions generally fall within the ranges 7000 - 13000 cm$^{-1}$, 11000-20000 cm$^{-1}$, and 19000-27000 cm$^{-1}$ respectively.

In the case of tetrahedral Ni(II) complexes the expected transitions are $^3T_1(F) \to ^3T_1(P)$, $^3T_1(F) \to ^3T_2$ and $^3T_1(F) \to ^3A_2$. Only two are observed. The absorption by a tetrahedrally coordinated Ni(II) is many fold intense than octahedrally coordinated Ni(II), since the former lacks centre of symmetry.$^{295}$

5.4 **Nephelauxetic series**

During complex formation when the metal d orbitals and the ligand orbitals overlap, the ligand lone pairs penetrate the metal d orbitals, screening the d electrons from the positive nucleus. This reduces the effective nuclear charge felt by the d electrons, which in turn leads to an expansion of the d orbitals. This expansion effectively increases the separation between the d orbitals and the inter electronic repulsion decreases.
The value of Racah parameter \( B \) for free ions determined from the emission spectra of free metal ions are not the same as those obtained for the complexed metal ion from the absorption spectra. The values obtained for the complexes \( B_1 \) are always lesser than \( B \) for free ion. The difference between \( B \) and \( B_1 \) values suggest that the radial distribution of the d-electron is not the same in the free ion and its complex. Since Racah parameter is an interelectronic repulsion parameter, the lower value of \( B_1 \) indicates that the d-electrons of the metal ion in a complex suffer lesser inter-repulsion than in the free ion. The lesser repulsion can be explained in terms of the expansion of charge cloud of d-electrons in the complex leading to co-valent interaction between the metal and ligand. A covalency factor \( \beta \) can be defined as \( \beta = \frac{B_1}{B} \). \( \beta \) is also known as nephelauxetic ratio.

It is possible to arrange the ligands in the order of decreasing \( \beta \), as

\[
F^- > H_2O > \text{urea} > NH_3 > \text{ethylene diamine}
\approx C_2O_4^{2-} > NCS^- > Cl^- > CN^- > Br^- > S^{2-} \sim I^-
\]

and the arrangement is known as nephelauxetic ligand series. The smaller value of \( \beta \), the more covalent the complex. For an ionic complex \( \beta \) is close to unity.

5.5 Evaluation of Dq, \( B_1 \) and \( \beta \) parameters

As an experimental spectrum is fitted to the energy expressions, we can calculate the values of the spectral parameters such as Dq, \( B_1 \) and \( \beta \).
There exist several procedures to fit the spectra to the theoretical expressions. After the spectrum has been assigned to the expected transitions, the transition energy ratios have to be approximately used for evaluating the parameter $B^I$ and Dq.

For high-spin octahedral and tetrahedral complexes of $d^1$, $d^6$, $d^9$ and $d^4$ metal ions, it is easy to deduce 10Dq values from the lone transition. The Orgel diagrams are sufficient for this purpose. But for the high spin cubic complexes of $d^2$, $d^8$, $d^3$ and $d^7$ ions, there are several procedures available for the calculation of ligand field parameter 10Dq and the inter electronic repulsion parameter $B^I$ and C ($C = 4B$). The Racah parameter (B) values for many free ions are available from their emission spectra. A covalency factor or nephelauxetic ratio $\beta$ is then calculated as $B^I/B$ to ascertain the percentage of the covalent character of the M-L bond.

Two methods are very popular for evaluating these spectral parameters 1) Graphical method and 2) Numerical method. Graphical method is adopted to calculate the ligand field parameters.\textsuperscript{290}

5.6 Results

The parameters Dq, $B^I$ and $\beta$ are evaluated for [Co(trien)(NO\textsubscript{3})\textsubscript{2}], [Co(o-tol)\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}], [Ni(en)\textsubscript{3}](NO\textsubscript{3})\textsubscript{2}, [Ni(trien)(NO\textsubscript{3})\textsubscript{2}] and [Ni(o-tol)\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}] before and after gamma irradiation. The absorption bands and their assignments are given in tables 30 and 31. Graphical method is used for the
evaluation of ligand field parameters. The results are given in tables 32 and 33. The electronic spectra of nickel(II) complexes are given in figures 51, 52 and 53.

5.6.1 Calculation of $B^I$, $Dq$ and $\beta$ of tris(ethylenediamine)nickel(II) nitrate

For unirradiated $[\text{Ni(en)}_3(\text{NO}_3)_2]$, three transitions are assigned as:

$^3A_2g \rightarrow ^3T_2g(F) \quad \nu_1 \quad 11415 \text{ cm}^{-1}$

$^3A_2g \rightarrow ^3T_1g(F) \quad \nu_2 \quad 18339 \text{ cm}^{-1}$

$^3A_2g \rightarrow ^3T_1g(P) \quad \nu_3 \quad 29112 \text{ cm}^{-1}$

From the results Racah parameters are calculated as

$\nu_3/\nu_1 = 29112/11415 \approx 2.55, \quad Dq/ B^I = 1.35$ (from table)

$\nu_2/B^' = 34$ (from table)

Therefore $B^I = 857 \text{ cm}^{-1}$

$B = 1080 \text{ cm}^{-1}$ for $\text{Ni}^{2+}$

Since $Dq/ B^I = 1.35$, $Dq = 1156 \text{ cm}^{-1}$ or $10 Dq = 11560 \text{ cm}^{-1}$

$\beta = 857/1080 = 0.7940$

For irradiated $[\text{Ni(en)}_3(\text{NO}_3)_2]$

Three transitions are assigned as

$^3A_2g \rightarrow ^3T_2g(F) \quad \nu_1 \quad 11494 \text{ cm}^{-1}$

$^3A_2g \rightarrow ^3T_1g(F) \quad \nu_2 \quad 18416 \text{ cm}^{-1}$

$^3A_2g \rightarrow ^3T_1g(P) \quad \nu_3 \quad 29411 \text{ cm}^{-1}$
From the results Racah parameters are calculated as

\[ \frac{v_3}{v_1} = \frac{29411}{11494} = 2.55, \quad \frac{Dq}{B_1} = 1.322 \text{ (from table)} \]
\[ \frac{v_3}{B_1} = 34 \text{ (from table)} \]

Therefore \( B_1 = 862.5 \text{ cm}^{-1} \)

Since \( \frac{Dq}{B_1} = 1.322 \), \( Dq = 1140 \text{ cm}^{-1} \) or \( 10 \times Dq = 11400 \text{ cm}^{-1} \)

\[ \beta = \frac{862.5}{1080} = 0.7986 \]

Three spin allowed transitions are possible for nickel(II) and cobalt(II) in an octahedral environment. Only two bands are observed for both the irradiated and unirradiated samples in the case of all the complexes except \([\text{Ni(enh)}_3](\text{NO}_3)_2\). Dq and covalency factor \( \beta \) were evaluated by graphical method. From the knowledge of transition energy ration \( \frac{v_i}{v_j} \), the value of \( \frac{Dq}{B_1} \) is obtained from the graph. \( B_1 \) is calculated from available transition energies and \( \beta \), covalency factor is obtained from the relation \( \beta = \frac{B_1}{B} \) where \( B \) is the Racah parameter for the free metal ion and \( B_1 \) that for complexed metal ion.

5.7 Discussion

The Racah parameter \( B \) for a given metal ion depends on the nature of the ligand bound to the metal ion. For the complexed metal ion, the value of \( B \) will be less than that for free metal ion. The decrease in the value of \( B \) is related to the percentage of covalency in the metal – ligand bond. The Racah parameter \( B \) depends on inter electronic repulsion within the d-orbitals. When the d-orbitals overlap with the ligand orbitals the metal – ligand bond becomes partially covalent. As a result, d-charge cloud expands,
interelectronic repulsion decreases and B value is lowered. For the complexed metal ion the parameter is represented by $B'$. The ratio $B'/B = \beta$ gives a measure of covalency in the metal – ligand bond. Lower the value of $\beta$, greater is the covalency.

Electronic spectra of transition metal complexes generally give rise to broad bands because the transitions are spread over a range of energies. Various factors such as vibrational phenomena, distortion to lower symmetry, spin-orbit coupling and Jahn-Teller affect the nature of electronic spectra. In the present studies it is found that the spectral bands are broadened after irradiation of the sample. Upon irradiation it is possible that the field strength fluctuates over a greater range and broadening of the band results.

If all the ligands in an octahedral complex are not the same, the symmetry of the molecule will be less than $O_h$ symmetry. But when the $O_h$ symmetry is distorted, the orbital degeneracy of $E_g$ and $T_{2g}$ states will be lifted and splitting of bands occur. If the perturbation by the low symmetry component is small, splitting will be limited and a broad band results. This mechanism may also be operating in the complexes upon irradiation. A broadened band below 400 nm indicates the presence of nano particles.

### 5.7.1 Cobalt(II) and nickel(II) complexes ethylenediamine

#### 5.7.1.1 Tris(ethylene diamine)cobalt(II)nitrate

It is observed that the band maxima appeared almost in the same position for both unirradiated and irradiated complexes and the bands
are broad. Since the results are ambiguous probably due to low resolution, they are not included.

5.7.1.2 Tris(ethylene diamine)nickel(II)nitrate

The parameters Dq, β and B₁ for the unirradiated and irradiated samples of [Ni(en)]_3(NO₃)_2 are found to be approximately the same. In this metal complex nitrate ion is not coordinated to the metal ion. Therefore the effect of damaged nitrate is negligible on the field strength. It is also noted that further broadening of the bands is less pronounced in this case. We can conclude that irradiation has not much affected the crystal field strength due to ethylenediamine which is coordinated to the metal ion (Table 33).

5.7.2 Cobalt(II) and nickel(II) complexes of triethylene tetramine

5.7.2.1 Dinitratotriethylenetetraminecobalt(II)

It is found that the band maxima are shifted to higher frequencies. The β values have increased upon irradiation indicating lesser covalent character for the metal-ligand bond. The damaged nitrate ion in the coordination sphere presents a field of different strength so that 10Dq has changed. Broadening of the band can also be due to the damaged nitrate coordinated to the metal ion (Table 32).

5.7.2.2 Dinitratotriethylenetetraminenickel(II)

Irradiation causes significant changes in the values of 10Dq, B₁ and β. The increase in the value of β upon irradiation is much more than in the
case of cobalt(II) complex. The damaged nitrate presents a field of different strength so that the ligand field parameters have changed. The spectral bands of the irradiated complexes are much broader indicating greater fluctuation of metal – nitrate bond (Table 33).

5.7.3 Cobalt(II) and nickel(II) complexes of o-toluidine

5.7.3.1 Dinitratobis(o-toluidine)cobalt(II)

As in the cobalt(II) complex of triethylenetetramine, here also the β value has increased upon irradiation (Table 32). The percentage of increase is small, when compared to that in nickel(II) complex.

5.7.3.2 Dinitratobis(o-toluidine)nickel(II)

It is observed that the value of β has increased upon irradiation. The magnitude of increase is comparable with that observed in [Ni(trien)(NO\(_3\))\(_2\)]. This implies lesser covalent character for the metal ligand bond. It is possible that the damaged nitrate, which is coordinated to the metal presents a field of different strength so that 10Dq and β have changed. As in the other nickel(II) complexes here also irradiation causes broadening of spectral bands.

5.8 Summary

In the present work, electronic spectra of cobalt(II) and nickel(II) complexes of ethylenediamine, triethylenetetramine and o-toluidine were studied. From the available data, 10Dq, B\(_1\) and β were determined by
The bands in the uv-visible spectra of irradiated samples appear broad and shift in $\lambda_{\text{max}}$ is observed. Upon irradiation $\beta$ values increased indicating lesser covalent nature for the metal ligand bond. In dinitratotriethylenetetraminecobalt(II) the percentage increase in $\beta$ value upon irradiation is 1.4% while percentage increase in nickel complex is 21.6%. In dinitratobis(o-toluidine)cobalt(II) the percentage increase in $\beta$ value is 3% while in nickel complex the percentage increase is 11%. The percentage increase of $\beta$ is more pronounced in nickel(II) complexes, especially when nitrate ion is inside the coordination sphere. Effect of irradiation is more in nickel(II) complexes than in cobalt(II) complexes.
Fig. 51. Electronic spectra of [Ni(en)$_3$](NO$_3$)$_2$

a. Unirradiated  b. Irradiated
Fig. 52. Electronic spectra of [Ni(trien)(NO$_3$)$_2$]

a. Unirradiated, b. Irradiated
Fig. 53. Electronic spectra of [Ni(o-tol)$_2$(NO$_3$)$_2$]

a. Unirradiated, b. Irradiated
### Table 30
Electronic absorption bands of cobalt(II) complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Band assignments</th>
<th>Band positions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Unirradiated</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Irradiated</td>
</tr>
<tr>
<td>[Co(trien)(NO$_3$)$_2$]</td>
<td>$^4T_{1g}(F)\rightarrow^4A_{2g}$</td>
<td>15384</td>
</tr>
<tr>
<td></td>
<td>$^4T_{1g}(F)\rightarrow^4T_{1g}(P)$</td>
<td>20325</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15649</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20661</td>
</tr>
<tr>
<td>[Co(o-tol)$_2$(NO$_3$)$_2$]</td>
<td>$^4T_{1g}(F)\rightarrow^4A_{2g}$</td>
<td>14388</td>
</tr>
<tr>
<td></td>
<td>$^4T_{1g}(F)\rightarrow^4T_{1g}(P)$</td>
<td>18382</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13568</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18115</td>
</tr>
</tbody>
</table>
Table 31
Electronic absorption bands of Ni(II) complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Band assignments</th>
<th>Band positions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Unirradiated</td>
</tr>
<tr>
<td>[Ni(en)$_3$(NO$_3$)$_2$]</td>
<td>$^3$A$_{2g}</td>
<td></td>
</tr>
</tbody>
</table><p>ightarrow ^3$T$<em>{2g}$(F) | 11415          | 11494         |
|                        | $^3$A$</em>{2g}ightarrow ^3$T$<em>{1g}$(F) | 18399          | 18416         |
|                        | $^3$A$</em>{2g}ightarrow ^3$T$<em>{1g}$(P) | 29112          | 29411         |
| [Ni(trien)(NO$<em>3$)$<em>2$] | $^3$A$</em>{2g}ightarrow ^3$T$</em>{1g}$(F) | 18183          | 18335         |
|                        | $^3$A$</em>{2g}ightarrow ^3$T$<em>{1g}$(P) | 27998          | 28715         |
| [Ni(o-tol)$<em>2$(NO$<em>3$)$<em>2$] | $^3$A$</em>{2g}ightarrow ^3$T$</em>{1g}$(F) | 14771          | 15389         |
|                        | $^3$A$</em>{2g}ightarrow ^3$T$</em>{1g}$(P) | 25387          | 25641         |</p>
Table 32
Racah parameters for the unirradiated and irradiated cobalt(II) complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>10Dq cm(^{-1})</th>
<th>β</th>
<th>B' cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated [Co(trien)(NO(_3))(_2)]</td>
<td>8310</td>
<td>0.8410</td>
<td>943</td>
</tr>
<tr>
<td>Irradiated [Co(trien)(NO(_3))(_2)]</td>
<td>7940</td>
<td>0.8530</td>
<td>956</td>
</tr>
<tr>
<td>Unirradiated [Co(o-tol)(_2)(NO(_3))(_2)]</td>
<td>7725</td>
<td>0.7511</td>
<td>841.3</td>
</tr>
<tr>
<td>Irradiated [Co(o-tol)(_2)(NO(_3))(_2)]</td>
<td>7461</td>
<td>0.7746</td>
<td>867.6</td>
</tr>
</tbody>
</table>
Table 33
Racah parameters for the unirradiated and irradiated nickel(II) complexes

<table>
<thead>
<tr>
<th>Complexes</th>
<th>10Dq cm⁻¹</th>
<th>β</th>
<th>B' cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated <a href="NO_3">Ni(en)_3</a>_2</td>
<td>11560</td>
<td>0.7940</td>
<td>857</td>
</tr>
<tr>
<td>Irradiated <a href="NO_3">Ni(en)_3</a>_2</td>
<td>11400</td>
<td>0.7986</td>
<td>862.5</td>
</tr>
<tr>
<td>Unirradiated [Ni(trien)(NO_3)_2]</td>
<td>12260</td>
<td>0.5679</td>
<td>613.4</td>
</tr>
<tr>
<td>Irradiated [Ni(trien)(NO_3)_2]</td>
<td>11950</td>
<td>0.6915</td>
<td>746.9</td>
</tr>
<tr>
<td>Unirradiated [Ni(o-tol)_2(NO_3)_2]</td>
<td>9590</td>
<td>0.7837</td>
<td>846.5</td>
</tr>
<tr>
<td>Irradiated [Ni(o-tol)_2(NO_3)_2]</td>
<td>9152</td>
<td>0.8703</td>
<td>940.1</td>
</tr>
</tbody>
</table>