CHAPTER V

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

5. 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 characterize 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 antibonding 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 antibonding orbitals located primarily on the metal atom to antibonding orbitals located primarily on the ligands are termed metal to ligand charge transfer transitions. (4) The electronic transitions, which involve electrons being excited from one ligand orbital to another ligand orbital.

The electronic spectrum can be recorded by irradiating the solution of a compound and by measuring the absorbance versus wavelength or wave number. The absorbance can also be called as ‘optical density’ and defined by $A = \log \frac{l_0}{l}$ where $l_0$ and $l$, 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 Laporte rule transitions are allowed only between gerade and ungerade states i.e., $g \rightarrow u$. The transitions $g \rightarrow g$ and $u \rightarrow u$ 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 Laporte rule can be violated. If the d-orbital wave function is mixed with some p-character which has ungerade symmetry, the transition moment integral does not vanish and transitions occur. The extent of d-p mixing influences the band intensity. When the d and p wave functions are mixed, the inversion center about the central atom is removed.

There are two important mechanisms by which the center 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 spfn 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 $10^{-4} - 10^{-6}$, if allowed fully. But when they are both spin forbidden and Laporte 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.\(^{217}\)

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 ions 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 centrosymmetric 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 lower symmetry components, vibrational coupling, spin orbit coupling, Jahn-Teller effect etc.\textsuperscript{218,219}

5.2.2.1. Lower Symmetry Components

If all the ligands in a hexa coordinate complex are not identical, the actual symmetry of the molecule will be lowered from $O_h$ to other point groups such as $D_{4h}$, $C_{4v}$, $C_{3v}$ etc., depending on the nature of the hetero group substitution. The degeneracy of E and T terms will necessarily be partially or wholly lifted. This splitting may be small, resulting in increased band width, or may result in several absorption peaks.

5.2.2.2. Vibrational coupling

In the case of an electronically allowed transition, if there is no change in equilibrium internuclear distance, a progression in the totally symmetric mode which distorts along the appropriate coordinate can be expected. This
leads to broadening of an otherwise narrow transition. When the measurement is made in fluid medium, each of these lines is associated with a rotational subset. If the measurement is made in the solid state, each electronic line will couple to a manyfold of lattice modes providing another broadening mechanism. In the case of a vibronic transition, the electronic state will couple with every odd mode of vibration permitted by the selection rules. In the solid state, lattice vibrations will also couple. Each of these vibronic origins will, in general, have a progression based thereon.

5.2.2.3. Spin-orbit coupling

This is another mechanism by which some broadening of the band takes place. Spin-orbit coupling has been treated as a small perturbation. $\lambda$ is a measure of this coupling phenomenon and ranges between 100 - 1000 cm$^{-1}$ for 3d metal ions. Spin-orbit coupling becomes more pronounced in the case of 4d and 5d metal complexes.

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. Nephelauxetic Series (Variation of Racah Parameter B)

The Racah parameter B vary as a function of the ligands bound to the metal ion. The value of B is always reduced from that observed with the free metal ion. It is evident that B increases with increasing oxidation state and with the number of electrons in the d shell. The primary factor is the size of the ion; the larger the ion, the larger the mean radial displacement of the d shell, and the smaller the mutual interelectronic repulsion. The reduction of B in a complexed ion, is generally attributed to one or both of following two mechanisms.

5.3.1. Central field covalency.

If the lone pairs of the ligands penetrate the d shell, they will tend to screen the d electrons from the nucleus, decrease the effective charge experienced by the d electrons and expand the d shell. Thus B is expected to decrease if the metal ligand bond becomes partially covalent. By transferring some charge to the metal ion, the ligand will reduce the effective positive charge on the metal and allow for some expansion of the d shell.
5.3.2. Symmetry restricted covalency

In an octahedral complex, if there is some covalent bonding between metal and ligand, a small amount of sigma or pi electron density of the metal, may be transferred to the ligands. Such delocalisation will also decrease the mean distance between d electrons and hence reduce the value of B. However central field covalency is probably the major contributor to the reduction of B in transition metal complexes. The greater the reduction in B, as represented by the ratio: \[ \beta = \frac{B_{\text{in complex}}}{B_{\text{in free ion}}} \], greater the covalency in the metal-ligand bond and the smaller the effective charge experienced by the d electrons. For a given ion, ligands are ordered according to the value of B in the corresponding complexes and the nephelauxetic series is obtained. The value of B also tends to decrease, for a given metal and ligand, with decreasing coordination number.

5.4. Spectrochemical Series (Variation of 10 Dq)

The crystal field splitting parameter 10Dq can be obtained from the absorption spectrum of the metal complex. This parameter is a measure of the extent to which the metal d-orbitals are split by the surrounding ligands. There are several factors which determine the magnitude of the ligand field splitting.

5.4.1. Nature of the metal ion

For metal ions of the same group and with the same charge, 10 Dq increases by 30% to 50% from 3d to 4d and from 4d to 5d transition series. The trend observed is 3d < 4d < 5d.
5.4.2. Oxidation state of the metal ion

Dq value increases with increase in oxidation state for the same ligand environment. The 10 Dq value for M(III) complexes is about 40-80% greater than that for M(II) complexes. Metal complexes belonging to a particular nd series with similar oxidation state and ligand environment show similar 10 Dq values.

5.4.3. Coordination number of the complex

Other factors being equal, \((10 \text{ Dq})_i = \frac{4}{9} [10 \text{ Dq}]_0\)

5.4.4. Nature of the ligands

The most common ligands can be arranged in a series according to increasing 10 Dq values, i.e., increasing ligand field strength and for any chosen central metal ion. This series is called the spectrochemical series.

\[ I^- < Br^- < S^{2-} < Cl^- < SCN^- - N_3^- < \text{Urea} \]
\[ \sim OH < Ox^{2-} < O^{2-} < H_2O < P_y - NH_3 < en \]
\[ < \text{bipy-phen} < NO_2^- < CH_3^- < CN^- < CO \]

The given order is according to the increase of 10Dq value.

5.5. Evaluation of Dq, B¹ and β Parameters

An experimental spectrum is fitted to the energy expressions and with the help of this assignment, the values of the spectral parameters can be calculated. After the spectrum has been assigned to the expected transitions, the transition energy ratios have to be appropriately used for evaluating the
parameters $B^1$ and $D_q$. For high spin octahedral and tetrahedral complexes of $d^1$, $d^6$, $d^9$ and $d^4$ metal ions, $10D_q$ values can be deduced from the lone transition. For high spin cubic complexes of $d^2$, $d^8$, $d^3$ and $d^7$ ions, there are several procedures available for the calculation of the ligand field parameter $10D_q$ and the inter-electronic repulsion parameter $B^1$. 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 $B^1/B$ to ascertain the percentage of covalent character of the M-L bond.

Two methods are used for evaluating these spectral parameters.

(1) Graphical method (2) Numerical method (due to Konig). Every method has its limitations and also advantages.

5.5.1. Graphical method

This method is most popular and used by many workers. Tanabe-Sugano energy level diagrams were presented quantitatively and these diagrams are accepted for all quantitative calculations. This graphical method is useful for ions with $d^2$, $d^8$, $d^3$ and $d^7$ configurations. The transition energy ratios of various possible spin allowed transitions corresponding to complexes of $T_1$ and $A_2$ ground states are calculated from Tanabe-Sugano diagrams.

Graphs with theoretical plots of $\frac{D_q}{B}$ versus $\frac{\nu_i}{\nu_j}$ for $T_1$ and $A_2$ ground states are available. From the assigned spectrum, it is possible to know the transition energy ratio $\frac{\nu_i}{\nu_j}$ for any given complex and to find the corresponding $\frac{D_q}{B}$.
From the known transition energy of \( \nu_1, \nu_2 \) or \( \nu_3 \), \( B^1 \) can be evaluated. From \( Dq/B \) value, \( Dq \) can be calculated.

5.6. Electronic Spectra of Cobalt(II) and Nickel(II) Complexes

5.6.1. 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\(^{220}\). Several cases are reported in which equilibrium exists between octahedral and tetrahedral structures\(^{221}\).

The electronic spectra of cobalt (II) complexes have been largely studied by Liehr\(^{222}\). The six-coordinate high spin cobalt (II) is a commonly encountered 3d\(^7\) system and in a high spin octahedral environment, the likely transitions are

\[
^4T_{1g}(F) \rightarrow ^4T_{2g} \quad \nu_1 \quad E \sim 8Dq
\]

\[
^4T_{1g}(F) \rightarrow ^4A_{2g} \quad \nu_2 \quad E \sim 18Dq
\]

\[
^4T_{1g}(F) \rightarrow ^4T_{1g}(P) \quad \nu_3 \quad E \sim 6Dq + 15B^1
\]

(\( Dq \) and \( B^1 \) are ligand field parameters)
It can be seen that the energy difference $\nu_1 - \nu_2$ is exactly equal to 10Dq.

Unfortunately the $\nu_2$ 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 8000-10,000 cm$^{-1}$ of intensity, 1-10 L mol$^{-1}$ 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$^{-1}$ with intensity 5-20 L mol$^{-1}$ cm$^{-1}$. The transition to $^4A_{2g}$ is very weak often appearing as a shoulder near 12000 cm$^{-1}$.

\[
^4T_{1g}(F) \rightarrow ^4T_{2g} \quad \nu_1 \quad \sim 8000-10000 \text{ cm}^{-1}
\]
\[
^4T_{1g}(F) \rightarrow ^4A_{2g} \quad \nu_2 \quad \sim 12000 \text{ cm}^{-1}
\]
\[
^4T_{1g}(F) \rightarrow ^4T_{1g}(P) \quad \nu_3 \quad \sim 20000 \text{ cm}^{-1}
\]

The allowed transitions in tetrahedral fields of cobalt(II) complexes are

\[
^4A_2 \rightarrow ^4T_2(F) \quad \nu_1 \quad E \sim 10Dq
\]
\[
^4A_2 \rightarrow ^4T_1(F) \quad \nu_2 \quad E \sim 18Dq
\]
\[
^4A_2 \rightarrow ^4T_1(P) \quad \nu_3 \quad E \sim 12Dq + 15 B^1
\]

5.6.2. 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,
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 nickel(II) complexes the expected transitions are \(^3T_1(F)\rightarrow ^3T_1(P), ^3T_1(F)\rightarrow ^3T_2\) and \(^3T_1(F)\rightarrow ^3A_2(F)\). 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 center of symmetry\(^{223}\).

5.7. Results

In the present work, spectral parameters Dq, B\(^1\) and \(\beta\) are evaluated for [Co(dien)\(_2\)](NO\(_3\))\(_2\), [Ni(dien)\(_2\)](NO\(_3\))\(_2\), [Co(py)\(_2\)](NO\(_3\))\(_2\), [Ni(py)\(_2\)](NO\(_3\))\(_2\), [Co(2-apy)\(_2\)](NO\(_3\))\(_2\), and [Ni(2-apy)\(_2\)](NO\(_3\))\(_2\)] before and after gamma irradiation. Electonic absorption bands of diethylenetriamine, pyridine and 2-aminopyridine complexes are listed in Tables 28,29 and 30 respectively. Graphical method is used for the evaluation of spectral parameters. The results are given in Tables (31-33). The electronic spectra of cobalt(II) and nickel(II) complexes of pyridine and 2-aminopyridine are given in figures (39-42) respectively.
Calculation of $B'$, $D_q$ and $\beta$ of Dinitratobis(pyridine)nickel(II)

Unirradiated $[\text{Ni(py)}_2(\text{NO}_3)_2]$

$^3\text{A}_2g \rightarrow ^3\text{T}_{1g}(F)$ \quad $\nu_2=15458.1 \text{ cm}^{-1}$

$^3\text{A}_2g \rightarrow ^3\text{T}_{1g}(p)$ \quad $\nu_3=25864.5 \text{ cm}^{-1}$

$$\frac{\nu_3}{\nu_2} = \frac{25864.5}{15458.1} = 1.67$$

$$\frac{\nu_3}{B'} = 30.4(\text{Table})$$

$D_q = \frac{B'}{B} = 1.12(\text{Table})$

$B' = 850.8 \text{ cm}^{-1}$

$D_q = 1.12 \times 850.8 = 952.9$

$$\beta = \frac{B'}{B} = \frac{850.8}{1080} = 0.787$$

Irradiated $[\text{Ni(py)}_2(\text{NO}_3)_2]$

$^3\text{A}_2g \rightarrow ^3\text{T}_{1g}(F)$ \quad $\nu_2=14905.1 \text{ cm}^{-1}$

$^3\text{A}_2g \rightarrow ^3\text{T}_{1g}(p)$ \quad $\nu_3=26099.4 \text{ cm}^{-1}$

$$\frac{\nu_3}{\nu_2} = \frac{26099.4}{14905.1} = 1.75$$

$$\frac{\nu_3}{B'} = 27.55(\text{Table})$$

$D_q = \frac{B'}{B} = 0.936(\text{Table})$

$B' = 947.4 \text{ cm}^{-1}$

$D_q = 947.4 \times 0.936 = 886.7$

$$\beta = \frac{B'}{B} = \frac{947.4}{1080} = 0.877$$
Three spin allowed transitions are possible for nickel(II) and cobalt(II) in an octahedral environment. In the case of all the complexes, only two bands were observed for both the irradiated and unirradiated samples. From the data available, LFSE and covalency factor $\beta$ were evaluated by graphic method.\textsuperscript{224} From the knowledge of transition energy ratio $\frac{v_i}{v_j}$, the value of $Dq/B^I$ is obtained from graph. $B^I$ is calculated from the available transition energies and $\beta$, covalency factor is obtained from the relation $\beta = \frac{B^I}{B}$ where $B$ is the Racah parameter for free metal ion and $B^I$ that for complexed metal ion.

5.7.1. Cobalt(II) and nickel(II) complexes of diethylenetriamine

5.7.1.1. Bis(diethylene triamine)cobalt (II) nitrate

The bands in the UV-visible spectra of irradiated samples appear broad. Electronic spectra of irradiated and unirradiated samples were analyzed. As the results are ambiguous, probably due to low resolution, they are not included.

5.7.1.2. Bis (diethylene triamine)nickel(II) nitrate

The band in the UV-visible spectrum of the irradiated sample appears broad and shift in $\lambda_{\text{max}}$ is observed. Decrease in LFSE is nominal in the irradiated sample and practically no change is observed in $B^I$ and $\beta$ values.
5.7.2. Cobalt(II) and nickel(II) complexes of pyridine

5.7.2.1. Dinitrato bis (pyridine) cobalt(II)

Broadening of spectral bands and shift in $\lambda_{\text{max}}$ occurs upon irradiation in $[\text{Co(py)}_2(\text{NO}_3)_2]$ (Fig. 39). LFSE is lowered and Racah parameter $B^1$ and covalency factor $\beta$ values increased upon irradiation.

5.7.2.2. Dinitrato bis (pyridine) nickel (II)

UV-visible spectral bands are broadened in the irradiated sample and $\lambda_{\text{max}}$ is changed (Fig. 40). In the irradiated sample lowering of LFSE and increase of $B^1$ and $\beta$ values are observed.

5.7.3. Cobalt(II) and nickel(II) complexes of 2-aminopyridine

5.7.3.1. Bis(2-aminopyridine) dinitrato cobalt(II)

In the irradiated sample $\lambda_{\text{max}}$ is shifted from that of the unirradiated one (Fig. 41). LFSE is lowered upon irradiation. Increase in Racah parameter $B^1$ and nominal increase in $\beta$ are observed in the irradiated sample.

5.7.3.2. Bis(2-amino pyridine)dinitrato nickel(II)

Solid state reflectance spectra showed broadening of the UV-visible spectral bands of the irradiated samples and shift in $\lambda_{\text{max}}$ (Fig. 42). LFSE of the irradiated sample is decreased while $B^1$ and $\beta$ values are increased upon irradiation.
5.8. Discussion

The Racah parameter B for a given metal ion varies as a function of the ligand bound to the metal ion. The value of this parameter will be always less for the complexed ion than that for free ion. The reduction of the value of B in a complexed ion is related to the extent of covalency in the metal-ligand bond. The metal-ligand bond becomes partially covalent when the d-orbitals overlap with the ligand orbitals. As a result, the interelectronic repulsion within the d-orbitals decrease and B value is lowered. For the complexed ion the parameter is represented as $B^1$. The ratio $\frac{B^1}{B} = \beta$ 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 distortion affect the electronic absorption spectra. Generally, one or more of these factors operate on the system to cause broadening of the band. In the present study it is found that the spectral bands are broadened after irradiation of the sample. The ligand field parameter Dq is very sensitive to change in metal ligand distance. As the metal-ligand bond vibrates, electronic transition will occur over a range of energies and a broad band results. Upon irradiation it is possible that the filed strength fluctuates over a greater range and broadening of the band results.
If all the ligands in a hexa coordinate complex are not the same the actual symmetry of the molecule will be lowered from $O_h$ symmetry. But when the octahedral symmetry gets distorted, the orbital degeneracy of $E_g$ and $T_{2g}$ levels will be lifted and splitting of bands occur. If the perturbation by the low symmetry component is small, splitting will be small, so that electronic transitions give rise to broad bands. This mechanism may also be operating in the complexes of cobalt(II) and nickel(II) upon irradiation.

5.8.1. Nickel(II) complex of diethylenetriamine

5.8.1.1. Bis(diethylenetriamine) nickel(II) nitrate

In the present study it is found that LFSE and $\beta$ are not affected significantly by irradiation in $[\text{Ni(dien)}_2](\text{NO}_3)_2$ (Table 31). This implies that no significant change in field strength is experienced by nickel(II) in $[\text{Ni(dien)}_2](\text{NO}_3)_2$. The nitrate ion is not coordinated to the metal ion and therefore the effect of damaged nitrate is negligible. The broadening of the spectral bands are less pronounced in $[\text{Ni(dien)}_2](\text{NO}_3)_2$ since the nitrate ion is outside the co-ordination sphere.

5.8.2. Cobalt(II) and nickel(II) complexes of pyridine

5.8.2.1. Dinitrato bis (pyridine) cobalt(II)

Upon irradiation LFSE is lowered, $B^l$ and $\beta$ values are increased (Table 32). Irradiation reduces the field strength experienced by cobalt(II) in $[\text{Co(py)}_2(\text{NO}_3)_2]$. The damaged nitrate ion in the coordination sphere presents
a field of different strength so that LFSE is lowered. Since ß is increased it can be concluded that metal-ligand bond becomes less covalent. Broadening of the spectral bands is pronounced since the damaged nitrate ion is inside the coordination sphere.

5.8.2.2. Dinitrato bis(pyridine) nickel(II)

The results observed are similar to \([\text{Co(py)}_2(\text{NO}_3)_2]\) but the effect of irradiation is more pronounced. Significant lowering of LFSE is observed. The metal-ligand bond becomes less covalent as evidenced by an increase in the ß value. ß increases by 11.4% and LFSE is lowered by 6.9% upon irradiation (Table 32).

5.8.3. Cobalt(II) and nickel(II) complexes of 2-aminopyridine

5.8.3.1. Bis(2-amino pyridine)dinitrato cobalt(II)

Damaged nitrate ion inside the co-ordination sphere produces lowering of LFSE and increase the value of B\(^1\) and ß (Table 33). The metal-ligand bond becomes less covalent after irradiation.

5.8.3.2. Bis(2-amino pyridine)dinitrato nickel(II)

The results are similar to \([\text{Co(2-apy)}_2(\text{NO}_3)_2]\). Lowering of LFSE and increase in B\(^1\) and ß values are observed upon irradiation (Table 33). ß value increased by 8.9% in the irradiated sample.

Maximum lowering of LFSE, 6.9% is observed in \([\text{Ni(py)}_2(\text{NO}_3)_2]\). Compared to cobalt(II) complexes, B\(^1\) and ß values are more affected in
nickel(II) complexes. Increase in $\beta$ values are 11.4% in $[\text{Ni(py)}_2(\text{NO}_3)_2]$ and 8.9% in $[\text{Ni(2-apy)}_2(\text{NO}_3)_2]$ whereas the same for $[\text{Co(py)}_2(\text{NO}_3)_2]$ and $[\text{Co(2-apy)}_2(\text{NO}_3)_2]$ are insignificant.

**Summary**

In the present work electronic spectra of cobalt(II) and nickel(II) complexes of diethylenetriamine, pyridine and 2-aminopyridine were studied. From the data available, LFSE, $B^1$ and $\beta$ were evaluated by graphical method. The bands in the UV-visible spectra of the irradiated samples appear broad and shift in $\lambda_{\text{max}}$ is observed. Upon irradiation LFSE is lowered, $B^1$ and $\beta$ values are increased. Since $\beta$ increases, it can be concluded that metal-ligand bond becomes less covalent. Lowering in LFSE is more pronounced in pyridine and 2-aminopyridine complexes, since the damaged nitrate ion is inside the coordination sphere. In $[\text{Ni(dien)}_2(\text{NO}_3)_2]$, lowering in LFSE is insignificant. The nitrate ion is not coordinated to the metal ion and therefore the effect of damaged nitrate is negligible. Compared to cobalt (II) complexes, the effect of irradiation is more in nickel (II) complexes.
Fig. 39. Electronic spectra [a] un irradiated [Co(py)$_3$(NO$_3$)$_3$] [b] irradiated [Co(py)$_3$(NO$_3$)$_3$]
Fig. 40. Electronic spectra

[a] un irradiated [Ni(py)$_2$(NO$_3$)$_2$]

[b] irradiated [Ni(py)$_2$(NO$_3$)$_2$]
Fig. 41. Electronic spectra

[a] unirradiated [Co(2-apy)$_2$(NO)$_3$]

[b] irradiated [Co(2-apy)$_2$(NO)$_3$]
Fig. 42. Electronic spectra (a) unirradiated [Ni(2-apy)$_2$(NO$_3$)$_2$] (b) irradiated [Ni(2-apy)$_2$(NO$_3$)$_2$].
<table>
<thead>
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<th>Sample</th>
<th>Band assignment</th>
<th>Band position (cm(^{-1}))</th>
<th>Unirradiated</th>
<th>Irradiated to 800 kGy</th>
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<td><a href="NO(_3)">Ni(dien)(_2)</a>(_2)</td>
<td>(^3)A(<em>{2g}) → (^3)T(</em>{1g})(F)</td>
<td>18656.7</td>
<td>18621.9</td>
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<tr>
<td></td>
<td>(^3)A(<em>{2g}) → (^3)T(</em>{2g})</td>
<td>11600.9</td>
<td>11587.4</td>
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### Table 29

Electronic absorption bands of \([\text{Co(py)}_2(\text{NO}_3)_2]\) and \([\text{Ni(py)}_2(\text{NO}_3)_2]\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Band assignment</th>
<th>Band position (cm(^{-1}))</th>
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<tbody>
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<td></td>
<td><strong>Unirradiated</strong></td>
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<td>([\text{Co(py)}_2(\text{NO}_3)_2])</td>
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<td>(^4\text{T}<em>{1g}(\text{F}) \rightarrow ^4\text{T}</em>{1g}(\text{P}))</td>
<td>21812.1</td>
</tr>
<tr>
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<td>(^3\text{A}<em>{2g}\rightarrow ^3\text{T}</em>{1g}(\text{F}))</td>
<td>15458.1</td>
</tr>
<tr>
<td></td>
<td>(^3\text{A}<em>{2g}\rightarrow ^3\text{T}</em>{1g}(\text{P}))</td>
<td>25864.5</td>
</tr>
<tr>
<td>Sample</td>
<td>Band assignment</td>
<td>Band position (cm⁻¹)</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>[Co(2-apy)₂(NO₃)₂]</td>
<td>(^4\text{T}<em>{1g}(F)\rightarrow (^4\text{A}</em>{2g})</td>
<td>16077.2</td>
</tr>
<tr>
<td></td>
<td>(^4\text{T}<em>{1g}(F)\rightarrow (^4\text{T}</em>{1g}(P))</td>
<td>19120.5</td>
</tr>
<tr>
<td>[Ni(2-apy)₂(NO₃)₂]</td>
<td>(^3\text{A}<em>{2g}\rightarrow (^3\text{T}</em>{1g}(F))</td>
<td>14981.2</td>
</tr>
<tr>
<td></td>
<td>(^3\text{A}<em>{2g}\rightarrow (^3\text{T}</em>{1g}(P))</td>
<td>25806.4</td>
</tr>
<tr>
<td>Sample</td>
<td>$B'$ (cm$^{-1}$)</td>
<td>(LFSE) (cm$^{-1}$)</td>
</tr>
<tr>
<td>----------------------------</td>
<td>------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>Unirradiated [Ni (dien)$_2$] (NO$_3$)$_2$</td>
<td>965.6</td>
<td>11587.9</td>
</tr>
<tr>
<td>800 kGy [Ni (dien)$_2$] (NO$_3$)$_2$</td>
<td>963.8</td>
<td>11566.3</td>
</tr>
</tbody>
</table>
Table 32

Spectral parameters of [Co(py)$_2$ (NO$_3$)$_2$] and [Ni (py)$_2$ (NO$_3$)$_2$] evaluated by graphical method

<table>
<thead>
<tr>
<th>Sample</th>
<th>$B'$ (cm$^{-1}$)</th>
<th>(LFSE) (cm$^{-1}$)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated [Co(py)$_2$ (NO$_3$)$_2$]</td>
<td>918.4</td>
<td>10561.6</td>
<td>0.945</td>
</tr>
<tr>
<td>800kGy [Co(py)$_2$ (NO$_3$)$_2$]</td>
<td>922.6</td>
<td>10517.4</td>
<td>0.950</td>
</tr>
<tr>
<td>Unirradiated [Ni (py)$_2$ (NO$_3$)$_2$]</td>
<td>850.8</td>
<td>9529</td>
<td>0.787</td>
</tr>
<tr>
<td>800kGy [Ni (py)$_2$ (NO$_3$)$_2$]</td>
<td>947.3</td>
<td>8867.2</td>
<td>0.877</td>
</tr>
</tbody>
</table>
Table 33

Spectral parameters of [Co(2-apy)2(NO3)2] and [Ni(2-apy)2(NO3)2] evaluated by graphical method

<table>
<thead>
<tr>
<th>Sample</th>
<th>$B'$ (cm$^{-1}$)</th>
<th>(LFSE) (cm$^{-1}$)</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unirradiated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Co(2-apy)2(NO3)2]</td>
<td>846.4</td>
<td>8582.6</td>
<td>0.872</td>
</tr>
<tr>
<td>800kGy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Co(2-apy)2(NO3)2]</td>
<td>853.6</td>
<td>8485.3</td>
<td>0.879</td>
</tr>
<tr>
<td>Unirradiated</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(2-apy)2(NO3)2]</td>
<td>896.6</td>
<td>9119.2</td>
<td>0.830</td>
</tr>
<tr>
<td>800kGy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ni(2-apy)2(NO3)2]</td>
<td>976.0</td>
<td>9037.9</td>
<td>0.904</td>
</tr>
</tbody>
</table>