CHAPTER - II

(A) PHYSICAL MEASUREMENTS AND ANALYTICAL ESTIMATIONS

(B) METHODS OF CALCULATIONS

The various techniques which have been used in deducing the structure and geometry of the compounds have been discussed in brief.

(A) PHYSICAL MEASUREMENTS AND ANALYTICAL ESTIMATIONS

1. Magnetic Susceptibility:

The magnetic susceptibility of the complexes in powder form were carried out at room temperature using Guoy’s balance and Mercury(II) tetra thio cyanato cobaltate \([\text{Hg} \text{Co(CNS)}_4]\), [for which \(X_y = 10.44 \times 10^{-6}\) c.g.s. units at 20°C] was used as calibrating agent. The assembly consisted of a semimicro single pan balance and a Layhold’s electromagnet. The specimen tube (20 cm length with 0.2 mm diameter) was suspended from a pan by silver string. The magnetic field of \(1.20 \times 10^3\) gauge generated by an electromagnet fed from an A.C. main power controlled supply was used. The sample tube was suspended in closed glass chamber to avoid any air damping. Tube constant was checked from time to time to ensure the satisfactory working of the apparatus.

2. Mossbauer Measurements:

Mossbauer studies were carried out with ECI Mossbauer Spectrophotometer MBS 35 (physics Department, I.I.T. Hauz Khas, New Delhi) with constant acceleration device operating in a multiscaler mode with time operated electrodynamic device Co\(^{57}\) diffused into copper was used as source which was kept at the same temp. as the absorbed. Samples of the compound were powdered and placed in plastic cuvettes which were used as absorbers having thickness 5–10 mg/cm\(^2\) based on Iron of natural isotopic composition and cooled at the liquid nitrogen temperature. Temperature was monitored by using thermo couple. The Mossbauer absorption spectra were obtained in transmission geometry.
using a Mossbauer spectrometer in conjunction with a multichannel analyzer. Velocity scans were calibrated using the quadropole splitting of a polycrystalline sample Na$_2$[Fe(CN)$_6$NO] 2H$_2$O. Sufficient counts were stored in each channel and data from multi channel analyzer were reduced by means of a least squares filling programme using an IBM 360 computer.

The isomeric shift $\delta$ are measured relative to the mid point of the spectrum of an iron foil absorber at 300°K and 78°K. To convert to the nitroprusside scale $+0.257 \text{ mm/sec}$ was added.

Following conventions $\delta$ is taken as +ve when the source is moved towards the absorber. Liquid air was used for low temperature work (78°K) which was poured into the vacuum sealed double walled pyrex Dewar flask and it was fixed in a stand to avoid any vibration in the process of vapourising liquid air. To attain the temperature, the system was put on for about an hour before starting any observations. For measuring the temperature, Chromel-Alumel thermo couple was used and the voltage was measured on micro voltmeter and standard calibration table was consulted to convert the obtained voltage into temperature.

3. **Electronic Spectral Studies**:

The reflectance as well as soln. (aqueous & non-aqueous) spectra of metal chelates derived from 2-thiouryl & Benzothizole acetic acid and its derivatives of 4 methyl benzaldehyde, 4 hydroxy-3-aldehydodiphenyl, 2 Acetyl Thiophene; 2 Acetyl Furan and 2 Acetyl pyridine were recorded on UNICAM-SP-700 UV & VISIBLE SPECTROPHOTOMETER, using solvent blanks with complex solutions. For reflectance spectral, the complexes intimately mixed with MgO (a white inert compound) and a thin and uniform layer of the mixture was subjected to the spectral analysis in each case. Pure MgO (A.R. grade) was used as a blank.

4. **Infrared Measurements**:

IR spectra of ligand and metal chelates in the range 4000 cm$^{-1}$ – 400 cm$^{-1}$ and and 400 cm$^{-1}$ – 200 cm$^{-1}$ were recorded on Beckman I.R. 5A
spectrophotometer and Perkin Elmer 621 grating I.R. spectrophotometer respectively using KBr pellet as well as Nujol mull at room temp. The far I.R. spectra (Range 400 - 200 cm⁻¹) were also measured by using Nujol Mull as reference solvent supported between polyethylene sheets. Atmospheric moisture was removed from spectrophotometer by flushing dry Nitrogen.

5. **N.M.R. Measurements:**

N.M.R. spectroscopy is used to determine the structure of the compounds. The ¹H NMR spectra of the organic compounds were recorded in Micro Analytical Section, Chemistry Department, Indian Institute of Technology, New Delhi using a working frequency of 60 MHz. Chemical shifts (relating to tetramethyl silane (TMS) 0.0 ppm on δ scale) of the protons in the ¹H NMR spectra were recorded at room temp. 301±1°K.

6. **Conductance Measurements:**

Molar conductance measurements were carried out of ~ 10⁻³M solutions in nitromethane as well as DMF using a pye conductivity Bridge (made by Pye W.G. & Co. Ltd., England) at room temp. 302±2°K in triple distilled water.

7. **pH Measurements:**

The pH of the solutions (where ever required) were measured with an Phillip pH meter fitted with glass and saturated calomel electrodes (combined) operated at 9 volt DC/220V AC.

8. **Molecular Weight and Melting Point Determination:**

The Molecular weight of organic compounds were determined by using Osmometric Method and Benzil as reference compound. The melting points of organic compounds as well as complexes were recorded on a dip type thermometric equipment by using silicone liquid as a medium and heating directly by electricity (Dipped electrical spiral).

9. **Thermogravimetric Analysis (TGA) & Differential Thermal Analysis (DTA):**
Thermogravimetric analysis of the complexes as well as organic ligands was carried out on a DuPont model 950 Thermo Balance under polythermal conditions in the temp. range 30–700°C. The recording was carried out at furnace heating rate 10°C/minute. The specimen (50–100 mg) and the ref. compound calcinated Al₂O₃ (Both nearly similar amounts) were placed in quartz ampules. The thermal measurements in pure oxygen (A.R.) atmosphere were made by using a combined chromel/Alumel thermo couple. The change in the mass specimen on heating was measured by using a MC-Bain Balance with calibrated quartz spring (21).

In all the present metal complexes, metal % is analytically estimated. The residue was dissolved in conc. HCl (A.R.) and gravimetrically estimated by using standard methods.

10. **Chemical Analysis of Elements**:

   (a) **Micro-analysis of carbon, Hydrogen and Nitrogen**:

   The analysis of C, H and N were done at the Micro-Analytical Division, CDRI, Lucknow. The elemental analysis was carried out on Perkin Elmer model 240°C elemental analyzer.

   (b) **Estimation of Sulphur and Halogens**:

   The percentage of sulphur in compounds was determined by standard methods while halogen estimations were carried out by Volhard’s method and the ionisable chlorine was estimated as silver chloride. (22)

   (c) **Determination of water of Crystallisation**:

   The water contents per chelates (in ionized sphere) unit as the water of crystallization was estimated by Karl-Fisher method, where the particular complex is heated at 110°C till constant weight and the loss in weight correspond to the number of water molecules present in ionized sphere of the complex. (23)
(d) **Metal estimations:**

The metals content in the complexes have been determined by standard methods after decomposing the complex several times with conc. HNO₃ and dissolving the residue in water. Sometimes a few drops of dil. HCl were also added. E.D.T.A was used as titrant and Eriochrome Black T and Xylene Orange as indicators. Iron was determined by using 1:10 phenan throline, while halides were determined gravimetrically as silver halide. Cobalt content in Co(II) complexes was estimated gravimetrically as anhydrous Cobalt Sulphate. In some cases percentage metal content Ni, Co, Cr, Cu, V were estimated by Atomic Absorption spectrophotometrically using a Pye Unicam S.P.-191 Atomic Absorption spectrophotometer.

(C) **METHODS OF CALCULATIONS:**

1. **Magnetic Susceptibility:** The magnetic susceptibility measurements were made by using Guoy's Technique. [HgCo(CNS)₆] was used as calibrant for determining the tube constant by using the following formula:

   \[ \chi = -\frac{1}{W} KoV + C (\Delta W) \]

Where

- \( W \) = Weight of the specimen under investigation in gms.
- \( \Delta W \) = Change in weight under the influence of applied magnetic field.
- \( X \) = Specific Susceptibility.
- \( C \) = Tube constant.
- \( Ko \) = Volume susceptibility of air = \( 0.029 \times 10^{-6} \) c.g.s. units at 20°C per gm atom.
\[ V = \text{Volume of the tube upto the mark.} \]
\[ \text{KoV} = \text{A constant for allowing the displaced air} \]

With our magnetic tube C comes out to be 151.45x10^{-6} \text{ (Tube I)}, 160.95x10^{-6} \text{ (Tube II)} and KoV as 1202x10^{-6} \text{ (Tube I)} and 1224x10^{-6} \text{ (Tube II)} in c.g.s. units at 30°C per gm atom. Knowing the molecular wt. of the complex, its molar susceptibility (\(X_m\)) can be calculated:
\[ X_m = \chi \times \text{mol wt. of the complex.} \]

By applying diamagnetic corrections of the ligand portion \(X_m\) can be calculated:
\[ X_m' = X_m + (\text{diamagnetic correction of the organic molecule under interaction}) \]

The effective magnetic moment:
\[ \mu_{\text{eff}} = 2.827 \left( X_m' T \right)^{1/2} \text{ B.M.} \]

and \(\mu_{\text{eff}} = n (n+2)^{1/2} \)

Where, \( T = \text{Absolute Temperature} \), \(X_m' = \text{The molar susceptibility after correcting diamagnetic contribution} \) and \( n = \text{No. of unpaired electrons} \).

### Table 2.1: Transition metal ions with Electronic spectral terms and calculated Magnetic moments in B.M. Units

<table>
<thead>
<tr>
<th>Ion</th>
<th>3d electron</th>
<th>Term</th>
<th>(\mu_{\text{eff. (Calcd.)}})</th>
<th>Reported</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(^{3+})</td>
<td>3d(^5)</td>
<td>(^1S_0)</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Ti(^{4+})</td>
<td>3d(^1)</td>
<td>(^3D_{2})</td>
<td>1.73</td>
<td>1.77-1.79</td>
</tr>
<tr>
<td>V(^{5+})</td>
<td>3d(^2)</td>
<td>(^3F_2)</td>
<td>2.83</td>
<td>2.76-2.85</td>
</tr>
<tr>
<td>V(^{4+})</td>
<td>3d(^3)</td>
<td>(^4F_{5/2})</td>
<td>3.87</td>
<td>3.68-4.00</td>
</tr>
<tr>
<td>Ion</td>
<td>Configuration</td>
<td>$^5$D_0</td>
<td>$^6$S_{5/2}</td>
<td>S.O. (4.80-5.60)</td>
</tr>
<tr>
<td>-------</td>
<td>---------------</td>
<td>---------</td>
<td>-------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>3d$^4$</td>
<td>4.90</td>
<td>5.92</td>
<td>5.2-6.00</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>3d$^5$</td>
<td>6.8</td>
<td></td>
<td>4.90</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>3d$^5$</td>
<td>5.0-5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>3d$^6$</td>
<td>3.87</td>
<td>2.83</td>
<td>4.4-5.2</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>3d$^7$</td>
<td>2.9-3.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>3d$^8$</td>
<td>1.73</td>
<td></td>
<td>1.8-2.2</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>3d$^9$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$^{+}$</td>
<td>3d$^{10}$</td>
<td>0.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*S.O.* = Spin-only value of magnetic moments.
Table 2.2: Inner transition metals and their magnetic moment values in BM Units

<table>
<thead>
<tr>
<th>Ions</th>
<th>4f electrons</th>
<th>Term</th>
<th>(\mu_{\text{eff}})</th>
<th>S.O.</th>
<th>Ions</th>
<th>4f electrons</th>
<th>Term</th>
<th>(\mu_{\text{eff}})</th>
<th>S.O.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(^{3+})</td>
<td>0</td>
<td>1(^1S)</td>
<td>0.00</td>
<td></td>
<td>Tb(^{3+})</td>
<td>8</td>
<td>7(^6F_5)</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>Ce(^{3+})</td>
<td>1</td>
<td>2(^2F_{5/2})</td>
<td>2.56</td>
<td></td>
<td>Dy(^{3+})</td>
<td>9</td>
<td>6(^6H_{15/2})</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>Pr(^{3+})</td>
<td>2</td>
<td>3(^3H_{4})</td>
<td>3.62</td>
<td></td>
<td>Ho(^{3+})</td>
<td>10</td>
<td>5(^5I_8)</td>
<td>10.6</td>
<td></td>
</tr>
<tr>
<td>Nd(^{3+})</td>
<td>3</td>
<td>4(^4I_{9/2})</td>
<td>3.68</td>
<td></td>
<td>Er(^{3+})</td>
<td>11</td>
<td>4(^4I_{15/2})</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>Pm(^{3+})</td>
<td>4</td>
<td>5(^5I_4)</td>
<td>2.83</td>
<td></td>
<td>Tm(^{3+})</td>
<td>12</td>
<td>3(^3H_6)</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>Sm(^{3+})</td>
<td>6</td>
<td>7(^7F_0)</td>
<td>3.40</td>
<td>3.41</td>
<td>Lu(^{2+})</td>
<td>14</td>
<td>5(^5S_{7/2})</td>
<td>7.94</td>
<td></td>
</tr>
<tr>
<td>Gd(^{3+})</td>
<td>7</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

II. **Stretching Force Constant:** The value of stretching force constant (K) for \(\nu(M-N)\), \(\nu(M-O)\), \(\nu(M-Cl)\) and \(\nu(M-S)\) bonds have been calculated by using the formula:

\[
K = 4 \pi^2 C^2 \mu^2
\]

Where, \(C\) = Velocity of light
\(
\mu\) = The reduced mass of the atom involved in the corresponding stretching frequency.

**Ligand Field Parameters**

III. **Ligand Field Splitting Energy:** (10Dq or \(\Lambda\))

It is the orbital separation energy between \(\nu_o\) or (t_{2g}) and \(\nu_g\) or (e_{g}) often represented by 10Dq or \(\Lambda\). In all the systems 10 Dq has been calculated using the eqn. suggested by Figgis\(^{27}\) and Ballhausen\(^{28}\) except for \(d^6\) complexes where Ballhausen energy equation\(^{29}\) have been used.

IV. **Racah’s Inter-Electronic Repulsion Parameter:**

Where interactions between two or more electrons are involved, it is possible to write down the energy for each term, above the ground term, which arises as an expression involving several parameters. The two parameters (\(F_0\), \(F_2\), \(F_4\)) or the Racah’s inter-electronic repulsion parameters
(A,B,C)\textsuperscript{(39)}. These parameters are sufficient if attention is restricted to d-electrons. If, for example, f-electrons are considered other parameters to extend the set must be incorporated. Excitation energies of some multiple terms in spherical symmetry expressed in Racah parameters (B) and (C) of inter-electronic repulsion are given in Table No. 2.3 and 2.4.

**Table 3: Relevant Excitation Energies of some of the terms for d\textsuperscript{n} configuration are given below**

<table>
<thead>
<tr>
<th>Ground Term</th>
<th>d\textsuperscript{5}</th>
<th>Ground Term</th>
<th>d\textsuperscript{3} and d\textsuperscript{7}</th>
<th>Ground Term</th>
<th>d\textsuperscript{2} and d\textsuperscript{8}</th>
</tr>
</thead>
<tbody>
<tr>
<td>6S</td>
<td>0</td>
<td>4F</td>
<td>0</td>
<td>3F</td>
<td>0</td>
</tr>
<tr>
<td>4G</td>
<td>10B+5C</td>
<td>2G</td>
<td>4B+3C</td>
<td>1D</td>
<td>5B+2C</td>
</tr>
<tr>
<td>4P</td>
<td>7B+7C</td>
<td>4P</td>
<td>15B</td>
<td>3P</td>
<td>15B</td>
</tr>
<tr>
<td>4D</td>
<td>17B+5C</td>
<td>2P</td>
<td>9B+3C</td>
<td>1G</td>
<td>12B+2C</td>
</tr>
<tr>
<td>4F</td>
<td>22B+7C</td>
<td>2H</td>
<td>9B+3C</td>
<td>1S</td>
<td>22B+7C</td>
</tr>
</tbody>
</table>

Only one parameter is necessary for the description of the energy difference between the multiplet terms of p\textsuperscript{n} system, while two parameters are necessary for d\textsuperscript{n} systems and three parameters for f\textsuperscript{n} systems. Actually the variation of the ionic charge as a function of the inter-electronic repulsion parameters is very regular for a given electron configuration.

**VI. Ligand Field Stabilization Energy: (L.F.S.E.):**

Ligand field stabilization energy is simply given by the energy gains in units of Dq for the ground state. Following Table 2.5 represents the values of L.F.S.E. for different electronic configurations. Actually L.F.S.E.
Table 2.4: Free ion values of B & C for different gaseous ions based on electronic configurations

<table>
<thead>
<tr>
<th>Electronic Conf.</th>
<th>Ion</th>
<th>B</th>
<th>C</th>
<th>Electronic Conf.</th>
<th>Ion</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d^2</td>
<td>Ti^{4+}</td>
<td>718</td>
<td>2629</td>
<td>4d^3</td>
<td>Mo^{4+}</td>
<td>610</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V^{3+}</td>
<td>861</td>
<td>4165</td>
<td>4d^6</td>
<td>Rh^{3+}</td>
<td>720</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr^{4+}</td>
<td>1039</td>
<td>4238</td>
<td>4d^7</td>
<td>Rh^{2+}</td>
<td>620</td>
<td>4002</td>
</tr>
<tr>
<td>3d^3</td>
<td>Sc^{3+}</td>
<td>480</td>
<td>-</td>
<td>4d^8</td>
<td>Pd^{1+}</td>
<td>683</td>
<td>2620</td>
</tr>
<tr>
<td></td>
<td>V^{1+}</td>
<td>765</td>
<td>2855</td>
<td>5d^2</td>
<td>Os^{4+}</td>
<td>780</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr^{3+}</td>
<td>918</td>
<td>3850</td>
<td>5d^3</td>
<td>Re^{4+}</td>
<td>650</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn^{4+}</td>
<td>1064</td>
<td>-</td>
<td>-</td>
<td>Ir^{3+}</td>
<td>810</td>
<td></td>
</tr>
<tr>
<td>3d^4</td>
<td>Cr^{2+}</td>
<td>810</td>
<td>3430</td>
<td>5d^4</td>
<td>Os^{4+}</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn^{3+}</td>
<td>1140</td>
<td>3675</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3d^5</td>
<td>Mn^{2+}</td>
<td>960</td>
<td>3525</td>
<td>5d^5</td>
<td>Ir^{3+}</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe^{2+}</td>
<td>1058</td>
<td>3901</td>
<td>5d^6</td>
<td>Pt^{4+}</td>
<td>720</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co^{3+}</td>
<td>1100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3d^7</td>
<td>Co^{2+}</td>
<td>971</td>
<td>4366</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3d^8</td>
<td>Ni^{2+}</td>
<td>1041</td>
<td>4831</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

is known as the difference between the lowest energy level of a term split by a ligand field and the centre of gravity of the term in the ligand field.

Table 2.5: L.F.S.E. values for different electronic configurations

<table>
<thead>
<tr>
<th>Electronic Configuration</th>
<th>L.F.S.E. for Octahedral Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak field</td>
</tr>
<tr>
<td>d^1</td>
<td>4 Dq</td>
</tr>
<tr>
<td>d^2</td>
<td>6 Dq</td>
</tr>
<tr>
<td>d^3</td>
<td>12 Dq</td>
</tr>
<tr>
<td>d^4</td>
<td>6 Dq</td>
</tr>
<tr>
<td>d^5</td>
<td>0 Dq</td>
</tr>
<tr>
<td>d^6</td>
<td>4 Dq</td>
</tr>
<tr>
<td>d^7</td>
<td>6 Dq</td>
</tr>
<tr>
<td>d^8</td>
<td>12 Dq</td>
</tr>
<tr>
<td>d^9</td>
<td>6 Dq</td>
</tr>
</tbody>
</table>
Table 2.4: Free ion values of B & C for different gaseous ions based on electronic configurations

<table>
<thead>
<tr>
<th>Electronic Conf.</th>
<th>Ion</th>
<th>B</th>
<th>C</th>
<th>Electronic Conf.</th>
<th>Ion</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d²</td>
<td>Ti⁺²</td>
<td>718</td>
<td>2629</td>
<td>4d³</td>
<td>Mo⁻³</td>
<td>610</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V⁺³</td>
<td>861</td>
<td>4165</td>
<td>4d⁶</td>
<td>Rh⁻³</td>
<td>720</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr⁺⁴</td>
<td>1039</td>
<td>4238</td>
<td>4d⁷</td>
<td>Rh⁺²</td>
<td>620</td>
<td>4002</td>
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<tr>
<td>3d³</td>
<td>Sc⁺³</td>
<td>480</td>
<td></td>
<td>4d⁸</td>
<td>Pd⁺²</td>
<td>683</td>
<td>2620</td>
</tr>
<tr>
<td></td>
<td>V⁺²</td>
<td>765</td>
<td>2855</td>
<td>5d²</td>
<td>Os⁺⁶</td>
<td>780</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cr⁺³</td>
<td>918</td>
<td>3850</td>
<td>5d³</td>
<td>Re⁺⁴</td>
<td>650</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn⁺⁴</td>
<td>1064</td>
<td></td>
<td></td>
<td>Ir⁺⁶</td>
<td>810</td>
<td></td>
</tr>
<tr>
<td>3d⁴</td>
<td>Cr⁺²</td>
<td>810</td>
<td>3430</td>
<td>5d⁴</td>
<td>Os⁺⁴</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn⁺³</td>
<td>1140</td>
<td>3675</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3d⁵</td>
<td>Mn⁺²</td>
<td>960</td>
<td>3525</td>
<td>5d⁵</td>
<td>Ir⁺³</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co⁺²</td>
<td>1058</td>
<td>3901</td>
<td>5d⁶</td>
<td>Pt⁺⁴</td>
<td>720</td>
<td></td>
</tr>
<tr>
<td>3d⁶</td>
<td>Fe⁺²</td>
<td>1100</td>
<td>4366</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Co⁺³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3d³</td>
<td>Ni⁺²</td>
<td>1041</td>
<td>4831</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

is known as the difference between the lowest energy level of a term split by a ligand field and the centre of gravity of the term in the ligand field.

Table 2.5: L.F.S.E. values for different electronic configurations

<table>
<thead>
<tr>
<th>Electronic Configuration</th>
<th>L.F.S.E. for Octahedral Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weak field</td>
</tr>
<tr>
<td>d¹</td>
<td>4 Dq</td>
</tr>
<tr>
<td>d²</td>
<td>6 Dq</td>
</tr>
<tr>
<td>d³</td>
<td>12 Dq</td>
</tr>
<tr>
<td>d⁴</td>
<td>6 Dq</td>
</tr>
<tr>
<td>d⁵</td>
<td>12 Dq</td>
</tr>
<tr>
<td>d⁶</td>
<td>0 Dq</td>
</tr>
<tr>
<td>d⁷</td>
<td>4 Dq</td>
</tr>
<tr>
<td>d⁸</td>
<td>6 Dq</td>
</tr>
<tr>
<td>d⁹</td>
<td>12 Dq</td>
</tr>
<tr>
<td>d¹₀</td>
<td>6 Dq</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Strong field</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4 Dq (3F₂-15F₄)</td>
</tr>
<tr>
<td></td>
<td>8 Dq (15F₂-275F₄)</td>
</tr>
<tr>
<td></td>
<td>20 Dq (-5F₂+255F₄)</td>
</tr>
<tr>
<td></td>
<td>25 Dq (-5F₂-255F₄)</td>
</tr>
<tr>
<td></td>
<td>18 Dq (7F₂-105F₄)</td>
</tr>
<tr>
<td></td>
<td>12 Dq</td>
</tr>
<tr>
<td></td>
<td>6 Dq</td>
</tr>
</tbody>
</table>
electrons in 'd' sub-shell. It has been found\textsuperscript{[31]} that it increases with the increase in oxidation state and No. of electrons in 'd' sub-shell. Further its value is smaller when the size of the ion is large because it explains the mean radial displacement of the 'd' sub-shell, consequently reduction in mutual attraction. As the oxidation state increases, size increases and for a given oxidation state, the size decreases in the free ion with the increasing number of d-electrons. Since the size of the ion is related to the effective nuclear charge experienced by the d-electrons, it follows that B is not only a measure of the size, but also effective nuclear charge.

The value of B decreases on complexation as compared with that of free ion value. This reduction implies that the mean radial displacement of the d-electron has increased and that the effective charge experienced by these electrons has decreased. The reduction in the value of B is the measure of covalency in the metal-ligand bond and decrease of the effective charge experienced by d-electrons.

Therefore,

Nephelauxetic Ratio = B (in complex)/B (in free ion) = β

If, \( β = 1.0 \) 100\% Ionic character
\( B = 0.5 \) 100\% Covalent character

Thus, the value of between 0.5 and 1.0 clearly suggests the partial covalent character of the bond concerned. It has been reported\textsuperscript{[32]} that the inter electronic repulsion forces between d-electrons are decreased on complex formation, the decrease may be from 5\% to 40\% for the 3d series of metal complexes.

VIII. \textbf{Condon-Shortley Parameters (F_2, F_4)}:

The value of fundamental condon shortley repulsion parameters (F_2 and F_4) are related to B and C as:

\[
B = \left[ \frac{F_2 + \frac{5F_4}{441}}{49} \right] \quad \text{and} \quad C = \frac{35F_4}{441}
\]
putting the values of B and C in the above relationship we may calculate $F_2$ and $F_4$ for the complexes under study. The increased value of $F_2$ and $F_4$ during complexation are considered due to expanded radial functions\(^{(33)}\) of the d-electrons.

**IX. $\beta_{55}$ and $\beta_{55'}$:** The values of $\beta_{35}$ and $\beta_{55}$ have been evaluated in some complexes using the following relation:

\[
\frac{B \text{ (spin allowed)}}{B_0} = \beta_{35} \\
\frac{B \text{ (spin forbidden with t_{2g} set)}}{B_0} = \beta_{55}
\]

Where, $B_0$ is the value of B in free ion. The ratio of $\beta_{35}$ and $\beta_{55}$ sometimes expressed as $(1 - \alpha) = \beta_{35}/\beta_{55}$ is the covalency parameter and the differential expansion of $\sigma(t_{2g})$ and $\sigma(e_g)$ metal orbitals is a function of this difference.

**X. Spin Orbit Coupling Constant ($\lambda$)**

The spin orbit coupling constant of the ions where complete quenching is expected has been calculated using the formula.

\[
\mu = \mu_0 (1 - \alpha/10 \ Dq)
\]

where, $\mu = \text{observed magnetic moment in B.M.}$, $\mu_0 = \text{spin only moment in B.M.}$, $\alpha = \text{a constant}$, $10 \ Dq = \text{Ligand field splitting energy.}$

**XI. Lande's Splitting Factor ($g$) in octahedral Fields:**

The value of Lande's splitting factor has been calculated by the given formula

\[
g = (2.8 \lambda)/10 \ Dq
\]

where, $\lambda = \text{Spin--orbit coupling constant}$, $10 Dq = \text{Ligand Field splitting Energy.}$

**XII. Ligand Field Theory of Spin--allowed transitions in dn configurations:** $n = 3, 7, 8.$

**Numerical Procedure for the determination of Accuracy of Inter-electronic repulsion parameters**
$d^7$: Configuration: Co(II)

From the equivalence of $d^7$ and $d^{10-n}$ electron systems, $d^5$ and $d^7$ configuration should give rise to the same type and number of terms. Therefore, in octahedral Cobalt(II), we will have to deal again with the $^4A_g$, $^4T_{2g}$, $^4T_{2g}(F)$ and $^4T_{1g}(P)$ states.

Further, since $d^7$ and $d^{10-n}$ ligand field systems are inter-related on account of the spherically symmetrical half filled $d^5$ configuration, therefore, apart from multiplicity, the energy expressions of $d^2$ and $d^7$ systems are identical. If experimentally observed spin allowed transitions in Co(II) octahedral complexes are in the order of increasing energy viz.

$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ (v$_1$) \hspace{1cm} (i)

$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ (v$_2$) \hspace{1cm} (ii)

$^4T_{1g}(F) \rightarrow ^4T_{1g}(F)$ (v$_3$) \hspace{1cm} (iii)

Now, by following the weak field coupling scheme, the energies of these transitions are given as under:-

\[ v_1 = \frac{\gamma}{2} \left[ (10Dq + 15B) + \frac{\gamma}{2} [(10Dq+15B)^2 - 12B.10Dq]^{1/2} \right] \] (iv)

\[ v_2 = \frac{\gamma}{2} \left[ (30Dq - 15B) + \frac{\gamma}{2} [(10Dq+15B)^2 - 12B.10Dq]^{1/2} \right] \] (v)

\[ v_3 = \left[ (10Dq - 15B)^2 - 12B.10Dq \right]^{1/2} \] (vi)

Further, the values of $10Dq$ and Racah inter-electronic repulsion parameter $B$ can be determined according to the following four different methods:

(a) **Fitting the First and Second Bands:**

The expressions of $v_1$ and $v_2$ from equations (iv) and (v) give

\[ 10Dq = v_2 - v_1 \]

\[ B = (2v_1^2 - v_1 v_2 / (12v_2 - 27v_1)) \] (vii)

(b) **Fitting the First and Third Bands:**

The expressions of $v_1$ and $v_3$ from equation (iv) and (vi) give:

\[ 10Dq = 2v_1 - v_3 + 15B \]
\[ B = \frac{1}{3} \left[ -2v_2 - v_3 \right] \pm \left\{ v_1^2 + v_2^2 + v_1 v_3 \right\}^{1/2} \] (viii)

It should be noted that the positive sign of \( B \) has a physical significance.

(c) **Fitting the second and third Bands:**

The expressions of \( v_2 \) and \( v_3 \) from equations (v) and (vi) give:

\[
10Dq = \frac{1}{3} (2v_2 - v_3) + 5B
\]

\[
B = \frac{1}{510} \left[ 7(2v_3 - 2v_2) + \{81v_3^2 + 16v_3(v_1 - v_3)\}^{1/2} \right] (ix)
\]

Hence, also only the positive value of \( B \) has a physical significance.

(d) **Fitting the Difference between First and Second Bands:**

If all the three \( d-d \) bands are observed, then from equations (iv) and (vi) as simple relation between the band energies in \( d^7 \) systems can be obtained as under:

\[
10Dq = (v_2 - v_3)
\]

\[
B = (v_2 + v_3 - 3v_1)/15 \quad (x)
\]

**d\(^8\) Configuration : Ni(II)**

The ground state of octahedral \( d^8 \) as well as \( d^5 \) system is an \( A_{2g} \) state and the order of excited state in both the configuration is the same i.e. the spin allowed transitions.

\[
^3A_{2g} \rightarrow ^3T_{2g} (F) \quad (v_1) \quad (xi)
\]

\[
\rightarrow ^3T_{1g} (F) \quad (v_2) \quad (xii)
\]

and

\[
\rightarrow ^3T_{1g} (P) \quad (v_3) \quad (xiii)
\]

Therefore, if one ignores multiplicity, the energy expression of \( d^9 \) and \( d^5 \) systems, become identical due to the relationship between \( d^9 \) and \( d^{2+} \) ligand field systems.

If experimentally observed spin-allowed transitions in Ni(II) octahedral complexes are in the order of increasing energy, then by
following the weak field coupling scheme, the energies of these transitions are computed as under:

\[ \nu = 10 Dq \quad (xiv) \]

\[ \nu_2, \nu_3 = \frac{1}{2} (15B + 30Dq) = \frac{1}{2} \{(15B - 10Dq)^2 + 12B \cdot 10Dq\}^{1/2} \quad (xv) \]

The value of Racah parameter B may then be calculated according to the following five different methods.

(a) **Fitting the second Band:** The value of transition \( \nu_2 \) in the above equation can be found out by putting the value of B and 10Dq obtained from the following expression:

\[ B = (2\nu_2^2 + \nu_3^2 - 3\nu_1 \nu_2) / (15\nu_2 - 27\nu_1) \quad (xvi) \]

\[ 10Dq = \nu_1 \]

(b) **Fitting the Third Band:** In this procedure, similar to above, \( \nu_3 \) is used instead of \( \nu_2 \). The following expression is used for the value of B:

\[ B = (2\nu_2^2 + \nu_3^2 - 3\nu_1 \nu_3) / (15\nu_3 - 27\nu_1) \quad (xvii) \]

\[ 10Dq = \nu_1 \]

(c) **Fitting the sum of second and third Bands:**

If all the three d-d transitions are observed then the following extremely simple relation may be used for B:

\[ B = (\nu_2 + \nu_3 - 3\nu_1)/15 \quad (xviii) \]

\[ 10Dq = \nu_1 \]

(d) **Fitting the Difference of Second and Third Bands:**

A considerable simplification is also achieved if the difference between the \( \nu_2 \) and \( \nu_3 \) is taken as a basis for the calculation of B. Thus the following expression where only the positive sign of B has a physical significance, may be used

\[ B = \frac{1}{35} [3\nu_1 + (25(\nu_3 - \nu_2)^2 - 16\nu_1^2)^{1/2}] \quad (xix) \]

(e) **Fitting the second and third Bands:**
If only the second and third bands were observed in octahedral d⁵ or tetrahedral d⁷ complex ion. The value of 10Dq and B may be calculated from the following expression:

\[ B = \frac{v_2 + v_3 - 30Dq}{15} \]

\[ 10Dq = \frac{1}{34}\left[9(v_2 + v_3)^2 + 81(v_2^2 + v_3^2) - 178v_2v_3\right] \]

(XX)

XIII. Spectrochemical Series:

All of the electronic spectral measurements were made in ethanolic medium. The value of Ligand Field Splitting Energy (L.F.S.E.) in octahedral complexes with our ligands “TBT”, “MB-TBT”, “HO-DP-TBT”, “AT-TBT”, “AF-TBT”, “BR-TBT” and “F-TBT” suggest that these ligands fall in the spectrochemical series some where in between water and pyridine:

\[ I^- < Br^- < SCN^- < NO_3^- < F^- < Urea < OH^- < ONO_2^- < OAc^- < C_2O_4^{2-} < H_2O < NCS^- < C_7H_5N < NH_3 < SO_3^- < diphenyl Phenanthrene < NO_2^- < CN^- < C=O^- \]

The corresponding series for present ligands incorporated with various metal ions is in the following manner: Mn(II) < Co(II) < Ni(II) < Fe(III) < Mn(III) < Vo(II) < Ti(III) < Cr(III) < Co(III)

XIV. Nephelauxetic Series:

The position of our ligands “TBT”, “MB-TBT”, “HO-DP-TBT”, “AT-TBT”, and “AF-TBT” in the nephelauxetic series are based on increasing value of (1/β) and are found some where in between \( C_2O_4^{2-} \) and \( Cl^- \) ions as

\[ F^- < H_2O < Urea < NH_3 < NCS^- < CN^- < C_2O_4^{2-} < Cl^- < Br^- < I^- \]

It corresponds well with the ideas of the reducing characters of the ligands where only the last ligand HB-TBT has a tendency to lose a proton.

XV. Crystal Field Parameters and NSH Parameters:

The NSH approach (Normalized Spherical Harmonic Hamiltonian) (using the parameters Dq, DS, DT etc.) has several far-reaching advantages with respect to low symmetry complexes when compared with
the more classical crystal field approach (Using Dq, Ds, Dt etc. as parameters). The main disadvantage of the NSH approach is the lack of an immediate appreciation of the chemical significance of the parameters rather, they provide a group theoretical appreciation of the molecule. Both types of parameters are inter related as

\[ DQ = 6 \left( \sqrt{21} \right) Dq - 3.5 \sqrt{21} Dt \]

\[ DS = 7 Ds \]

\[ DT = 3.5 \sqrt{15} Dt \]

\[ DI = \frac{4}{9} \left( Dqe - Dqa \right) \]

When Dqe is the classical equatorial field strength and Dqa is the classical axial field strength.

The corresponding NSH parameters are DQE (Equatorial Field strength) and DQA (Axial Field strength) defined by

\[ DQE = DQ - \left( \frac{\sqrt{7}}{\sqrt{5}} \right) DT \]

\[ DQA = DQ + 2 \left( \frac{\sqrt{7}}{\sqrt{5}} \right) DT \]

and the global DQ value, defining the totally symmetric A1g component of the field is linked theoretically as

\[ DQ = \frac{1}{6} \left( 4DQE + 2DQA \right) \]

The parameters Dq and Dt have been used to calculate the degree of distortion of the complexes. The extent of distortion prevailing in the complexes has also been calculated by using NSH Hamiltonian parameters. The ratio DT/DQ is a measure of tetragonal distortion. The value reported\(^{34,35}\) for a limiting case of tetragonally distorted molecule is 0.4226.
STRUCTURE SHEET

(1.) 2 THIOUREYL 6 BENZOTHIAZOLE ACETIC ACID ("TBT")

(2.) 4 METHYL BENZILIDENE 2 THIOUREYL-6-BENZOTHIAZOLE ACETIC ACID (MB - TBT)

(3.) 4' HYDROXY 3' ALDEHYDODIPHENILIDENE 2 THIOUREYL-6-BENZOTHIAZOLE ACETIC ACID

"HODP TBT"
(4.) \( \text{2'-ACETYL THIOPHENE - 2'-THIOURYL - 6'-BENZOTHIAZOLE ACETIC ACID (AT-TBT)} \)

(5.) \( \text{2'-ACETYL PYRIDINE - 2'-THIOURYL - 6'-BENZOTHIAZOLE ACETIC ACID (AP-TBT)} \)

(6.) \( \text{2'-ACETYL FURANILIDINE - 2'-THIOURYL - 6'-BENZOTHIAZOLE ACETIC ACID (AF-TBT)} \)
MOL. FORMULA : (C_{19}H_{12}O_{3}N_{3}S_{2})
MOL. WT. : 395
M.P. : 275 °C

(1, 3'-ALDEHYDE BENZOTHIURAZOLE, 2-THIOBENZYL-6-BENZO[d]IMIDAZOLE ACETIC ACID [BF - TBI])
CHAPTER II
REFERENCES


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ELECTRONIC SPECTRAL STUDIES ON IRON(III) COMPLEXES WITH 2-THIOURYL-6-BENZO-THIAZOLE ACETIC ACID AND ITS DERIVATIVES