CHAPTER-II
CHROMIUM(III), 3d³

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CHAPTER (II)

CHROMIUM (III), 3d³

1.1 INTRODUCTION:

Chromium might be expected to form compounds with oxidation states from 0, (+I) to (+VI)². Hexavalent chromium is potent toxins mutagens and carcinogens to both plants and animals⁴. Whereas, the trivalent state of chromium is important in the biological system. The most important characteristics of chromium in coordination chemistry is that the complexes of chromium(III) are substitutionally inert.

Due to lack of toxicity chromium(III) complexes are used as potential supplements and drugs. Chromium picolinate and chromium nicotinate are the most popular chromium complexes, which are used in the production of drugs⁵,⁶,⁷. Chromium(III) is an essential nutrient for mammals, so pharmaceuticals compounds are recommended as a source of this element⁸. Chromium was demonstrated to be essential for human in 1975⁹,¹⁰,¹¹. The biological significance of chromium is still a matter of considerable discussion¹²,¹³. The glucose tolerance factor (GTF)¹⁴ is an active Cr(III) substance and has never been isolated in pure form. GTF is a substance which,

(a). involved in maintaining normal glucose,

(b). prevents and cure impairment of glucose removal when given in the diet or by
stomach tube and
c. results in impairment of intravenous glucose tolerance when it is deficient in
diet. Chromium containing bimolecular, chromodulin is a naturally occurring
oligopeptide of glycine, cystine, aspartate and glutamate with carboxylates
comprising more than half of the total amino acid residues. Chromodulin
[low molecular weight chromium] plays a key role to understand the role of
chromium at a molecular level because the molecule has been found to bind to
activated insulin receptor, stimulating its kinase activity.

Chromium also shows a number of other biological effects. The most
important medical aspects of Cr salts are that in larger amount it is carcinogenic
and a variety of allergic responses. To the study of biochemistry of Cr(III)
allows us to make a judgment that how Cr is essential for mammalian
carbohydrate and lipid metabolism. Genetic alteration induced in cells by
treatment with Cr(VI) induced chromosomal abnormalities and mutation.

1.2 EARLIER WORK ON CHROMIUM(III) COMPLEXES:
Chromium(III) complexes of phenyl pyruvic acid semicarbazone (Ppysc) and 4-
methyl phenyl pyruvic acid semicarbazone (4-Ppysc), phenyl pyruvic acid
thiosemicarbazone (4-Ppysc) have been synthesized by Chandra et.al. These
complexes were characterized by elemental analysis, magnetic moments, IR and
electronic spin resonance spectral studies. All the complexes were found to have
composition \([\text{Cr}^{111}X]_2\), (where \(X = \text{Cl, Br, I and NO}_3\)). These complexes have six co-ordinated octahedral geometry. Chromium(III) complexes of acetone, ethyl-methyl ketone and 2-nethylcyclohexanone semicarbazones and thiosemicarbazones have been synthesized by Chandra et al\(^{25}\). The complexes were found to have [CrL\(_2\)Cl\(_2\)]Cl and [CrL\(_2\)NO\(_3\)]NO\(_3\) compositions. These complexes were characterized by physicochemical techniques viz- magnetic moments, electronic and electron spin resonance spectral studies. On the basis of above spectral data all the complexes were found to have an octahedral geometry.

Chromium(III) complexes of cyclohexanone semicarbazones and cyclohexanone thiosemicarbazones have been synthesized by Chandra et al\(^{26}\). The complexes were found to have the [Cr(L)X\(_2\)] and [Cr(Chsc\(_2\)Cl\(_2\)] Cl, [Cr(Chsc\(_2\)(NO\(_3\))\(_2\)]NO\(_3\) and [Cr(Chsc\(_2\)(NO\(_3\))\(_2\)]NO\(_3\) compositions. These complexes were characterized by magnetic moments, electronic spectra and E.S.R spectral studies.

Chromium(III) complexes of furfuraldehyde and indole-3-carboxyaldehyde semicarbazones and thiosemicarbazones were synthesized by Garg et al\(^{27}\). These complexes were found to have [Cr Cl\(_3\) L] and [Cr Cl\(_3\) L\(_2\)] compositions. I.R data suggest that L co-ordinated through the azomethine nitrogen and oxygen /sulphur. A tetragonal geometry has been suggested for these complexes with the help of IR, magnetic moments. Ligand field parameters were also calculated. Chromium(III) and Iron(III) complexes of salicylaldehyde semicarbazones were prepared by Gerbeleau et al\(^{28}\). The complexes were found to have
[Co (sesa) (Hsesa)] H₂O, [Fe (sesa)₂], and [Fe (sesa) (Hsesa)] compositions. On the basis of spectral data the complexes were found to have an octahedral geometry.

Chromium(III) complexes of 2-hydroxy acetophenone and 2-hydroxy naphthaldehyde semicarbazones and thiosemicarbazones were synthesized by Chandra et al.²⁹ The complexes have [Cr (ligand)₂]Cl composition. These complexes were characterized by elemental analysis, molar conductance, magnetic moments, IR, electronic and ESR spectral studies. Chromium(III) complexes of methylhydrazine carboxylate were synthesized by Magied et al.³⁰. These complexes were characterized by elemental analysis, molar conductance, magnetic moments, IR, electronic and ESR spectral studies.

Chromium(III) complexes of 1-(2- furan thiocarbo)-3-thiosemicarbazone have been synthesized by Singh et al.³¹. These complexes were found to have [Cr (hftsc) (acac)₂] composition. These were characterized by elemental analysis, magnetic susceptibility, I.R, electronic and N.M.R spectral data. Chromium(III) complexes of 1-isonicotinoyl-4-benzoyl-3-thiosemicarbazone (IBtsc) have been synthesized by Singh et al.³². These complexes were characterized by elemental analysis, magnetic susceptibility measurements, U.V, I.R, N.M.R and F.A.B mass spectral data. The above spectral data suggest octahedral geometry.

Chandra et al.³³ also prepared chromium(III) complexes with 2-methylcyclohexanone thiosemicarbazone and 2-methylcyclohexanone -4- methyl-
3-thiosemicarbazones. These complexes were found to have $[\text{CrL}_2X_3]$ composition, [where $X=\text{Cl}^-$, $\text{SCN}^-$, $\text{NO}_3^-$ and $1/2\text{SO}_4^-$]. These complexes were characterized by elemental analysis, molar conductance and magnetic moment measurements, electronic, I.R. and E.P.R spectral studies. On the basis of above spectral data an octahedral geometry has been suggested for all the complexes.

Chromium(III) complexes of 2-pyridincarbaldehyde thiosemicarbazone have been synthesized by Yakuphanoglu et al. These complexes were used for the analysis of film thickness effect on the optical absorption edge and optical constants. The thickness of films causes important changes in refractive index and real part and imaginary part of the dielectric constant. The most significant results of the present study are to indicate that thickness of the film can be used to modify in optical band gaps and optical constant of this films.

Chromium(III) complexes of cis-3, 7-di-methyl 2, and 6-Octa diensemicarbazones were prepared by Nagar et.al. They have the general composition $[\text{CrL}_2\text{Cl}_2]$ and $[\text{CrL}_2\text{Cl}_2]\text{Cl}$. Structure of the complexes were determined by using elemental analyses, molar conductivity, magnetic measurements, IR and electronic spectral data. Synthesized complexes, as well as ligand were screened for their antibacterial activity. All the complexes exhibit strong inhibitory action against Gram(+) bacteria Staphylococcus aureus and Gram (-) bacteria coli.
1.3 PRESENT WORK:

The present work is related to the synthesis and characterization of chromium(III) complexes with four ligands \([\text{pvsc} \ (L^1), \ \text{pvtsc} \ (L^2), \ \text{ptasc} \ (L^3) \ \text{and} \ \text{ptatsc} \ (L^4)]\).

These complexes were characterized by the elemental analysis, molar conductance, magnetic moment, I.R and electronic spectral studies.

\[ \text{(p-vanillin semicarbazone)} \]
\[ \text{(p-vanillin thiosemicarbazone)} \]

\[ \text{(pvsc, L}^1\text{)} \]
\[ \text{(pvtsc, L}^2\text{)} \]

\[ \text{(p-toluinaldehyde semicarbazone)} \]
\[ \text{(p-toluinaldehyde thiosemicarbazone)} \]

\[ \text{(ptasc, L}^3\text{)} \]
\[ \text{(ptatsc, L}^4\text{)} \]
PREPARATION OF THE COMPLEXES:
A hot ethanolic solution (20mL) of the chromium salt (CrCl₃.6H₂O or Cr(NO₃)₃.6H₂O (0.001mole) was mixed with a hot ethanolic solution of the semicarbazones and thiosemicarbazones of p-vanillin or p-tolualdehyde (0.44g, 0.002mol). The mixture was refluxed on a water-bath for about 6-10 hrs at 65-80°C. After refluxing the mixture was concentrated to half of its original volume. On cooling overnight in a refrigerator the green to violet coloured crystals of the complexes precipitated out. It was filtered, washed with 50% ethanol and dried under vacuum over P₂O₅.

1.4 RESULT AND DISCUSSION:
On the basis of elemental analysis all the complexes were found to have the general composition CrL₂X₂ (where L = pvsc(L¹), pvts(L²), pttsc(L³), ptatsc(L⁴), and X=Cl, NO₃⁻). The molar conductance of these complexes has been measured in DMSO solution. This indicates that chloro complexes are 1:1 electrolyte in nature, so the complexes may be formulated as [Cr(L)₂Cl₂] Cl, whereas the nitrato complexes are 1:2 electrolyte in nature, and may be formulated as [Cr(L)₂NO₃] (NO₃)₂ Table-1.

MAGNETIC MOMENT:
Generally the magnetic moment of chromium(III) complexes at room temperature lies near 3.87 B.M. i.e. equal to spin only value. For the Cr(III) compounds the magnetic moment is reduced below the spin only value because of the
(1-4λ/10 Dq) effect. The spin-orbit coupling constant for Cr(III) is rather small. To determine actual magnetic moment, consider the actual degree of reduction and the effect which reduce the magnetic susceptibility measurements.

The magnetic moments of the complexes under study at room temperature lie in the range of 3.73 to 3.82 B.M. corresponding to three unpaired electrons Table-3.

**IR SPECTRA:**
A comparative study of the spectra of the ligands and their complexes show that all the ligands behave as bidentate. A band corresponding to ν (N-H) observed at 3295-3215 cm⁻¹ in all the ligands. On complex formation the position of this band remains unchanged. Which indicates that NH group does not coordinate to the metal ion. A new band for ν(C = N) group, observed at 1627-1595 cm⁻¹, the position of this band shifted to a lower frequency 35-45 cm⁻¹ in the spectra of the metal complexes which indicate that coordination takes place through azomethine nitrogen. Which is further supported by the appearance of a medium intensity band in the range ~ 439-411 cm⁻¹ attributable to ν (M-N). A strong band at 1675/835 cm⁻¹ is observed due to ν (C = O/S) spectra of the ligands. On complex formation this band is also shifted to the lower frequency in complexes which suggests that coordination takes place through O/S atom of ν(C=O/S) group respectively. Thus it has been concluded that all the ligands act as bidentate³⁶.
Figure 1-5 IR Spectrum Of [Cr(pvsc)2(NO3)] (NO3)2
Figure 1. IR Spectrum Of [Cr (ntasc).Cl]. Cl
Figure 1.7  IR Spectrum Of [Cr (ptatse)$_2$Cl$_2$] Cl
Figure 1.8: IR Spectrum of (C=C=O) CHCl
Figure 1.9 IR Spectrum of [Cr(pvts)c2Cl2] Cl
BANDS DUE TO ANION:

In case of the nitrato complexes 1505-1475 cm\(^{-1}\) \((v_1)\), 1325-1275 cm\(^{-1}\) \((v_4)\), 1045-1020 cm\(^{-1}\) \((v_2)\) and 808-803 cm\(^{-1}\) \((v_6)\) infra red bands are observed corresponding to both the coordinated\(^{36}\) and uncoordinated nitrato group. In the present complexes these bands lie in the range of 1546-1429 cm\(^{-1}\) \((v_1)\), 1290-1271 cm\(^{-1}\) \((v_5)\), 1136-1022 cm\(^{-1}\) \((v_2)\), and 838-804 cm\(^{-1}\) \((v_6)\) (Figs. 1.3-1.5). The separation between \(v_1\) and \(v_5\) is found \(> 186\) which indicates the bidentate nature of the nitrato group. A broad band at near 1392 cm\(^{-1}\) corresponding to uncoordinated nitrate.

ELECTRONIC SPECTRA:

Chromium(III) \(d^3\) case, the spin quantum number \(S=3/2\). The ground configuration is \(t_{2g}^3e_g^0\). The excited configuration is \(t_{2g}^2e_g^1\), which is six fold orbitally degenerate and second excited configuration, \(t_{2g}^1e_g^2\), is three fold orbitally degenerate. The ground state can be written by considering spin of \(3/2\) as it is an orbital singlet. The free ion split in quartet terms i.e. \(^4F\) and \(^4P\). These terms in octahedral field are split into \(^4A_{2g}, ^4T_{1g}, ^4T_{2g}\) and \(^4T_{1g}(P)\) respectively.

Thus three spin allowed transition are expected as follows\(^{37}\)

\[ ^4A_{2g} \rightarrow ^4T_{2g}, \quad v_1, \quad E=10 Dq \]
\[ ^4A_{2g} \rightarrow ^4T_{1g}(F), \quad v_2, \quad E=18 Dq \]
\[ ^4A_{2g} \rightarrow ^4T_{1g}(P), \quad v_3, \quad E=12 Dq+15 B \]

If we consider all three configurations, splitting and energy levels can be represented as
BANDS DUE TO ANION:

In case of the nitrato complexes 1505-1475 cm\(^{-1}\) (\(v_1\)), 1325-1275 cm\(^{-1}\) (\(v_4\)), 1045-1020 cm\(^{-1}\) (\(v_2\)) and 808-803 cm\(^{-1}\) (\(v_6\)) infra red bands are observed corresponding to both the coordinated\(^{36}\) and uncoordinated nitrato group. In the present complexes these bands lie in the range of 1546-1429 cm\(^{-1}\)(\(v_1\)), 1290-1271 cm\(^{-1}\)(\(v_3\)), 1136-1022 cm\(^{-1}\)(\(v_2\)), and 838-804 cm\(^{-1}\)(\(v_6\)) (Figs-1.3-1.5). The separation between \(v_1\) and \(v_5\) is found > 186 which indicates the bidentate nature of the nitrato group. A broad band at near 1392 cm\(^{-1}\) corresponding to uncoordinated nitrate.

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The free ion split in quartet terms i.e. \(^4\)F and \(^4\)P. These terms in octahedral field are split into \(^4\)A\(_{2g}\), \(^4\)T\(_{1g}\), \(^4\)T\(_{2g}\) and \(^4\)T\(_{1g}\)(P) respectively.

Thus three spin allowed transition are expected as follows\(^{37}\)

\[^4\]A\(_{2g}\) \(\rightarrow\) \(^4\)T\(_{2g}\), \(v_1\) \(E=10\) Dq

\[^4\]A\(_{2g}\) \(\rightarrow\) \(^4\)T\(_{1g}\)(F) \(v_2\) \(E=18\) Dq

\[^4\]A\(_{2g}\) \(\rightarrow\) \(^4\)T\(_{1g}\)(P) \(v_3\) \(E=12\) Dq+15 B

If we consider all three configurations, splitting and energy levels can be represented as
**Figure 111** Electronic Spectrum Of \([\text{Cr (pvsc)}_2\text{NO}_3] (\text{NO}_3)_2\)
$t_{2g}^3 \quad ^4A_{2g} \quad -12Dq$
$^2E_g \quad -12Dq + 9B + 3C - 50B^2/10Dq$
$^2T_{1g} \quad -12Dq + 9B + 3C - 24B^2/10Dq$
$^2T_{2g} \quad -12Dq + 15B + 5C - 176B^2/10Dq$
$e_{g}^1 \quad ^4T_{2g} \quad -2Dq$
$^4T_{1g} \quad 7.5B + 3Dq - 1/2(225B^2 + 100 Dq^2 - 180 DqB)^{1/2}$
$e_{g}^2 \quad ^4T_{1g} \quad 7.5B + 3Dq + 1/2(225B^2 + 100 Dq^2 - 180 DqB)^{1/2}$

**Electronic Spectra Of Chloro Complexes:**

Electronic spectra of the complexes show bands at $14183-14903 \text{ cm}^{-1}(v_1)$, $20745-21186 \text{ cm}^{-1}(v_2)$ corresponding to the spin allowed transitions $^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$, $^4A_{2g}(F) \rightarrow ^4T_{1g}(F)$. The band positions are given in Table-2. The $^4A_{2g}(F) \rightarrow ^4T_{1g}(P)$ transition expected, to appear above $30000 \text{ cm}^{-1}$, is usually not observed due to the charge transfer band in the ultra-violet region. On the basis of above transitions an octahedral geometry may be suggested for the complexes.

Values of ligand field parameters have been evaluated and presented in Table-3.

The thiosemicarbazone complexes have higher $Dq$ value as compared to the semicarbazone complexes. It is due to higher position of the sulphur atom as donor compared to the oxygen atom in the spectrochemical series. Thiosemicarbazide complexes are also known to have larger $Dq$ values as compared to the corresponding semicarbazide complexes$^{38}$. 
Electronic Spectra of Nitrato Complexes:

Electronic spectra of the complexes show bands 160778-16890 cm\(^{-1}\)(\(v_1\)), 20283-21321 (\(v_2\)) cm\(^{-1}\) (fig-1.9) Table-2 corresponding to \(^4A_{2g}(F) \rightarrow ^4T_{2g}(F)\), \(^4A_{2g}(F) \rightarrow ^4T_{1g}(F)\). The \(v_3\) transition is usually not observed because of charge transfer set in the ultra-violet region. It is important to note that the chloro complexes are green and the nitrato complexes are violet in colour. This difference in colour is associated with a marked difference in the electronic spectra as discussed below.

It has also been observed that the aqueous solution of the nitrato complexes, on keeping, undergo a colour change from violet-green. It is indicated that the green coloured species is comparatively more stable and hence, has a trans structure; the violet species, thus being cis.

For the same ligand the nitrato complexes show stronger ligand field than the corresponding chloro complexes. The extent of spectral shift from chloro to nitrato complex is of the order of approximately 2000 cm\(^{-1}\), which by no means may be attributed to the difference in the ligand field strengths of the two aninos.

LIGAND FIELD PARAMETERS:

The energy of the \(^4A_{2g} \rightarrow ^4T_{2g}(F)\) spin-allowed transition gives the value of 10Dq. The evaluation of B can be made by the use of any of the following formulae:\(^39\).

\[
B = \frac{(2v_1^2+v_2^2-3v_1v_2)}{(15v_2-27v_1)} \quad \text{(fitting the second band)}
\]

\[
B = \frac{(2v_1^2+v_3^2-3v_1v_3)}{(15v_3-27v_1)} \quad \text{(fitting the third band)}
\]

\[
B = \frac{(v_2+v_3-3v_1)}{15} \quad \text{(fitting the sum of the second and the third band maxima)}
\]
where $v_1$ and $v_2$ are the energies of the transitions $^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$, $^4A_{2g}(F) \rightarrow ^4T_{1_{eg}}$ (respectively).

The nephelauxetic parameter, $\beta$ is readily obtained using the relation:

$$\beta = \frac{B(\text{complex})}{B(\text{free ion})}$$

where $B$ for the free ion = 918 cm$^{-1}$. The value lies in the range of 0.31-0.84 indicate that the complexes have appreciable covalent character. The value of $C$ can be calculated by using the relation $C = 4B$.

**EPR Spectra:**

The spin-Hamiltonian for chromium(III) complexes ($S=3/2$) may be written as:

$$\mathcal{H} = g \beta S \cdot H + D \left( S_z^2 - \frac{5}{4} \right) + E \left( S_x^2 - S_y^2 \right)$$

The $^4F$ state of $d^3$ ion in octahedral symmetry has the orbital singlet state lowest in energy with all excited states at much higher energy. The $d^3$ ion has relatively long spin-lattice relaxation times and gives narrow ESR absorption line, even at room temperature. In an octahedral symmetry the ground state belongs to the $^4A_{2g}$ irreducible representation and is connected through the spin-orbit coupling to the excited $^4T_{2g}$ states only. For this reason, the $g$ and $A$ term are nearly isotropic, even in highly distorted crystal fields.
Figure 1. EPR Spectrum of [Cr(pvtsc)_2(NO_3)](NO_3)_2
In $d^9$ ions the symmetry of the crystal field is primarily exhibited through spin-spin terms $D$ and $E$. In the crystal field theory the value of $g$ can be calculated by the equation

$$g = 2.0023 - 8\lambda / \Delta E (T_{2g})$$

where $\lambda$ is the spin orbit coupling constant for the metal ion in the complexes.

On the basis of aforesaid study such as elemental analysis, molar conductance measurements, magnetic susceptibility, IR, electronic and EPR spectral data, the structures may be proposed for all the complexes.
L = LIGAND

L = LIGAND
### TABLE-1

**COLOUR AND ELEMENTAL ANALYSIS OF Cr(III) COMPLEXES:**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Colour</th>
<th>MP °C</th>
<th>Molar Conductance Ω Mole^2 cm^-1</th>
<th>Yield %</th>
<th>Elemental analyses found and (calculated) %</th>
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</thead>
<tbody>
<tr>
<td>[Cr(pvsc)_2Cl_2]Cl</td>
<td>Green</td>
<td>222</td>
<td>90</td>
<td>60</td>
<td>Cr</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.55</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(9.07)</td>
</tr>
<tr>
<td>[Cr(pvtscc)_2Cl_2]Cl</td>
<td>Green</td>
<td>218</td>
<td>95</td>
<td>65</td>
<td></td>
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<td>8.54</td>
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<td>(9.34)</td>
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<tr>
<td>[Cr(ptasc)_2Cl_2]Cl</td>
<td>Green</td>
<td>224</td>
<td>96</td>
<td>69</td>
<td></td>
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<td>10.06</td>
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<td></td>
<td></td>
<td>(10.36)</td>
</tr>
<tr>
<td>[Cr(ptatsc)_2Cl_2]Cl</td>
<td>Green</td>
<td>213</td>
<td>98</td>
<td>62</td>
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<td>10.38</td>
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<td>(10.83)</td>
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<tr>
<td><a href="NO_3">Cr(pvsc)_2NO_3</a>_2</td>
<td>Violet</td>
<td>229</td>
<td>205</td>
<td>71</td>
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<td></td>
<td>(8.33)</td>
</tr>
<tr>
<td><a href="NO_3">Cr(pvtscc)_2NO_3</a>_2</td>
<td>Brown</td>
<td>232</td>
<td>200</td>
<td>58</td>
<td></td>
</tr>
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<td></td>
<td></td>
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<td>8.11</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>(7.69)</td>
</tr>
<tr>
<td><a href="NO_3">Cr(ptasc)_2NO_3</a>_2</td>
<td>Dirty Brown</td>
<td>230</td>
<td>190</td>
<td>60</td>
<td></td>
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<td>9.20</td>
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<td>(9.01)</td>
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<tr>
<td><a href="NO_3">Cr(ptatsc)_2NO_3</a>_2</td>
<td>Violet</td>
<td>225</td>
<td>185</td>
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### Table 2
**Electronic Spectral Bands and Magnetic Moment of Cr(III) Complexes**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$v_1$ (cm$^{-1}$)</th>
<th>$v_2$ (cm$^{-1}$)</th>
<th>$v_3$ (cm$^{-1}$)</th>
<th>$\mu_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr (pvsc)$_2$ Cl$_2$]Cl</td>
<td>14903</td>
<td>20745</td>
<td>26446</td>
<td>3.76</td>
</tr>
<tr>
<td>[Cr (pvsc)$_2$ Cl$_2$]Cl</td>
<td>14183</td>
<td>21186</td>
<td>27397</td>
<td>3.78</td>
</tr>
<tr>
<td>[Cr (ptasc)$_2$ Cl$_2$]Cl</td>
<td>14224</td>
<td>20920</td>
<td>26041</td>
<td>3.75</td>
</tr>
<tr>
<td>[Cr (ptatsc)$_2$ Cl$_2$]Cl</td>
<td>14235</td>
<td>21008</td>
<td>-</td>
<td>3.70</td>
</tr>
<tr>
<td>[Cr (pvsc)$_2$ NO$_3$] (NO$_3$)$_2$</td>
<td>16778</td>
<td>20283</td>
<td>-</td>
<td>3.74</td>
</tr>
<tr>
<td>[Cr (pvsc)$_2$ NO$_3$] (NO$_3$)$_2$</td>
<td>16890</td>
<td>21000</td>
<td>-</td>
<td>3.76</td>
</tr>
<tr>
<td>[Cr (ptasc)$_2$ NO$_3$] (NO$_3$)$_2$</td>
<td>16077</td>
<td>20745</td>
<td>27397</td>
<td>3.82</td>
</tr>
<tr>
<td>[Cr (ptatsc)$_2$ NO$_3$] (NO$_3$)$_2$</td>
<td>16778</td>
<td>21321</td>
<td>-</td>
<td>3.83</td>
</tr>
</tbody>
</table>

### Table 3
**Ligand Field Parameters of Cr(III) Complexes**

<table>
<thead>
<tr>
<th>Complexes</th>
<th>$D_q$ (cm$^{-1}$)</th>
<th>$B$ (cm$^{-1}$)</th>
<th>$\beta$</th>
<th>LFSE (KJ.mol$^{-1}$)</th>
<th>$g_{\text{iso}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr (pvsc)$_2$ Cl$_2$]Cl</td>
<td>1490</td>
<td>580</td>
<td>.632</td>
<td>202</td>
<td>2.00</td>
</tr>
<tr>
<td>[Cr (pvsc)$_2$ Cl$_2$]Cl</td>
<td>1418</td>
<td>771</td>
<td>.840</td>
<td>203</td>
<td>2.01</td>
</tr>
<tr>
<td>[Cr (ptasc)$_2$ Cl$_2$]Cl</td>
<td>1422</td>
<td>717</td>
<td>.781</td>
<td>203</td>
<td>1.99</td>
</tr>
<tr>
<td>[Cr (ptatsc)$_2$ Cl$_2$]Cl</td>
<td>1423</td>
<td>730</td>
<td>.795</td>
<td>204</td>
<td>2.00</td>
</tr>
<tr>
<td>[Cr (pvsc)$_2$ NO$_3$] (NO$_3$)$_2$</td>
<td>1677</td>
<td>312</td>
<td>.340</td>
<td>240</td>
<td>2.02</td>
</tr>
<tr>
<td>[Cr (pvsc)$_2$ NO$_3$] (NO$_3$)$_2$</td>
<td>1689</td>
<td>372</td>
<td>.406</td>
<td>242</td>
<td>2.01</td>
</tr>
<tr>
<td>[Cr (ptasc)$_2$ NO$_3$] (NO$_3$)$_2$</td>
<td>1607</td>
<td>433</td>
<td>.472</td>
<td>230</td>
<td>2.03</td>
</tr>
<tr>
<td>[Cr (ptatsc)$_2$ NO$_3$] (NO$_3$)$_2$</td>
<td>1677</td>
<td>417</td>
<td>.454</td>
<td>240</td>
<td>2.02</td>
</tr>
</tbody>
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1.5 REFERENCES:


