 CHAPTER VIII

Magnetic susceptibility measurements of complexes of iso-quinoline and 8-hydroxy quinoline with ethereal blue perchromate;

(i) Prepared with phthalic acid.
(ii) Prepared with sulphuric acid.
Tjabbes\textsuperscript{1} employed for the first time magnetic susceptibility measurements in elucidating the structure of perchromates and persalts. He\textsuperscript{2} found the magnetic susceptibility of K\textsubscript{2}CrO\textsubscript{8} to be $3.89 \times 10^{-6}$ indicating penta or hepta valency of chromium.

Rodriguez and Horrau\textsuperscript{3} determined the magnetic susceptibility of Mg\textsubscript{2}K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{15}. The values had shown that the compound really contained the tetraperoxy chromate (V) ion.

While studying the magnetic susceptibility of the red potassium perchromate, Klemm and Werth\textsuperscript{4} found it to be paramagnetic with the magnetic moment of value 1.80 Bohr magnetons. They\textsuperscript{5} also determined the magnetic susceptibility of blue perchromate of potassium and pyridine and found these compounds to be diamagnetic and confirmed the views of Schwarz and Giese\textsuperscript{5} that the blue compound contained hexavalent chromium only.

Bhatnagar, Prakash and Hamid\textsuperscript{6}, and Fergusson and Wilkims\textsuperscript{7} measured the magnetic susceptibility of Cr(O\textsubscript{2})\textsubscript{2}3NH\textsubscript{3} derivative of diperoxy chromium and found 2.8 Bohr magnetons. The paramagnetic moment of the compound was consistent with the presence of the two unpaired electrons associated with Cr(IV).

Rai\textsuperscript{8} measured the magnetic moment of blue compound extracted with ether and ethyl acetate and found it to be paramagnetic in nature.

Pillai\textsuperscript{9} found the value of magnetic moment of the
quinoline complex of the blue perchromate to be 3.8 B.M. and
strychnine complex was found to be feebly paramagnetic.

In view of the above contradictions, I thought worth
while to confirm the presence of Cr(III) in the so-called blue
peroxychromic acid by carrying out the magnetic measurements of
its complexes with isoquinoline and 8-hydroxyquinoline.

**EXPERIMENTAL**

**Preparation of the complexes:** Complexes of isoquinoline and 8-hydroxy
quinoline with both blue perchromates obtained in presence of
phthalic acid and sulphuric acid were prepared as described in
Chapter V. As the magnetic measurements were to be made in the
powder, to ensure perfect packing in Guoy's tube, they were ground
to fine powder.

**MAGNETIC MEASUREMENTS:**

Magnetic susceptibility measurements of the complexes
were determined by Guoy's method as modified by Bose, A.10 The
electromagnet used was of Rutherford flat face type, giving the
field strength of 6000 to 8000 gauss. After making necessary
arrangements, the balance was first standardized either with A.R.
carbon tetrachloride or distilled water.

The weight of the empty Guoy's tube was determined at
first without the field and then with the field on. To ensure
perfect and tight packing and to guard against preferential
orientation of the particles, the fine powder of the complexes was
gently rammed up to the mark into Guoy's tube and then weighed
with out the field and with the field on. The tube was emptied
washed and then filled up to the same mark with water and weighed
with out the field and with the field on. The effective density
of each of the complexes was also determined. Calculations were
made from the formula given below:

\[
\frac{\Delta W_{\text{substance}}}{\Delta W_{\text{water}}} = \frac{K_{\text{substance}} - K_{\text{air}}}{K_{\text{water}} - K_{\text{air}}}
\]

\[K_{\text{air}} = 0.028 \times 10^{-6}\]

The formula for the determination of susceptibility of
the powder used is:

\[\chi = \frac{K_{\text{substance}}}{\rho_{\text{eff.}}}\]

where \(\rho_{\text{eff.}}\) = effective density

\(\chi\) = mass susceptibility.

The molecular susceptibility \(\chi_M\) is given by the expression:

\[\chi_M = \chi \times M\]

and finally, \[\mu_B = 2.841\sqrt[4]{\chi_M \times T}\]

where \(\mu_B\) is the Bohr magneton and \(T\) = absolute temperature.
**Table 8.1**

Magnetic Susceptibility Measurements of 8-Hydroxy Quinoline Complex of Etheeral Blue Perchomate Prepared with Phthalic Acid

\[
\text{Current passed: } 2.5 \text{ amp.} \\
\chi_{\text{air}}: 24.16 \times 10^{-6} \\
K_{\text{air}}: +0.031 \times 10^{-6} \\
\text{Temperature: } 22.6^\circ C \\
\chi_{\text{water}}: -0.720 \times 10^{-6} \\
K_{\text{water}}: -0.751 \times 10^{-6}
\]

<table>
<thead>
<tr>
<th></th>
<th>Wt. of the empty tube in gms.</th>
<th>Wt. of the tube &amp; 8-hydroxyquinoline complex (gms.)</th>
<th>K \times 10^6 \gamma_{\text{eff.}}</th>
<th>Pull on the 8-hydroxyquinoline complex corrected for density \chi x 10^{-6}</th>
<th>\chi_M x 10^{-6}</th>
<th>\mu B</th>
</tr>
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<tr>
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<td>5.468</td>
<td>0.5912</td>
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(182)
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<thead>
<tr>
<th>Wt. of the empty tube in gms.</th>
<th>Wt. of the tube &amp; 8-hydroxyquinoline complex (gms.)</th>
<th>Pull on the complex corrected for empty tube (gm.)</th>
<th>$K \times 10^6$</th>
<th>$\gamma\text{eff.} \times 10^6$</th>
<th>$\chi \times 10^6$</th>
<th>$\chi_M \times 10^6$</th>
<th>$/\mu B$</th>
</tr>
</thead>
<tbody>
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<td>Without any field on</td>
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<td>10.01</td>
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<td>4.491</td>
<td>0.4493</td>
<td>10.00</td>
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### Table 8.3

**Magnetic Susceptibility Measurements of Isoquinoline Complex of Ethereal Blue Perchromate**

Prepared with Phthalic Acid \((\text{C}_9\text{H}_7\text{N})_5\text{C}_8\text{H}_{4}O_4\cdot\text{Cr}_2(\text{CrO}_4)_3\)**

<table>
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<tr>
<th>Current passed: 2.5 amp.</th>
<th>Temperature: 22.6°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi_{\text{air}}): (24.16 \times 10^{-6})</td>
<td>(\chi_{\text{water}}): (-0.720 \times 10^{-6})</td>
</tr>
<tr>
<td>(K_{\text{air}}): (+0.031 \times 10^{-6})</td>
<td>(K_{\text{water}}): (-0.720 \times 10^{-6})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Wt. of the empty tube in gms.</th>
<th>Wt. of the tube &amp; isoquinoline complex (gms.)</th>
<th>Pull on the complex corrected for empty tube (gm.)</th>
<th>(K \times 10^{6})</th>
<th>(\beta_{\text{eff.}})</th>
<th>(\chi \times 10^{-6})</th>
<th>(\chi_{M} \times 10^{-6})</th>
<th>(\mu_{B})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without any field on.</td>
<td>With the field on.</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>1</td>
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<td>15.7670</td>
<td>15.7776</td>
<td>0.0106</td>
<td>1.7616</td>
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<tr>
<td>13.8406</td>
<td>13.8406</td>
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<td>1.7616</td>
<td>0.5780</td>
<td>3.047</td>
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</tbody>
</table>

(141)
**TABLE 8.4**

**MAGNETIC SUSCEPTIBILITY MEASUREMENTS OF ISOQUINOLINE COMPLEX OF ETHERAL BLUE PERCHROMATE**

\[
(G_7H_7N)_5Cr_2(CrO_{10})_3
\]

Current passed : 2.5 amp.

\[
\chi_{\text{air}} = 24.16 \times 10^6
\]

\[
K_{\text{air}} = +0.031 \times 10^6
\]

Temperature : 22.6°C

\[
\chi_{\text{water}} = -0.720 \times 10^6
\]

\[
K_{\text{water}} = -0.720 \times 10^6
\]

<table>
<thead>
<tr>
<th>Wt. of the empty tube in gms.</th>
<th>Wt. of the tube &amp; isoquinoline complex(gms.)</th>
<th>Pull on the complex corrected for empty tube (gm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without any field on</td>
<td>Without field on</td>
<td>K \times 10^6 \rho_{\text{eff.}} \times 10^6 \chi_M \times 10^6 \mu_B</td>
</tr>
<tr>
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<td>13.7834</td>
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</table>
The values of 3.64 and 3.98 Bohr magnetons obtained in the case of 8-hydroxyquinoline complexes of ethereal blue perchromate prepared with sulphuric acid as well as phthalic acid, as shown in tables 8.2 and 8.1, explicitly confirm the presence of Cr(III) in these complexes contrary to the belief of some authors that only hexavalent chromium is present in all the complexes of blue peroxychromic acid.

The low values corresponding to 3.029 and 3.356 Bohr magnetons observed in the case of isoquinoline complexes (undecomposed) of ethereal blue perchromate will be discussed under "General Discussion".

REFERENCES