CHAPTER VI

MAGNETIC SUSCEPTIBILITIES AND IR SPECTRA OF SOLID COMPLEXES
MAGNETIC SUSCEPTIBILITIES OF METAL-NOSA COMPLEXES

There are various types of magnetic behaviours of substances, such as, diamagnetism, paramagnetism, van Vleck paramagnetism, ferromagnetism, etc. When an external magnetic field is applied (i) diamagnetic polarization is produced in all substances and it is due to the accelerating effect of the field on orbital electrons; it acts in a direction opposite to the applied field, (ii) paramagnetic polarization is produced in some substances resulting from the interaction of the applied field with the permanent magnetic dipoles in atoms and molecules. The atoms and the molecules tend to line up in such a manner that their own magnetic fields reinforce the applied field, i.e., they line up with the field. In general, paramagnetic polarization is much greater in magnitude than diamagnetic polarization. Ferromagnetic polarization which is relatively rare, results in an increase of the order of a million times, in the intensity of the field within a substance. It has been observed for a few metals, alloys and compounds. Paramagnetic effects are comparatively more important for co-ordination compounds.

The magnetic susceptibility of a system containing only one kind of paramagnetic particle may be expressed by the equation.
\[ X = N \alpha + \frac{N \mu^2}{3kT} \]  

where \( X \) = Specific magnetic susceptibility,

\( N \) = Avogadro number,

\( \alpha \) = Molecular diamagnetic susceptibility,

\( k \) = Boltzmann constant,

\( T \) = Absolute temperature,

\( \mu \) = Permanent magnetic dipole moment.

Thus, the magnetic dipole moment is related to the magnetic susceptibility in a manner which is quite analogous to the relationship between electrical dipole moment and dielectric constant.

The contribution of the spin dipole moments of unpaired electrons to the magnetic susceptibility of a substance is not directly proportional to the number of unpaired electrons, but rather to \( n(n+2) \), where \( n \) is the number of such electrons. This resultant magnetic moment which is due to 'n' unpaired electrons may be expressed by

\[ \mu = \sqrt{n(n+2)} \]  

where \( \mu \) is expressed in Bohr magnetons (1 Bohr magneton = 5.56 x 10^(-3) erg gauss^-1 mol^-1). \( \mu \) may have to be corrected for diamagnetic susceptibility which may be obtained by taking the sum of atomic susceptibility(1). Another correction is required for orbital contribution. For example, the orbital
moments of the unpaired electrons of the transitional metals are not free to move and orient themselves with respect to the applied field, as are those of rare earths. Their magnetic effects are overcome by interaction of the surrounding molecules and the ions. The magnetic susceptibility of a metal chelate depends both on the nature of the ion as well as on the ligand. For example, \( \overset{\text{Fe(Cl)}}{\text{Fe}}_6 \) \( \text{Cl} \) \( -3 \) has \( \mu = 2.3 \) and \( \overset{\text{Fe}}{\text{Fe}}_6 \) \( \text{Cl} \) \( -3 \) has \( \mu = 5.9 \). The low magnetic moment of \( \overset{\text{Fe(Cl)}}{\text{Fe}}_6 \) \( \text{Cl} \) \( -3 \) is explained by the donation of electrons to the metal forming a covalent bond. There is a strong evidence for covalent structure of \( \overset{\text{Fe(Cl)}}{\text{Fe}}_6 \) \( \text{Cl} \) \( -3 \), which forms \( d^2sp^3 \) octahedral complex. The fluoride complex, on the other hand, is ionic. Thus, the determination of magnetic susceptibility may throw light on the extent to which the bonds are 'essentially covalent' or 'essentially ionic'. However, the classification of bonds as ionic or covalent on the basis of measurements of magnetic susceptibility has been challenged\(^{(2)}\). The magnetic susceptibility measurements may be considered useful as giving information about the structure which will have to be verified by other physical methods. Measurements of magnetic susceptibility over a wide range of temperature will yield results which will be of greater theoretical value\(^{(3)}\).
EXPERIMENTAL

The nickel, copper, cobalt, manganese, silver, zinc, cadmium, and lead metal ion solutions were mixed in equimolar proportions with NQSA. NQSA solution was prepared in hot water. On mixing, the complexes were obtained by double decomposition. To a metal ion solution, NQSA solution was added slightly in excess. The precipitates formed were thoroughly washed with water, followed by washing with a little quantity of alcohol and ether. In the case of Fe(II) complex, it was obtained by evaporating to dryness. The nickel complexes were prepared by taking different nickel salts like, nickel chloride, nickel sulphate and nickel nitrate. The precipitates were allowed to dry at room temperature.

Magnetic susceptibility was measured employing Guoy's balance. The field strength was about 7500 gauss and the current applied was 6 amps. The measurements of magnetic susceptibilities were carried out using finely powdered samples at room temperature (32°C). One Guoy tube was used and its constant was determined using $\text{HgCo(CNS)}_4$. The observations for determining constants of tube A, following Lewis and Figgis(4), are as follows:

1. Weight of the empty tube (without field) = 11.21298 g.
2. Weight of the empty tube (with field) = 11.20647 g.
3. Change in weight due to field = -0.00651 g.
   = -6.51 mg = d
4. Weight of the tube + Hg\[\text{Co(CNS)}_4\] = 12.63918 g.

5. Weight of Hg\[\text{Co(ClS)}_4\] = 1.42620 g.

6. Weight of the tube + Hg\[\text{Co(ClS)}_4\] = 12.69697 g.

7. Weight of Hg\[\text{Co(ClS)}_4\] = 1.49050 g.

8. Change in weight of Hg\[\text{Co(ClS)}_4\] = 0.06430 g.

\[dW = (1.49050 - 1.42620)\]

9. Weight of Hg\[\text{Co(ClS)}_4\] = 1.42620 g.

10. Apparent change in weight of Hg\[\text{Co(ClS)}_4\]

\[dW = dW' - d\]

\[= 64.30 - (-6.51)\]

\[= 70.81 \text{ mg.}\]

11. \(X\) for Hg\[\text{Co(ClS)}_4\] at 20°C = 16.44 x 10^{-6}

12. The correction for the displaced air is

\[\infty = 0.029\]

Now,

\[E.d.W = X \times m - \infty\]
\[ \beta = \frac{X \times m - \alpha}{dw} \quad (2) \]

\[ = \frac{16.44 \times 1.42620 - 0.029}{70.81} \]

\[ \beta = 0.3307 \]

Thus, the two constants \( \alpha \) and \( \beta \) for a particular tube were determined. The values of \( \alpha \) and \( \beta \) for the tube used were 0.029 and 0.3307 respectively.

Rearranging equation (2),

\[ X = \frac{\alpha + \beta \cdot dw}{m}. \]

\( X \) for an unknown samples can now be calculated. Here, \( dw \) would be equal to the apparent change in weight of the substance minus the change in weight of the tube (with air) for the field on and off and \( m \) is the mass of the sample. Experiments were carried out at room temperature 32°C. From \( X \), the molecular magnetic susceptibility \( X_m \) can be calculated. Results are shown in Tables 6.1 and 6.2.

The tube was filled with different samples and their weights were noted with and without magnetic field. Care was taken to pack the samples uniformly. Several observations were taken and the mean (\( dw \) and \( m \)) of results which agreed fairly well with one another were recorded in Tables 6.1 and 6.2.
The formula of the complexes were checked by conductometric and potentiometric methods as well as volumetric titration of metal ions with EDTA. All the complexes were found in 1:1 composition. Measurements of magnetic susceptibility at a single temperature is also of somewhat limited use(2).

Nickel complexes are yellowish green in colour. They are paramagnetic, insoluble in water and also insoluble in organic solvents like ethanol, acetone, chloroform, carbon tetrachloride and ether. Sr. No. 1, 2, 3 (Table 6.1) nickel-NQSA complexes were prepared by taking different nickel salts like nickel sulphate, nickel chloride, and nickel nitrate, however, magnetic susceptibility data (Table 6.1) are nearly the same. This indicates that the anion of the salt does not form part of the complex.

The copper complex was yellowish green in colour. It is insoluble in water and organic solvents like ethanol, acetone, chloroform, carbon tetrachloride and ether. It is found to be paramagnetic with molar magnetic susceptibility equal to 1190.

The cobalt complex is light brown in colour. It is insoluble in water and organic solvents like ethanol, acetone, chloroform, carbon tetrachloride and ether. It is found to be paramagnetic with molar magnetic susceptibility equal to 7032.
The manganese complex is yellow in colour. It is also insoluble in water and organic solvents such as ethanol, acetone, chloroform, carbon tetrachloride and ether. It is found to be paramagnetic with molar magnetic susceptibility equal to 11078.

The iron(II) complex is found to be black in colour. It is soluble in water, ethanol and acetone but insoluble in chloroform, carbon tetrachloride and ether. It is paramagnetic with molar magnetic susceptibility equal to 2354.

It can be concluded that all the complexes studied viz., Cu, Ni, Co and In show paramagnetic behaviour which is the characteristic of transition metal ions. They are found to be insoluble in water and also in common organic solvent. They must be having no resultant charge.

The silver complex is reddish brown in colour. It is insoluble in water and organic solvents such as acetone, ethanol, chloroform, carbon tetrachloride and ether. It is found to be diamagnetic with molar magnetic susceptibility equal to -15.5.

The zinc complex is shining yellow in colour. It is insoluble in water and organic solvents like ethanol, acetone, chloroform, carbon tetrachloride and ether. It is found to be diamagnetic with molar magnetic susceptibility equal to -76.4.

The cadmium complex is yellow in colour. It is insoluble in water and organic solvents like ethanol, acetone, chloroform, carbon tetrachloride and ether. It is found to be diamagnetic
with molar magnetic susceptibility equal to -39.3.

The lead complex is found to be yellow in colour. It is insoluble in water and organic solvents like, ethanol, acetone, chloroform, carbon tetrachloride and ether. It is found to be diamagnetic with molar magnetic susceptibility equal to -85.2.

The complexes of silver, zinc, cadmium and lead are found to be diamagnetic. These metals also show diamagnetism.

The metal ions in forms of suitable salt / salts (in the case of nickel complex) were mixed in 1:1 proportion, the complex separated out as precipitate. On further addition it was found that soluble complex can form. So only 1:1 type complexes were prepared and subjected to magnetic susceptibility and I.R. studies.

The metal ions used for solid complex formation were also titrated potentiometry and / or conductometrically. Most of them showed a sharp change or intersection at 1:1 composition. Thus 1:1 type of complexes are insoluble in water and some organic solvents. They can be employed for magnetic susceptibility and I.R. studies.

**IR SPECTRA OF METAL-NQSA COMPLEXES**

Infrared spectra of the ligand NQSA and its metal complexes were recorded on IA spectronon-2000 double beam spectrophotometer.

Since metal complexes of NQSA were insoluble in organic solvents, it was necessary to employ a method for handling solid samples. The potassium bromide pellet technique was
selected. The IR spectra of the HQSA (Fig. 6.1) and its metal complexes with various bivalent metals, such as, nickel, copper, cobalt, manganese, iron(II), silver, zinc, cadmium and lead are shown in Figs. 6.2 to 6.10.

The presence of quinoline (8 EQ) ring is indicated by usual bands(5). The bands assigned for HQSA (Fig. 6.1) are 3200 cm⁻¹ (OH), quinoline ring at 1600 cm⁻¹ and 1580 cm⁻¹. The 1580 cm⁻¹ either completely disappeared or shortened in all the metal complexes. This indicates the coordination between nitrogen of quinoline ring and cation. The hydroxyl group band at 3200 cm⁻¹ has completely disappeared in all the complexes indicating coordination through hydroxyl group.

A new broad band of weak to medium intensity at 2400-1800 cm⁻¹ is exhibited by all the metal complexes. This suggests that O - H ....O/H....H - O the bonding holds with HQSA. The probable general structure of the HQSA complex with a divalent ion can be shown as above.
INFRARED SPECTRA OF METAL COMPLEXES

FIG. 6-1
NQSA

FIG. 6-2
Ni-NQSA COMPLEX
INFRARED SPECTRA OF METAL COMPLEXES

**FIG. 6.3**
Cu-NQSA COMPLEX

**FIG. 6.4**
Co-NQSA COMPLEX
INFRARED SPECTRA OF METAL COMPLEXES

FIG. 6.5
Mn-NQSA COMPLEX

FIG. 6.6
Fe-NQSA COMPLEX
INFRARED SPECTRA OF METAL COMPLEXES

**FIG. 6.7**
Ag-NQSA COMPLEX

**FIG. 6.8**
Zn-NQSA COMPLEX
INFRARED SPECTRA OF METAL COMPLEXES

FIG. 6.9
Cd-NOSA COMPLEX

FIG. 6.10
Pb-NOSA COMPLEX
### Table 6.1

**Magnetic Susceptibilities of Meta-NQSA Complexes**

\[ \alpha = 0.029 \quad \beta = 0.3307 \quad d = -6.51 \text{ mg} \quad dw = dw^1 - d \]

<table>
<thead>
<tr>
<th>No.</th>
<th>Name of the complex</th>
<th>Apparent change in weight in mg</th>
<th>Weight of sample in cm³</th>
<th>Magnetic susceptibility X 10⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nickel-NQSA</td>
<td>13.65</td>
<td>0.55628</td>
<td>+8.1668</td>
</tr>
<tr>
<td>2</td>
<td>Nickel-NQSA</td>
<td>9.08</td>
<td>0.37984</td>
<td>+7.9816</td>
</tr>
<tr>
<td>3</td>
<td>Nickel-NQSA</td>
<td>9.82</td>
<td>0.42276</td>
<td>+7.7501</td>
</tr>
<tr>
<td>4</td>
<td>Copper-NQSA</td>
<td>8.06</td>
<td>0.75317</td>
<td>+3.5774</td>
</tr>
<tr>
<td>5</td>
<td>Cobalt-NQSA</td>
<td>38.62</td>
<td>0.59721</td>
<td>+21.4340</td>
</tr>
<tr>
<td>6</td>
<td>Manganese-NQSA</td>
<td>48.22</td>
<td>0.46738</td>
<td>+34.1806</td>
</tr>
<tr>
<td>7</td>
<td>Iron(II)-NQSA</td>
<td>13.83</td>
<td>0.63769</td>
<td>+7.2435</td>
</tr>
<tr>
<td>8</td>
<td>Silver-NQSA</td>
<td>-0.01</td>
<td>0.62453</td>
<td>-0.0411</td>
</tr>
<tr>
<td>9</td>
<td>Zinc-NQSA</td>
<td>-0.41</td>
<td>0.46644</td>
<td>-0.2235</td>
</tr>
<tr>
<td>10</td>
<td>Cadmium-NQSA</td>
<td>-0.30</td>
<td>0.66210</td>
<td>-0.1029</td>
</tr>
<tr>
<td>11</td>
<td>Lead-NQSA</td>
<td>-0.99</td>
<td>1.61048</td>
<td>-0.1352</td>
</tr>
</tbody>
</table>

* See discussion Page 211
<table>
<thead>
<tr>
<th>No.</th>
<th>Formula of the complex</th>
<th>Mol.wt.</th>
<th>Magnetic susceptibility</th>
<th>Molecular magnetic susceptibility</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>H</td>
<td>X \cdot 10^6</td>
</tr>
<tr>
<td>1</td>
<td>Ni-NQSA</td>
<td>327.9</td>
<td>+8.1668</td>
<td>2677.0</td>
</tr>
<tr>
<td>2</td>
<td>Ni-NQSA</td>
<td>327.9</td>
<td>+7.9816</td>
<td>2617.1</td>
</tr>
<tr>
<td>3</td>
<td>Ni-NQSA</td>
<td>327.9</td>
<td>+7.7501</td>
<td>2541.2</td>
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<tr>
<td>4</td>
<td>Cu-NQSA</td>
<td>332.7</td>
<td>+3.5774</td>
<td>1190.2</td>
</tr>
<tr>
<td>5</td>
<td>Co-NQSA</td>
<td>328.1</td>
<td>+21.4340</td>
<td>7032.5</td>
</tr>
<tr>
<td>6</td>
<td>Mn-NQSA</td>
<td>324.1</td>
<td>+34.1806</td>
<td>11078.0</td>
</tr>
<tr>
<td>7</td>
<td>Fe-NQSA</td>
<td>325.0</td>
<td>+7.2435</td>
<td>2354.1</td>
</tr>
<tr>
<td>8</td>
<td>Ag-NQSA</td>
<td>377.0</td>
<td>-0.0411</td>
<td>-15.494</td>
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<tr>
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<td>Zn-NQSA</td>
<td>334.5</td>
<td>-0.2285</td>
<td>-76.433</td>
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<tr>
<td>10</td>
<td>Cd-NQSA</td>
<td>334.6</td>
<td>-0.1029</td>
<td>-39.266</td>
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<tr>
<td>11</td>
<td>Pb-NQSA</td>
<td>476.3</td>
<td>-0.1852</td>
<td>-86.229</td>
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REFERENCES