SECTION 8

ANALYTICAL AND SPECTRAL MEASUREMENTS
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(A) Estimation of elements in the complexes

(i) Cobalt, copper, cadmium and mercury: The metal contents in the complexes were estimated by EDTA complexometric back titration method using erichrome black-T as indicator in the pH range 10.

(ii) Chloride, bromide, iodide, thiocyanate and selenocyanate: These were estimated gravimetrically as silver halides and pseudohalides in presence of dilute nitric acid.

(iii) Sulphur: It was estimated gravimetrically as barium sulphate in presence of hydrochloric acid.

(iv) Carbon, Hydrogen and Nitrogen: These analytical data were obtained, wherever necessary, from Central Drug Research Institute, Lucknow (India).

(B) Magnetic susceptibility measurements

In coordination chemistry, the simple measurement of the effective magnetic moment ($\mu_{\text{eff.}}$) has been, for many years, a powerful method for determining the spin multiplicity of transition metal ions. Precise measurements of the magnetic susceptibility reveals many characteristics of the transition metal ions and this method constitutes one of the most important experimental routes by which the chemist can easily get information on the structure and bonding in metal complexes. The extent to which the observed magnetic moment deviates from the calculated spin-only moment gives an indication of the magnitude of orbital contribution and in
suitable cases (e.g. Co(II) and Ni(II) in various symmetries) can tell about the geometry of the complex.

The magnetic susceptibility determinations were carried out on solid samples using a Gouy apparatus with a semi-micro balance and tapered magnet pole tips. The apparatus was calibrated with Hg[Co(SCN)]_4. The room temperature magnetic moment was measured for all the compounds and the values have been corrected for diamagnetism using Pascal's constant.

<table>
<thead>
<tr>
<th>Diamagnetic correction</th>
<th>(All values X 10^-6/g.atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl^-</td>
<td>23.4</td>
</tr>
<tr>
<td>Br^-</td>
<td>34.6</td>
</tr>
<tr>
<td>I^-</td>
<td>50.6</td>
</tr>
<tr>
<td>CNS^-</td>
<td>31.0</td>
</tr>
<tr>
<td>C=C-C-C=C</td>
<td>-10.6</td>
</tr>
<tr>
<td>NO_3^-</td>
<td>18.9</td>
</tr>
<tr>
<td>ClO_4^-</td>
<td>32.0</td>
</tr>
<tr>
<td>N (ring)</td>
<td>4.61</td>
</tr>
<tr>
<td>N (open chain)</td>
<td>5.57</td>
</tr>
<tr>
<td>S</td>
<td>15.0</td>
</tr>
</tbody>
</table>

(C) Infrared spectra :-

The regions of the electromagnetic spectrym of interest to coordination chemists varies from 0.01 to 300 μ. In the present investigation, the i.r. absorption between 200 - 5,000 cm^{-1} has been recorded on KBr phase using Beckman IR-12, Perkin-Elmer 577 and Perkin-Elmer 389 spectrophotometers using rock salt optics.
The region of the electromagnetic spectrum

<table>
<thead>
<tr>
<th>Region</th>
<th>Wavelength (μ)</th>
<th>Wave number (A°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Far U.V.</td>
<td>0.01 - 0.20</td>
<td>100 - 2,000</td>
</tr>
<tr>
<td>Near U.V.</td>
<td>0.20 - 0.38</td>
<td>2,000 - 3,8000</td>
</tr>
<tr>
<td>Visible</td>
<td>0.38 - 0.78</td>
<td>3,800 - 7,800</td>
</tr>
<tr>
<td>Near IR</td>
<td>0.78 - 3.0</td>
<td>7,800 - 30,000</td>
</tr>
<tr>
<td>Middle IR</td>
<td>3.0 - 30.0</td>
<td>30,000 - 300,000</td>
</tr>
<tr>
<td>Far IR</td>
<td>30.0 - 300,000</td>
<td>300,000 - 3000,000</td>
</tr>
</tbody>
</table>

The solid sample is ground and mixed with KBr and then the mixture is pressed in to a transparent disc. The weight percentage of sample is usually of the order of 1% and the total mass of the disc varies from 1 g to 10 mg, depending on the nature of the work.

(D) Conductance measurements:

The conductance measurements were made to determine whether the complex compounds are electrolytes or non-electrolytes. From this knowledge it can be predicted whether the anion is bonded to the metal ion or not. Conductance measurements were carried out either in acetone or dimethylformamide medium (10⁻³M) using Toshniwal conductivity bridge type Cl. 0102.

(E) Electronic spectra:

According to Beer Lambert law of light absorption, the amount of light absorbed is proportional to the number of absorbing molecules through which light passes. That is, if a substance is dissolved in a solvent the absorption by the solution will be proportional to the molecular concentration, provided the solvent itself does not absorb in that region. This law is expressed as
I = \text{I}_0 \cdot 10^{-abc} \text{ or } \log \frac{\text{I}}{\text{I}_0} = abc, \text{ where 'I' is the intensity of transmitted light, 'I}_0 \text{ the intensity of incident light, 'a' is absorptivity, a molecular property characteristic of the substance under examination and independent of concentration 'c', 'b' = cell length. Either of the expressions or the equivalent one long } \frac{1}{\text{I}} = abc, \text{ where 'T' is the transmittance, describes the absorption laws. The quantity that is usually measured with spectrophotometer is called the absorbance, 'A'. It is related to the quantities discussed in the above paragraph by } \log \frac{\text{I}_0}{\text{I}} = A = abc, \text{ when the concentration is expressed in moles per litre and the cell length 'b' in centimeters, the absorptivity, 'a' is called 'molar absorptivity' and is denoted by '£'. Accordingly '£' is expressed as follows: }

\[ £ = \frac{A}{b (cm) \times c (mole/lit)} = \frac{A}{bc} \times \frac{1000 \text{ cm}^2}{\text{mole}} \]

Invariably '£' is given without units, although as indicated, it has units of 1000 cm²/mole, it is also called the molar extinction coefficient.

In the present investigation, the visible spectra were recorded in chloroform and dimethylformamide solutions (10⁻²M) using Hilger Watt Uvispeck spectrophotometer. In recording the absorption spectra, two cells were used, one as the reference cell filled with the solvent and the other as the sample cell filled with the solution. Sometimes corresponding ligands were added to the solution of complexes to prevent dissociation. Silica cells were used for measurements below 350 µm and glass cells for measurements above 350 µm. Similarly for measurements below 320 µm, the blue photo cell and hydrogen lamp are necessary, for measurements between 320 – 400 µm blue photo cell, tungsten lamp with filter at position
for measurements between 400 - 625 μ, blue photo cell tungsten lamp and for measurements between 625 - 1000 μ, red photo cell and tungsten lamp were used.

(F) Thermal analysis measurements:

When a sample is heated various chemical changes (e.g., thermal decomposition, oxidation etc.) and several physical processes (solvent and water desorption, evaporation, sublimation etc.) may take place, with a consequent change in the weight of the sample. These processes are examined by thermogravimetry. The experiments were carried out on finely powdered samples on a platinum crucible using a derivatograph (MOM) supplied by the Hungarian optical works, Hungary in the ambient temperature of the furnace with heating rate of 10°C per minute. This instrument records simultaneously the derivative thermogravimetry (DTG), differential thermal analysis (DTA) and the temperature (T) photographically. Also recording was carried out in two other instruments made in German and they record DGT and DTA curves separately with the rise of temperature (10°C per minute).

(G) Molecular weight measurement [Rast method]:

The method involves the determination of the melting point of a pure solvent, usually camphor and the melting point of a solution of the substance under investigation, in camphor. The solution was prepared by mixing camphor (200 mg) and the substance (20 mg) in a neat and clean test tube and heated by dipping in hot glycerol at 180°C. On cooling it became solidified. Then it was
taken in a capillary tube of about 50 - 70 mm in length with an inner diameter of 3 - 4 mm constructed of soft glass. It was then sealed at a point 20 mm above the level of the solid and the melting point was taken. The molecular weight of the compound was then calculated using the equation

\[ M = \frac{1000KW}{TW} \]

where
- \( K \) = cryoscopic constant
- \( W \) = weight of the substance
- \( T \) = depression of melting point
- \( w \) = weight of camphor.
REFERENCES

2. A.I. Vogel, Loc. cit. p. 266
3. A.I. Vogel, Loc. cit. p. 569
4. A.I. Vogel, Loc. cit. p. 462

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