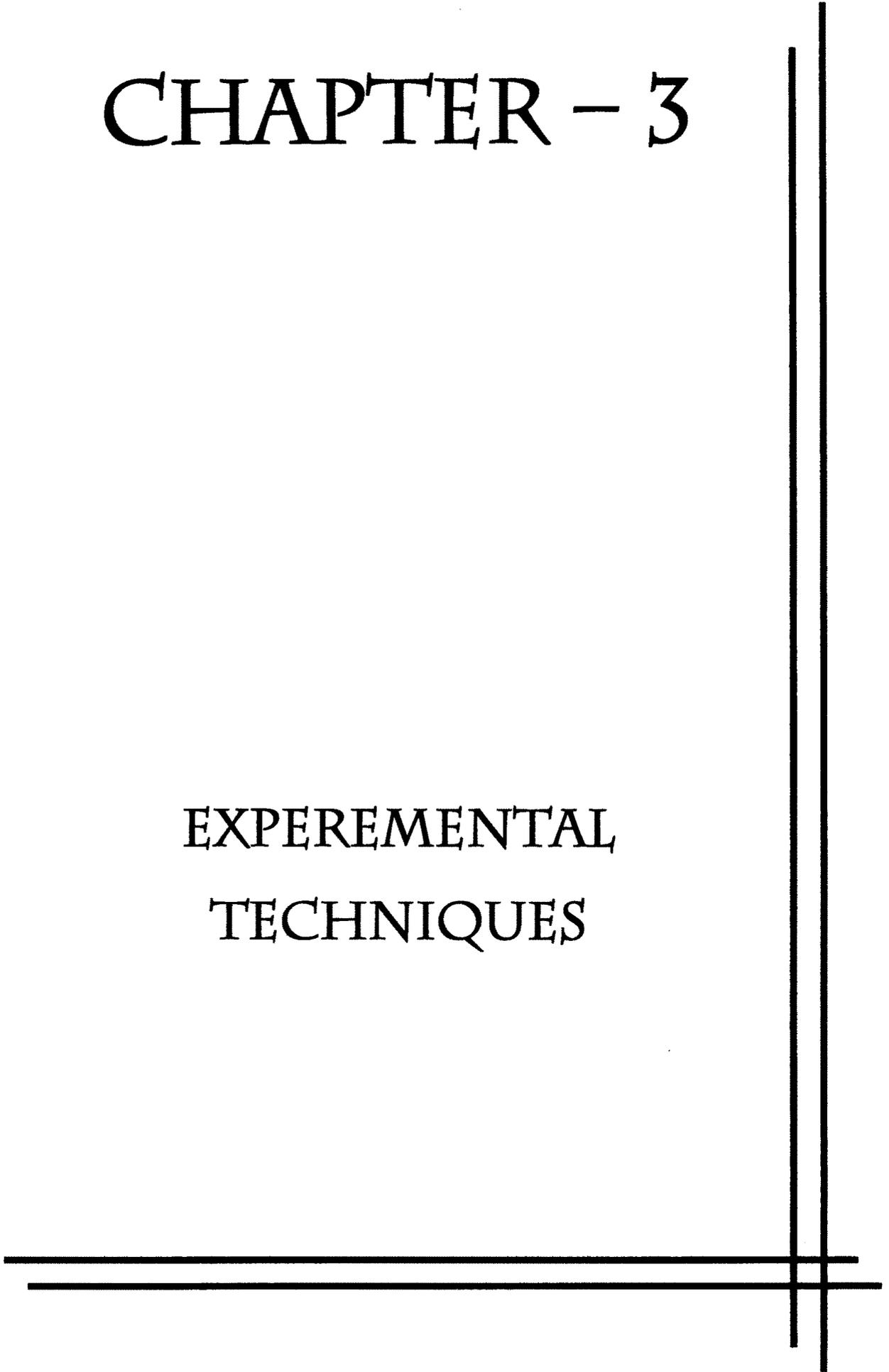


CHAPTER – 3

EXPEREMENTAL TECHNIQUES



3. A. GENERAL:

A wide variety of methods of variable precision and dependability are available for determining the structure of coordination compounds. These may be roughly divided into three groups: spectroscopic methods, microscopic methods and chemical methods.

(a) Spectroscopic methods generally provide specific structural information of high precision. The important methods in this group are:

IR and Raman spectrophotometry

UV-visible (electronic) spectrophotometry,

Magnetic resonance methods like NMR, NQR, ESR and Diffraction methods, Mass Spectrometry.

(b) Macroscopic physical methods indicate the general structure type rather than giving structural details. These involve measurements of gross physical properties such as melting point, boiling point, vapour pressure, thermogravimetric, electrical conductivity, magnetic susceptibility, etc.

(c) Chemical methods are based on chemical reactions of the compounds. The reliability of these methods is, in general, low and the information needs to be carefully interpreted.

In the present work, the following methods were used to obtain structural information on the coordination compounds studies.

3. B. ELEMENTAL ANALYSIS:

This involved the estimation of metal, nitrogen, carbon and hydrogen in all the solid chelates. Estimation of metal in each compound was carried out by gravimetric oxide method and EDTA titration as described by Flaschka[1], Carbon hydrogen and nitrogen were estimated on a “ Carlo-Erba 1108 ” C-H-N analyzer at Regional Sophisticated Instrumentation Center,(RSIC) Lacknow,India.

3. C. ELECTRICAL CONDUCTIVITY MEASUREMENTS:

The conductivity of the metal chelates in DMF was measured using “Equiptronics EQ-660 digital conductivity meter” and a calibrated conductivity cell at a room temperature. The cell constant of conductivity cell at room temperature. The cell constant of the conductivity cell was calculated using standard procedure [2].

The cell constant obtained for the cell is 1.01 cm^{-1} at 30°C . The conductivity of each solution was measured twice or thrice and the constant value observed was used in further calculations.

3. D. MAGNETIC SUSCEPTIBILITY MEASUREMENTS:

The Gouy method [3,4] used for magnetic susceptibility constants essentially of suspending a cylindrical sample of a substance in a non homogenous magnetic field With the lower end in the region of maximum field and the upper end in a region of effectively zero field conventional weighing technique.

The Gouy set-up should be calibrated [5-9] in terms of a substance of known susceptibility such as distilled water, benzene, aqueous nickel chloride solution, copper sulphate, mercury tetrathiocyanato cobaltate

Hg[Co(CNS)₄], [Ni(en)₃(S₂O₃)], [(NH₄)₂ Fe(SO₄)₂].6H₂O and K₃[Fe(CN)₆].

Magnetic susceptibility measurements in the present work were made at a room temperature (30°C) using a Gouy balance (Sartorius, Semi micro, Sardar Patel University, Vidhyanagar, India). The Gouy tube was calibrated using mercury tetrathiocyanato cobaltate, Hg [Co (CNS)₄] ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. units decrease per 30°C rise) and tube constant was verified using pure copper sulphate ($\chi_g = 5.9 \times 10^{-6}$ c.g.s. units at 30°C).

For determining magnetic moment, finely ground sample was carefully packed into a pyrex Gouy tube by introducing small quantity at a time and tapping it down after each addition. This operation was repeated until the sample filled into a fixed mark on the Gouy-tube. The tube was then suspended with its bottom at the center of the gap between the pole faces of the electro-magnet. The tube was weighed with and without applied magnetic field and deviation in weight of the tube (W) containing W gm of sample was calculated using the expression.

$$\chi_g = \frac{\alpha + \beta \cdot dw}{W}$$

Where α = correction due to displaced air.

$$= + 0.029 \times 10^{-6} \text{ c.g.s. units} \times \text{volume of air.}$$

β = Gouy tube constant

$dw = (\Delta W - \delta)$ here ΔW is apparent change (in mg) of the tube containing W grams of the sample on application of the field and δ is the deflection in weight of the empty tube on application of the field.

In order to minimize error due to packing of the solid into the tube, measurement with each sample was repeated three to four times, emptying the tube and repacking it a fresh each time the average change in weight was considered,

The gram susceptibility was multiplied by the molecular weight to obtain the molar susceptibility, χ_M . A correction was applied for the diamagnetism of the ligands and anions using Pascal's constant [10-12] to give the corrected molar susceptibility, χ'_M . The effective magnetic moment μ_{eff} was then calculated from the expression.

$$\mu_{\text{eff}} = 2.84 (\chi'_M \times T)^{1/2}$$

Where T = absolute temperature (°K)

3. E. SPECTROPHOTOMETRIC MEASUREMENTS:

(a) Electronic Spectral measurements :

The electronic spectra of the solid compounds were recorded in DMF (spectral grade) on Perkin – Elmer Lambda-19 UV-visible spectrometer at Sophisticated Instrumentation Center for Applied Research and Testing (SICART), Vidhyanagar, India.

(b) Infrared spectral measurements:

The FT-IR spectra of the compounds studied in the present work were recorded on a Perkin-Elmer Spectrum-GX spectrophotometer in KBr pellets at Sophisticated Instrumentation Center for Applied Research and Testing (SICART), Vidhyanagar, India.

(C) ^{13}C NMR Spectral measurements:

The ^{13}C NMR spectra in DMSO of all ligands studied in the present work were recorded on a Bruker DRX-300 FT-NMR Spectrometer using TMS $[(\text{CH}_3)_4\text{Si}]$ as an internal standard at Regional Sophisticated Instrumentation Center (RSIC), Lucknow, India.

3. F. THERMOGRAVIMETRIC ANALYSIS (TGA):

The thermograms of the chelates were recorded on Metler Toledo thermal analyzer at a heating rate $10^\circ\text{C min}^{-1}$ in air [Regional Sophisticated Instrumentation Center (RSIC), Nagpur, India] The thermograms were analyzed to obtain the information about the presence of water (lattice or coordinated) in the chelates and also to evaluate the activation energy for the chelates studied in the present work (chapter 4.F)

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