Chapter - 2
CHAPTER II
EXPERIMENTAL TECHNIQUES

Details about the general reagents used, the procedures adopted for the preparation of the ligands and various physico-chemical techniques employed in the elucidation of structure of the complexes are given in this chapter. Procedural details regarding the synthesis of the metal complexes are given in the appropriate chapters.

2.1. Reagents

The following metal salts were used:

\[ \text{CrCl}_3\cdot6\text{H}_2\text{O (BDH, AR); MnCl}_2\cdot4\text{H}_2\text{O (E. Merck, AR); FeCl}_3 \ (\text{Merck, GR); CoCl}_2\cdot6\text{H}_2\text{O (E. Merck, GR); NiCl}_2\cdot6\text{H}_2\text{O (BDH, GR); CuCl}_2\cdot2\text{H}_2\text{O (BDH, GR); CuBr}_2 \ (\text{Aldrich, 99\% pure); HgCl}_2 \ (\text{E. Merck, GR); HgBr}_2 \ (\text{Aldrich, 98\% pure) and HgI}_2 \ (\text{E. Merck, GR).} \]

Dimethylamine (40\% aqueous solution), diethylamine, piperidine, pyrrolidine, morpholine, carbon disulphide, cyclopentanone, isopropanol, isobutanol, n-propanol, n-butanol, sodium hydroxide, potassium hydroxide, 25\% ammonia solution, thionyl chloride, benzoylchloride and other reagents used for the present work are commercially available (BDH or E.Merck) chemicals.
of 99% purity. The solvents employed are either of 99% purity or purified by known laboratory procedures before use.  

Preparation of starting materials for the synthesis of complexes.

2-Aminocyclopent-1-ene-1-dithiocarboxylic acid (HACDA)

The reagent was prepared following a modified procedure of Takeshima et al.12. Cyclopentanone (22.2 ml, 0.25 mole) and 25% aqueous ammonia (100 ml) were taken in a stoppered conical flask. The flask was cooled to -0°C by keeping it in a bath containing a freezing mixture of ice and salt. Carbon disulphide (15 ml, 0.25 mole) was then added slowly with constant stirring to this cooled solution. The flask was shaken in an automatic shaker for eight hours, while keeping the same in the freezing bath. Ammonium salt of HACDA was separated as a yellow solid, which was filtered and washed with diethylether. The ammonium salt is not stable at room temperature; it loses ammonia on standing. The acid form is more stable than its ammonium salt, and was prepared by dissolving the crude product in water and slowly neutralising with 2N acetic acid under ice-cooling. The yellow crystals separated were collected, washed with water and dried over anhydrous calcium chloride.

Alkyl derivatives of HACDA

Alkyl derivatives of HACDA were prepared by the transamination reaction of HACDA. HACDA (7.9 g) and alkylamine, (9 ml of i-PrNH₂ or 10 ml of n-BuNH₂) were dissolved in methanol
This solution was refluxed for one hour. After cooling the solution to room temperature, water (200 ml) was added, and the solution was filtered to remove any solid impurities. To this filtrate, 2N acetic acid was added till the yellow product was separated. The crude product was then recrystallised from acetone.

Sodium dithiocarbamate

Sodium salts of dimethyl dithiocarbamate (Me₂dtc), diethylidithiocarbamate, (Et₂dtc), morpholine-N-carbodithioate, (Morphdtc), piperidine-N-carbodithioate (Pipdtc) and pyrrolidine-N-carbodithioate (Pyrrdtc) were prepared by the general procedure given below:

A 500ml three-necked flask was equipped with a separating funnel, electric stirrer and an air condenser. An aqueous solution of sodium hydroxide (20g, 0.5mole) and 0.5mole of the amine were taken in the flask. This was cooled in a freezing mixture of ice and salt. Carbon disulphide (31 ml, 0.5mole) was added dropwise from the separating funnel and the mixture was stirred for about two hours. The solid that separated out was washed several times with petroleum ether and recrystallised from water.

Potassium carbonodithioates (xanthates)

Potassium salts of isobutylxanthate (i-Buxant), isopropylxanthate (i-PrXant), n-butylxanthate (n-BuXant) and
n-propylxanthate (n-PrXant) were prepared by the general procedure given below:

Potassium hydroxide pellets (11.2g, 0.2 mole) was mixed with an excess of the appropriate alcohol, R-OH (~ 0.6mole) (R=i-Bu, i-Pr, n-Bu or n-pr). The reaction mixture was refluxed for three hours in a 500ml round bottomed flask. The potassium alkoxide solution was transferred into a 500ml beaker and cooled by placing in a freezing mixture of ice and salt. Carbon disulphide (12ml, 0.2mole) was added drop by drop with stirring till the precipitation was complete. The precipitated potassium xanthate was filtered and washed with diethylether.

Mixed benzoic-dithiocarbamic anhydrides

These compounds have the general formula Y-C(S)-S-COC\textsubscript{6}H\textsubscript{5} (where Y=Me\textsubscript{2}N-, Et\textsubscript{2}N-, C\textsubscript{4}H\textsubscript{8}N-, C\textsubscript{5}H\textsubscript{10}N-, OC\textsubscript{4}H\textsubscript{8}N-), were prepared by adopting the procedures of the earlier workers. Details about the preparation are given below:

Benzoylchloride (11.6 g, 0.1 mole) was added to ice cooled aqueous solution containing 0.1mole of the appropriate sodium dithiocarbamate. An yellow oily layer was formed immediately. On vigorous shaking for a few minutes, yellow crystals of mixed benzoic-dithiocarbamic anhydride separated out. The crude product was washed a few times with distilled water and finally with methanol. It was further purified by crystallisation from a mixture of n-hexane and diethylether.
These mixed anhydrides decompose on keeping to the corresponding amides with the loss of carbon disulphide. Further these decompositions are reported to be enhanced by light.\(^ {182}\) Therefore, the anhydrides were prepared afresh everytime for subsequent synthetic work.

**Mixed benzoic-xanthic anhydrides**

The mixed benzoic-xanthic anhydrides having the general formulae \(R{-}O{-}C(S){-}S{-}COC_6H_5\); were prepared by the procedure reported in the literature \(^ {184}\): Potassium alkylxanthate (0.1 mole) was dissolved in water and crushed ice was added. To this was added benzoylchloride (11.6ml, 0.1mole) drop by drop with vigorous shaking. The benzoylated product was extracted into the diethylether medium and dried using anhydrous sodium sulphate. The ether solution was filtered and the anhydride was separated as a yellow liquid by the evaporation of ether in vacuum.

2.2. Elemental analysis

**Estimation of metal ions**

In all the cases, the organic part of the complexes were completely eliminated before estimation of metals. A uniform procedure (except for the mercury complexes) was adopted for this purpose. A known weight of the complex (0.1-0.5mg) was treated with concentrated nitric acid (25ml) and bromine in carbon tetrachloride (20ml). This mixture was kept for more than
three hours. It was then evaporated to dryness on a water bath and converted to its sulphate by fuming with few drops of sulphuric acid two or three times. The resulting metal sulphate was dissolved in water, and this solution was used for the analysis of metal.

Metal analyses were carried out using standard procedures. Chromium in the solution was estimated using standard ferrous ion solution, after oxidising to dichromate using potassium persulphate and a little silver nitrate (catalyst). Manganese and nickel were estimated by EDTA method using Eriochrome Black T as indicator. A back titration procedure was adopted for the estimation of nickel. Iodometric method was employed for the estimation of copper in the complex.

Gravimetric procedures were adopted for the estimation of iron and nickel. Iron in the complex was estimated by precipitating the metal with ammonia solution and igniting the resulting hydroxide to the ferric oxide. Cobalt was estimated by precipitating it as [Co(Py)$_2$(SCN)$_2$] using ammonium thiocyanate and pyridine.

Halogen content was determined by peroxide fusion of the sample, followed by volumetric estimation using Volhard's method. The percentage of nitrogen present in the ligand and also in the complexes was determined by Kjeldahl's method. For sulphur estimation, the complexes were fused with Na$_2$CO$_3$ and Na$_2$O$_2$ and the
resulting sulphate was determined gravimetrically as barium sulphate.

2.3. Physical measurements

Conductivity measurements

The molar conductance of the complexes in nitrobenzene was determined at 28±2°C using a ELICO PR 9500 conductance bridge with a dip type cell and a platinum electrode. The concentration of the solutions used were about 10⁻³M.

Magnetic susceptibility measurements

The measurements were carried out using solid samples at room temperature, 28±2°C, on a Gouy type balance. The Gouy tube was standardised using Hg[Co(SCN)₄]₂, as recommended by Figgis and Nyholm 186. The effective magnetic moment, was calculated using the equation,

\[ \mu_{\text{eff.}} = 2.84 \left( \chi_M^{\text{corr.}} T \right)^{1/2} \text{ BM} \]

where \( \chi_M^{\text{corr.}} \) is the molar magnetic susceptibility corrected for diamagnetism of other atoms in the complex using Pascals constants 187 and \( T \) is the temperature (in °K).

EPR spectral measurements

The EPR spectra of a few complexes in chloroform were obtained at room temperature using Varian E-112 X/Q band EPR
spectrometer. Samples are taken in capillary tubes for the measurements. Spectra were calibrated using diphenylpicryl-hydrazyl (DPPH) as a field marker.

Electronic spectral measurements

Electronic spectra were recorded in solutions (in the cases of soluble complexes) or in the solid state by a mull technique following a procedure recommended by Venanzi et al. Mull spectra were recorded as follows. Samples were prepared in nujol and smeared over Whatman filter paper No.1. Reference filter paper was prepared by smearing a drop of nujol. The two filter paper bits were placed in the two windows of the spectrometer and the spectra were scanned in the desired region. Solution spectra were recorded using matched one cm quartz cells. The spectra were recorded on a Hitachi U-3410 spectrophotometer or on a Shimadzu UV-160A spectrophotometer.

Infrared spectral measurements.

Infrared and far infrared spectra of the complexes were recorded on Perkin Elmer 983 recording spectrometer. The spectra were recorded in the infrared region with the samples distributed in potassium bromide matrix and in the far infrared region with the samples smeared on polyethylene films.

Proton NMR spectral measurements

The proton nuclear magnetic resonance spectra of complexes, which have got sufficient solubility in chloroform, were taken in CDCl₃ using Hitachi R-600 FT NMR spectrophotometer. Tetramethylsilane (TMS) was employed as an internal reference.