

## CHAPTER

# 2

## General Experimental Methods and Techniques

**I**n this chapter an outline of the materials, procedures and various physicochemical techniques employed is presented.

### 2.1 Materials

The various metal salts used in the present investigation, like cupric chloride dihydrate, cupric sulphate pentahydrate and cupric nitrate hexahydrate, were of AR grade and obtained from B.D.H. (India). Cupric perchlorate hexahydrate was prepared from cupric carbonate by reacting with perchloric acid (50%) and crystallising the salt from the resulting solution over a steam bath.

The solvents used such as chloroform, acetonitrile, methanol, benzene, tetrahydrofuran and acetone were of commercial grade but were purified according to standard procedures. DMF of HPLC grade procured from Sisco Chemicals (India) and diethylether of Sarabhai Chemicals (India) were used as such.

Methylamine and ethylamine were obtained as 40% and 70% aqueous solutions, respectively from Merck Schuchardt. n-Butylamine and benzylamine were procured from S.D. Fine Chem (India). o-Aminophenol and p-aminophenol were of Fluka and 4-aminocantipyrine from Aldrich.

Aniline, ortho, meta and para-toluidines, meta and para-chloroanilines, ortho- and para-anisidines, glycine, phenyl alanine, ethylene diamine, acetyl acetone, benzoyl acetone, 8-hydroxy quinoline, salicylaldehyde, carbon disulphide and benzoyl chloride used for the preparation of various dithiocarbamic acid derivatives and metal complexes were of either Merck or B.D.H. The mineral acids, barium chloride and potassium dichromate were of AR grade. Sodium hydroxide, ammonia, acetic acid, potassium iodide and sodium thiosulphate were either Merck or B.D.H. sample.

The chloromethylated polystyrene of Aldrich/Fluka of mesh size 400-600  $\mu$  was dried in an oven below 100°C. This is known to contain 4.2 mM of chlorine per gram.

## 2.2 Preparative details

### 2.2.1 *Dithiocarbamate ligands*

A solution of carbondisulphide in acetone was added to an equimolar quantity of the corresponding amine dropwise. Required quantity of NaOH dissolved in minimum quantity of water was then added to the above solution while stirring. The sodium salt of the dithiocarbamate thus formed is not tried to separate in solid form. This solution as such is used for the study of interaction with cupric ions. Dithiocarbamate ligands derived from ethylamine, n-butylamine and benzylamine were prepared by this method. Also, ammonium salt of BuHDtc in the solid form was prepared by the reported method<sup>1</sup> for the spectral characterisation of a typical ligand.

A solution of carbondisulphide in DMF water mixture (2:1 v/v) was added dropwise to an equimolar quantity of the corresponding amine with stirring, keeping the solution cooled in cold water. Equimolar quantity of sodium hydroxide dissolved in minimum quantity of water was then added to the above solution dropwise with stirring. This solution was washed with ether and dissolved ether was removed by suction. Dithiocarbamates derived

from aniline, ortho, para and metatoluidines, ortho and para anisidines, ortho, meta and para chloroanilines and 4-aminoantipyrine were prepared by this method.

Solid ammonium dithiocarbamate was prepared from freshly distilled aniline as described in the literature.<sup>1</sup> Solid ammonium PhHDtc was necessary for interaction studies in non aqueous media.

Dithiocarbamate derived from glycine and phenyl alanine were prepared by dissolving a weighed quantity of the crystalline amino acid in required quantity of aqueous sodium hydroxide with stirring. This solution was mixed with some DMF and equimolar quantity of carbondisulphide was added dropwise with stirring. The ligand solution was washed with ether and dissolved ether was expelled by suction.

### 2.2.2 *Polymer supported primary amines*

Merrifield resin (2% crosslinked-chloromethyl polystyrene) was dried in an oven below 100°C overnight. The resin suspended in dioxan was refluxed with five fold excess of ethylene diamine in presence of pyridine for 9 h. The product was filtered, purified and dried in vacuum.

Merrifield resin dried in an air oven below 100°C overnight was suspended in DMF. The suspension of the resin was heated with five fold excess of ortho hydroxyaniline in presence of pyridine with stirring at about 80°C for 15 h, filtered, purified and dried in vacuum.

Polymer bound p-hydroxyaniline was prepared using Merrifield resin and p-hydroxyaniline by the same procedure as described above.

### 2.2.3 *Polymer supported primary amine dithiocarbamates*

To the polymer supported ethylene diamine suspended in acetone was added calculated amount of CS<sub>2</sub> and NaOH solution and stirred for 15 min so

that ethylene diamine function formed monodithiocarbamate. The resin, after the reaction, was filtered, purified and dried in vacuum. IR spectrum of the sample showed the formation of dithiocarbamate on the polymer support.

Calculated amount of CS<sub>2</sub> and sodium hydroxide solution were added to the polymer supported o-hydroxyaniline suspended in acetone and stirred for 1 h. The resin was filtered, purified and dried in vacuum. IR spectrum of the sample indicated the presence of dithiocarbamate function.

The polymer bound p-hydroxyaniline-dithiocarbamate was prepared from the polymer appended p-hydroxyaniline by the same procedure as described above.

## 2.3 Elemental analysis

### 2.3.1 Copper

Weighed quantity (0.1 g) of the copper complex was digested using concentrated sulphuric acid and perchloric acid. The resulting clear solution was evaporated to dryness and the residue was then extracted with distilled water into an iodine flask. The resulting Cu<sup>2+</sup> solution was brought to a pH of 4-5.5 by adding ammonia solution followed by acetic acid. The estimation of copper was done by iodometric titration.<sup>2</sup>

### 2.3.2 Sulphur

The estimation of sulphur content was carried out by gravimetric method. The sulphur in the complex was oxidised to sulphate using Br<sub>2</sub> followed by conc. HNO<sub>3</sub>. Nitrate ion was removed by evaporating the solution by adding large excess of HCl. The sulphate was then precipitated as BaSO<sub>4</sub> by adding hot solution of BaCl<sub>2</sub> solution with constant stirring.<sup>2</sup>

### 2.3.3 Carbon, hydrogen and nitrogen

The determination of percentage of carbon, hydrogen and nitrogen in the complexes was carried out using Heraeus CHN rapid analyser.

### 2.3.4 Chlorine capacity of polymer resin

Weighed quantity of chloromethylated polystyrene was fused with pure anhydrous pyridine. This was followed by the addition of conc.  $\text{HNO}_3$  and known volume of excess standard  $\text{AgNO}_3$  solution. The unreacted  $\text{AgNO}_3$  was estimated by Volhard's method.<sup>2</sup>

## 2.4 Spectral methods

*IR spectra:* The spectra were recorded using Shimadzu IR-470 spectrophotometer operating in the range of  $4000\text{--}400\text{ cm}^{-1}$ , the samples being made as KBr pallets using well dried potassium bromide. Spectra in the range of  $500\text{--}100\text{ cm}^{-1}$  were recorded in a Bruker IFS 66 V FT-IR spectrophotometer using polyethylene powder.

*Electronic spectra:* A Shimadzu -UV-160 A spectrophotometer having the spectral range  $1100\text{--}200\text{ nm}$  was used for electronic spectral studies. The spectra were recorded using nujol mull of the solid samples.

*$^1\text{H}$ NMR Spectra:* The proton NMR spectra of the compounds were recorded on a Jeol NMR spectrophotometer and also a Bruker WH 270 MHz FT NMR spectrophotometer using tetramethylsilane as internal standard.  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  were used as solvents.

*EPR Spectra:* The EPR spectra were recorded on a Varian E-112 EPR spectrometer. The organic radical DPPH was used as the 'g' marker. The samples were in the bead form for polymer supported dithiocarbamate complexes and the spectra were recorded without any further diamagnetic dilution. The measurements were made at room temperature.

## 2.5 Other analytical methods

### 2.5.1 *Molecular mass determination*

Molecular masses were determined in nitrobenzene by cryoscopic method using a Beckmann thermometer.

### 2.5.2 *Magnetic susceptibility*

Magnetic susceptibility of the complexes were measured at room temperature ( $28 \pm 2^\circ\text{C}$ ) using Gouy Balance with mercury(II) tetrathiocyanatocobaltate(II) as calibrant.

### 2.5.3 *Thermogravimetry*

The thermal experiments were carried out using either Delta Series TGA 7 thermal analyser or Seiko thermal analyser in an atmosphere of dry nitrogen, from room temperature to about  $800^\circ\text{C}$ . The kinetic parameters were calculated using a computer programme.

## References

1. C. C. Hadjikostas, G. A. Katsoulos and S. Shakhathreh, *Inorg. Chim. Acta*, **133**, 129 (1987).
2. A. I. Vogel, *A Text Book of Quantitative Inorganic Analysis*, ELBS, London, 1961.