

CONTENTS

| | Page No. |
|--|----------|
| CHAPTER 1 | |
| Thiosemicarbazones and their transition metal complexes: a brief prologue | |
| 1.1. General introduction | 1 |
| 1.2. Bonding and stereochemistry | 3 |
| 1.3. Characterization techniques | 8 |
| 1.3.1. Estimation of carbon, hydrogen and nitrogen | 8 |
| 1.3.2. Magnetic susceptibility measurements | 8 |
| 1.3.3. IR spectroscopy | 10 |
| 1.3.4. Electronic spectroscopy | 10 |
| 1.3.5. EPR spectroscopy | 11 |
| 1.3.6. NMR spectroscopy | 13 |
| 1.3.7. X-ray crystallography | 13 |
| 1.4. Significance of thiosemicarbazones and their metal complexes | 14 |
| 1.5. Objective and scope of the present work | 17 |
| References | 18 |
| CHAPTER 2 | |
| Synthesis and characterization of thiosemicarbazone ligands | |
| 2.1. Introduction | 24 |
| 2.2. Experimental | 26 |
| 2.2.1. Materials | 26 |
| 2.2.2. Synthesis of ligand precursors | 26 |
| 2.2.3. Synthesis of ligands | 28 |
| 2.3. Characterization techniques | 30 |
| 2.3.1. X-ray crystallography | 30 |
| 2.4. Results and discussion | 32 |
| 2.4.1. Crystal structure of H_2L^2 | 32 |
| 2.4.2. IR spectra | 37 |
| 2.4.3. Electronic spectra | 39 |
| 2.4.4. 1H NMR spectra | 40 |
| References | 45 |
| CHAPTER 3 | |
| Synthesis, spectral and structural studies of Cu(II) complexes of N(4)-ring incorporated thiosemicarbazones of aromatic aldehydes | |
| 3.1. Introduction | 48 |
| 3.2. Experimental | 49 |
| 3.2.1. Materials | 49 |

| | | |
|--------|--|----|
| 3.2.2. | Synthesis of the complexes | 49 |
| 3.2.3. | Physical measurements | 51 |
| 3.2.4. | X-ray crystallography | 52 |
| 3.3. | Results and discussion | 53 |
| 3.3.1. | Crystal structure of [CuL ⁴ bipy] | 54 |
| 3.3.2. | IR spectra | 59 |
| 3.3.3. | Electronic spectra | 64 |
| 3.3.4. | EPR spectra | 67 |
| | References | 75 |

CHAPTER 4

Synthesis, spectral and structural studies of Ni(II) complexes of N(4)-ring incorporated thiosemicarbazones of aromatic aldehydes

| | | |
|--------|--|-----|
| 4.1. | Introduction | 78 |
| 4.2. | Experimental | 79 |
| 4.2.1. | Materials | 79 |
| 4.2.2. | Synthesis of the complexes | 79 |
| 4.2.3. | Physical measurements | 81 |
| 4.2.4. | X-ray crystallography | 82 |
| 4.3. | Results and discussion | 84 |
| 4.3.1. | Crystal structures of the compounds [NiL ² py], [NiL ² α-pic] and [NiL ² β-pic] | 86 |
| 4.3.2. | Crystal structure of the compound [Ni ₂ L ₂ phen] | 96 |
| 4.3.3. | IR spectra | 102 |
| 4.3.4. | ¹ H NMR Spectra | 107 |
| 4.3.5. | Electronic spectra | 110 |
| | References | 114 |

CHAPTER 5

Synthesis and spectral studies of Co(III) complexes of salicylaldehyde N(4)-ring incorporated thiosemicarbazones: crystal structure of a sulfenato complex

| | | |
|--------|---|-----|
| 5.1. | Introduction | 117 |
| 5.2. | Experimental | 118 |
| 5.2.1. | Materials | 118 |
| 5.2.2. | Synthesis of the complexes | 118 |
| 5.2.3. | Physical measurements | 120 |
| 5.2.4. | X-ray crystallography | 120 |
| 5.3. | Results and discussion | 121 |
| 5.3.1. | Crystal structure of the compound [Co(L ⁴ O)phenN ₃] | 123 |
| 5.3.2. | IR spectra | 129 |
| 5.3.3. | Electronic spectra | 134 |
| | References | 137 |

CHAPTER 6

Synthesis, spectral and structural studies of Zn(II) complexes of salicylaldehyde N(4)-ring incorporated thiosemicarbazones

| | | |
|--------|--|-----|
| 6.1. | Introduction | 139 |
| 6.2. | Experimental | 140 |
| 6.2.1. | Materials | 140 |
| 6.2.2. | Synthesis of the complexes | 140 |
| 6.2.3. | Physical measurements | 142 |
| 6.2.4. | X-ray crystallography | 142 |
| 6.3. | Results and discussion | 144 |
| 6.3.1. | Crystal structure of the compound [Zn(HL ²) ₂] | 145 |
| 6.3.2. | IR spectra | 149 |
| 6.3.3. | Electronic spectra | 153 |
| 6.3.4. | ¹ H NMR spectra | 156 |
| | References | 160 |

CHAPTER 7

Synthesis and spectral studies of Cd(II) complexes of N(4)-ring incorporated thiosemicarbazones

| | | |
|--------|-------------------------------|------------|
| 7.1. | Introduction | 163 |
| 7.2. | Experimental | 164 |
| 7.2.1. | Materials | 164 |
| 7.2.2. | Synthesis of the complexes | 164 |
| 7.2.3. | Physical measurements | 165 |
| 7.3. | Results and discussion | 165 |
| 7.3.1. | IR spectra | 166 |
| 7.3.2. | Electronic spectra | 170 |
| 7.3.3. | ¹ H NMR spectra | 172 |
| | References | 176 |
| | Summary and conclusion | 178 |