

Summary and conclusion

This thesis describes the synthesis, structural and spectral characterization of four *N*(4)-ring incorporated thiosemicarbazones of benzaldehyde, 2-hydroxybenzaldehyde and 4-methoxybenzaldehyde and their metal complexes.

Chapter 1 gives a prologue of the bonding and stereochemistry of the thiosemicarbazones. The different analytical and spectroscopic techniques used for the analysis of the ligands and metal complexes are discussed.

Chapter 2 deals with the synthesis of four thiosemicarbazone ligands. The ligands synthesized are:

- benzaldehyde 3-hexamethyleneiminylthiosemicarbazone [HL¹]
- 2-hydroxybenzaldehyde 3-hexamethyleneiminylthiosemicarbazone [H₂L²]
- 4-methoxybenzaldehyde 3-hexamethyleneiminylthiosemicarbazone [HL³]
- 2-hydroxybenzaldehyde 3-tetramethyleneiminylthiosemicarbazone [H₂L⁴]

Crystal and molecular structure of the ligand H₂L² was described in detail. Thiosemicarbazones are synthesized by adapting a three step procedure reported elsewhere. The ligands are characterized by elemental analyses, IR, UV and ¹H NMR techniques. H₂L² crystallizes with one molecule per asymmetric unit into triclinic crystal system with a space group of *P2₁/n*. The molecule adopts *E* configuration about azomethine bond. The crystal structure data indicated that the ligand exists in the thione form.

Chapter 3 describes the synthesis of ten copper(II) complexes (**1-10**) using the four types of ligands. These are characterized by partial elemental analyses, IR, UV-vis and EPR spectra. Single crystal X-ray diffraction studies of one of the

complexes [CuL⁴bipy] (**10**) were carried out. The copper in the mononuclear complex is five coordinated and is having an approximate square pyramidal (SPY) geometry. The copper centre is coordinated by the phenolato oxygen, O1, azomethine nitrogen, N1, and the thiolato sulphur, S1, of the thiosemicarbazone and the pyridine nitrogens, N5 and N4, of bipyridine. Magnetic moments of the complexes were calculated from magnetic susceptibility measurements. Mononuclear Cu(II) complexes exhibit magnetic moments in the range 1.5–2.05 B.M, which are close to their spin-only value. Magnetic moment of binuclear Cu(II) complex [(CuL²)₂] (**2**) is 1.25 BM which is in the range of 1.15–1.40 BM, found for binuclear complexes. The EPR spectra of all the Cu(II) complexes were recorded both in polycrystalline state at 298 K and in DMF at 77 K. The g values and the various EPR spectral parameters were calculated. The g values calculated indicate that in all the complexes the unpaired electron is present in the d_{x²-y²} orbital. In the electronic spectral studies, the *d-d* transitions are found to be broad. So the three *d-d* transitions could not be resolved. IR spectral data indicates that the complexes with ONS donor ligands are tridentate coordinated through phenolic oxygen, azomethine nitrogen and thione/thiolate sulfur atoms and with NS donor ligands through azomethine nitrogen and thiolate sulfur atoms.

Chapter 4 includes the synthesis of ten nickel(II) complexes (**11-20**) using the four types of ligands. It also describes the X-ray diffraction studies of [NiL²py] (**13**), [NiL²α-pic] (**14**), [NiL²β-pic] (**15**) and [Ni₂L²₂phen] (**17**) of the complexes. The complexes **13**, **14** and **15** have distorted square planar structure and compound **17** is a typical binuclear complex having two types of coordination centers and also having different spin states. It is discussed in detail in this chapter. All the complexes except **17** are diamagnetic due to square planar nature of the complexes. The reason for paramagnetism in the compound **17** may be due to the presence of phenanthroline coligand present in the molecule. But the magnetic moment is

lower compared to the octahedral Ni(II) complexes. Some of the magnetic moments may be cancelled due to square planar coordination. IR, NMR and electronic spectral studies are also done.

Chapter 5 represents the synthesis, structural and spectral characterization of five Co(III) complexes (**21-25**). The thiosemicarbazones, heterocyclic bases viz., phenanthroline/bipyridine and azide/potassium thiocyanate ion act as ligands. Magnetic susceptibility measurements at 293 K suggest that the compounds are diamagnetic indicating the oxidation of cobalt(II) to cobalt(III) and hence corresponds to d^6 ion in strong field. Attempts to prepare the single crystals of the Co(III) compounds resulted in a sulfenato complex due to oxidation of thiol in the thiosemicarbazone moiety. In complex $[\text{Co}(\text{L}^4\text{O})\text{phenN}_3]$ (**24**), during the course of the synthetic reaction, the thiosemicarbazone may undergo oxidation at the sulfur center whereby it is converted into sulfenate, and the transformed thiosemicarbazone is coordinated to cobalt as a dianionic tridentate ONS donor. The oxidation at sulfur depends on the nucleophilicity of the sulfur atom and it is assumed that there is at least some π - back bonding character in the M-S bond. The coordination around the cobalt metal centre is found to be distorted octahedral. IR and electronic spectral studies are also done.

Chapters 6 and 7 portray the synthesis and characterization of ten zinc (**26-35**) and five cadmium metal complexes (**36-40**) of thiosemicarbazones. All the zinc complexes are prepared from ONS donor thiosemicarbazones and cadmium complexes are prepared from ONS/NS donor thiosemicarbazones. It was possible to isolate single crystals of $[\text{Zn}(\text{HL}^2)_2]$ (**26**) and it is studied in detail. The ligands coordinate to the Zn(II) ion, through azomethine nitrogen and thiolate sulfur atoms of the deprotonated form after thiolation, to form a highly distorted tetrahedral geometry. The phenolic group of the ligand is retained as such and is placed away

from the metal centre. All the complexes are diamagnetic as expected. These are characterized by elemental analysis, IR, electronic and ^1H NMR spectra.

Curriculum Vitae

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RESEARCH PUBLICATIONS/COMMUNICATED

1. Salicylaldehyde 4,4'-(hexane-1,6-diyl)-thiosemicarbazone, L. Latheef,
M.R.P. Kurup, E. Manoj, Acta Crystallogr. C 62 (2006) 16.

2. Synthesis and spectral characterization of zinc(II) complexes of N(4)-substituted thiosemicarbazone derived from salicylaldehyde: Structural study of a novel –OH free Zn(II) complex, L. Latheef, M.R.P. Kurup, E. Manoj, *Polyhedron* 26 (2007) 4107.
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5. Spectral studies of cobalt(III) salicylaldehyde N(4)-ring incorporated thiosemicarbazone complexes: crystal structure of a sulfenato complex, Leji Latheef, M.R.P. Kurup, Communicated.
6. Synthesis, spectral and structural studies of Ni(II) complexes of ONS donor thiosemicarbazone ligands, Leji Latheef, E.B. Seena, M.R.P. Kurup, Communicated