SYNOPSIS OF THE THESIS ENTITLED

METAL COMPLEXES OF AZO-DERIVATIVES OF PYRAZOLONES AND
β-DIKETO COMPOUNDS

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Azoderivatives of pyrazolones and β-diketones have generated interest in researchers from the early years of 19\textsuperscript{th} century. The importance of these compounds lies in their dyeing property. Many of the dyes used yester years were azo compounds. The metal complexes of these azo compounds are also found to be acting as dyes which are light fast due to their stable nature. Pyrazolones possess exceptional medicinal properties too.

The present work is intended for a systematic analysis of the versatile ligational behaviour of azo pyrazolones and azo beta diketones. The paradigm of the investigation is centred around the synthesis of the ligands and their coordination behaviour towards transition metals. Priority has been given to the structural details of the ligands and their metal complexes. The photophysical behaviour of one of the ligands when complexed with europium is also analysed.

A total of twenty two complexes have been synthesised and characterised of which twenty were of the first transition series (Cr, Fe, Co, Ni, Cu, Zn) and are synthesised to study the ligational behaviour of the ligands towards these metals. Two rare earth (europium) complexes were
synthesised, one with phenylazo dimedone and the other with dimedone to analyse and compare their photophysical behaviour.

The text of the thesis evolves in two parts: Part I comprises six chapters and describes the synthesis and characterization of several complexes of the first transition series. Part II consists of the synthesis, characterization and photophysical behaviour of the europium complexes.

PART I
SYNTHESIS AND CHARACTERIZATION

CHAPTER I : INTRODUCTION

This chapter outlines the general preamble to azo derivatives of pyrazolones and β-diketones. An account of the structural aspects of the substituent effects, azo-hydrazone keto-enol tautomerism and denticity of the ligands are provided with ample literature citation to substantiate the details and are included in Section A. Section B is exclusively set apart for the versatile application of the ligands and their metal complexes in day to day life. All the examples are supported with appropriate references of previous works. Section C mentions the objectives and scope of the present work.
CHAPTER II: MATERIALS AND METHODS

The reagents used, general procedures adopted and the instrumental facilities availed are presented in this chapter. A brief note is also included on the operating modes of the different instruments.

CHAPTER III: SPIRO-5,5-DIMETHYL-1,2,3-CYCLOHEXANETRIONE-2-PHENYLHYDRAZONE AND ITS METAL COMPLEXES

This chapter elaborates the synthesis and characterization of spiro-5,5-dimethyl-1,2,3-cyclohexanetrione-2-phenylhydrazone (phenylazodimedone) (LH) and its Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes. The ligand has been characterized by elemental analysis, electronic, IR, \(^1\)H NMR and mass spectral techniques. A structural depiction based on single crystal XRD method has also been included. The five metal complexes have been characterized by elemental analyses, electronic and IR spectral tools. The \(^1\)H NMR of the diamagnetic Zn(II) complex and mass spectrum of Cu(II) complexes were taken. Magnetic moments of the paramagnetic complexes were calculated and the general formulae of the complexes were found to be [ML\(_2\)] for bivalent metals like Co(II), Ni(II), Cu(II) or Zn(II) and [ML\(_3\)] for the trivalent Fe(III), where L = monoanion of the ligand.
CHAPTER IV : 3-METHYL-4-(PHENYLHYDRAZONO)-1-PHTHALAZINYL-2-PYRAZOLIN-5-ONE AND ITS METAL COMPLEXES

The ligational behaviour of 3-methyl-4-(phenylhydrazono)-1-phthalazinyl-2-pyrazolin-5-one (N-1 phthalazinyl phenylazo pyrazolone) (LH) with four metal ions, Cr(III), Fe(III), Ni(II) and Cu(II) was analysed in the chapter. Copper(II) formed two complexes different in physico-chemical behaviour. The ligand has been characterized by elemental analysis, electronic, IR, $^1$H NMR and mass spectral techniques. The metal complexes were characterized by elemental analyses, magnetic susceptibility studies, electronic and IR spectral measurements. The two copper complexes have been subjected to mass spectral and thermal (TG/DTG) studies. The complexes were found to be possessing octahedral geometry with general formulae \([M(LH)X_3]\) where \(M = \text{Cr(III)}, \text{Fe(III)}, \text{LH = ligand, } X = \text{halide ion,}\) \([M(LH)(OAc)_2(H_2O)]\) where \(M = \text{Ni(II) / Cu(II)}\) and the brown copper complex with the formula \([\text{CuL(OAc)}(H_2O)_2]\) where L is the mono anion of the ligand.

CHAPTER V : 3-ACETYL-5-PHENYLAZO-4-HYDROXY-6-METHYL-PYRAN-2-ONE AND ITS METAL COMPLEXES

This chapter deals with the synthesis and characterization of 3-Acetyl-5-phenylazo-4-hydroxy-6-methyl-pyran-2-one (phenylazo dehydroacetic acid) (LH) and its five metal complexes with Cr(III), Fe(III), Ni(II), Cu(II) and
Zn(II). The ligand has been characterised by elemental analysis, electronic, IR, $^1$H NMR and mass spectral techniques. The complexes have been characterised by elemental analyses, magnetic susceptibility measurements, electronic and IR spectra. The $^1$H NMR spectra of the diamagnetic Zn(II) complex and the mass spectrum of Cu(II) complex have also been analysed. The TG/DTG analyses of Cu(II) and Ni(II) complexes were also performed. Based on the above studies, complexes of Cr(III) and Fe(III) were found to be having general formula [ML$_2$X(H$_2$O)], where X = Cl and [ML$_2$(H$_2$O)$_2$] for Ni(II). ML$_2$ for M = Zn(II) and [ML(OAc)(H$_2$O)], where M = Cu(II) and L in all cases is the monoanion of ligand.

CHAPTER VI : 2,3-DIMETHYL-4-(2-HYDRAZONO-SPIRO-5,5-DIMETHYL-1,3-CYCLO-HEXANEDIONO)-1-PHENYL-3-PYRAZOLIN-5-ONE AND ITS METAL COMPLEXES

In this chapter the synthesis and characterization of the 2,3-Dimethyl-4-(2-hydrazone-spiro-5,5-dimethyl-1,3-cyclohexanediono)-1-phenyl-3-pyrazolin-5-one (antipyrinylazodimedone) (LH) and its Cr(III), Fe(III), Ni(II), Cu(II) and Zn(II) complexes have been described. The ligand has been characterized by elemental analysis, electronic, IR, $^1$H NMR and mass spectral analyses. The complexes have been characterized by elemental analyses, electronic, IR spectra and magnetic susceptibility measurements. The $^1$H NMR spectrum of the diamagnetic Zn(II) complex and the mass
spectra of Cu(II) and Zn(II) complexes have also been analysed. The complexes were assigned formulae [ML$_2$]Cl where M = Cr(III), [MLCl$_2$] where M = Fe(III) and ML$_2$ where M = Ni(II) / Cu(II) or Zn(II). L = monoanion of the ligand LH.

PART II

PHOTOPHYSICAL STUDIES

CHAPTER I: INTRODUCTION

The reminiscence of the photoluminescent behaviour of azodyes and rare earth metal complexes of β-diketones are highlighted in this chapter. The rare earth metal, europium with its remarkable luminescent property has been chosen for the study.

CHAPTER II: EUROPIUM CHELATE AS EMITTER IN OPTICAL DEVICES

The exposition of two europium complexes, one with phenylazodimedone and the other with dimedone in their photophysical behaviour have been compared in this chapter. Quantum yield studies of the complexes have been conducted. The incorporation of the complexes into four different polymers EVA, PS, PMMA and PEG and the absorption and the luminescence studies of the doped polymer films have been carried out. Other studies like IR, TG/DTG/DTA and SEM have also been conducted to
find out the nature of doping and the thermal stabilities of the polymer films. The studies have been attempted at to explore their possible applications as active layer in OLEDs/POFA.

References

The references are given in serial order at the end of each chapter in Part I and at the end of Part II.