Synthesis, Characterization and Biological Activity of Transition Metal Complexes of Substituted Acid Hydrazides

By

JAIPAL SINGH

Dean, P.G.S.

Thesis submitted to CCS Haryana Agricultural University in partial fulfilment of the requirements for the

degree of

Doctor of Philosophy

IN

CHEMISTRY

Department of Chemistry & Biochemistry

CCS Haryana Agricultural University

HISAR

1992

..... To

My

Sister

&

Brother

CERTIFICATE-I

This is to certify that the thesis entitled **"Synthesis Characterization and Biological Activity of Transition Metal Complexes of Substituted Acid Hydrazides"** submitted for the degree of Doctor of Philosophy in the subject of Chemistry to the CCS Haryana Agricultural University is a bonafide research work carried out by **Jai Pal Singh** under my supervision and no part of this thesis has been submitted for any other degree.

The assistance and help received during the course of investigation have been fully acknowledged.

Co-Major Advisor

Major Advisor

CERTIFICATE-II

This is to certify that the thesis entitled "**Synthesis, Characterization and Biologicl Activity of Transition Metal Complexes of Substituted Acid Hydrazides**" submitted to the CCS Haryana Agricultural University in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the subject of Chemistry has been approved by the Student's Advisory Committee after an oral examination on the same, in collaboration with the external examiner.

Major Advisor 29/8/93

External Examiner 29/8/93

Co-Major Advisor

Head of the Department

Dean, Post Graduate Studies 8/9

ACKNOWLEDGEMENTS

With high esteems and profound regard, I take the privilege to acknowledge the valiant efforts of Dr. M.P. Gupta, Associate Professor, Department of Chemistry and Biochemistry for his diligent guidance, generous advice, enduring interest and inexhaustible encouragement for enabling me to accomplish this work. No part of this work could have been accomplished without the sheen and inspiring guidance of my revered teacher.

I, from the bottom of my heart, owe a special debt of gratitude to Dr. Kuldip Singh Dhindsa [M.Sc.(Hons), Ph.D. (Pb.). D.H.E. (h.c.), F.R.S.C. (London, F.N.A.Sc.], Professor of Chemistry for his learned discourses. His superb guidance, educative criticism, benevolent attention and unstinted interest has been the only inspiration for me from the day one of this study.

I am covetous to thank Dr. N.K. Sangwan, Associate Professor of Chemistry for his generous, illustrious and emphatic help during the entire course of studies. I esteem the members of my advisory committee Dr. V.K. Gupta, Professor, Department of Soils, Dr. M.R. Saharan, Associate Professor of Biochemistry and Dr. S.P.S. Karwasra, Professor, Department of Soils for their constant help, constructive criticism and critical amendments during the course of study and preparation of this manuscript. My special thanks are due to Dr. Rajesh Malhotra, Assistant Professor, Department of Chemistry and Biochemistry for his wise counsel and pain-staking help throughout the course of investigation and preparation of this manuscript.

I do acknowledge the Professor & Head, Department of Chemistry and Biochemistry for providing me all the facilities during research work.

The conglomerate of my entire feeling goes to my revered parents and brother and sister for their silent wishes, everlasting inspiration and unremitting encouragement throughout the study.

I value and cherish the association with my friends Dr. Vinod, Mamta, Hem, Suman, Jyoti, Jai Singh, Satwinder, Sunil, Parveens, Ajay, Vivek, Shashi, Anil, Anita, Jagdev, Neelkamal, Anu, S.P. Sharma and Satya for their help, encouragement and moral support during the times of stress and strain. I also extend my thanks to Mr. Ram Swarup for his timely and cordial help.

Lastly, my very special thanks are due to Late Shakunt aunti for her inspiring love, care, affection and wishes during the investigation.

December 9, 1992 **(Jai Pal Singh)**

CONTENTS

****

LIST OF TABLES

LIST OF FIGURES

Fig. No.	Description
16.	Antifungal activity of compounds ML_X-ML_{XVIII} against Fusarium oxysporum.
17.	Antifungal activity of compounds ML_X-ML_{XVIII} against Colletotrichum capsicum.
18.	Antifungal activity of compounds ML_X-ML_{XVIII} against Rhizoctonia solani.
19.	Antibacterial activity of compounds ML_X-ML_{XVIII} against Escherichia coli.
20.	Antibacterial activity of compounds ML_X-ML_{XVIII} against Bacillus subtilis.

CHAPTER I

Introduction

CHAPTER-I

INTRODUCTION

The last few decades have seen an astonishingly large growth in research activity in the field of 'Inorganic Biochemistry'. This has been due to the realization of importance of the vital functions that some of the metal ions perform in biochemical and biophysical processes occurring in the cell's dynamic environment. The role these metal ions play in combination with the organic biomolecules of the cell, makes them so vital in the maintenance of living systems that life would not have been possible, at least in its present form, without the involvement of these essential components. The biological functions affected by these metal ions include the charge balance of proteins, ionic gradient across membranes, nerve impulse transmission, osmotic and buffering equilibria, biological oxygen transport, electron transport chains, redox reactions, gene expression, gene regulation and enzymatic catalysis. The metal ions act as cofactors in the enzymatic catalysis, serve as substrate binders, bring the substrate in a particular configuration and conformation suitable for catalytic activity and provide a suitable three dimensional conformation to the protein molecule as a result of charge balance and interaction with different groups. Besides, these are also involved in the catalytic processes in certain cases.

More than a dozen metal ions are now considered to be essential that perform various structural and functional roles in biology. It is, therefore, critical for the cell to acquire and maintain the levels of these metal ions within a' concentration window' where enough is present to meet the requirements

of the cell but not enough to be toxic. The low levels of the essential metal ions will lead to deficiency symptoms whereas their excess concentration as also even the low levels of non-essential metal ions termed 'villainous' metal ions may harm cells through inactivation of enzymes or by catalysing the oxidative degradation of lipids, proteins and nucleic acids (Diana and Thoman, 1990). The cell maintains a homeostatic control of metal ions via sequestration, storage and excretory mechanisms and specific metal chelators are synthesized by the cell machinery for this purpose. Ionophores, siderophores, azurins, plastocynins, ferritins, transferrins and the recently identified and studied 'Zinc binding fingers' (Sout and Summers, 1990) are some of the molecules synthesized by the living systems for this purpose.

The structural and functional aspects of biomolecules on complexation with metal ions are a function of the resultant physico-chemical manifestations arising from the interaction of these molecules with the metal ions. The configuration, conformation, stability, kinetic lability and relative metal-ligand bond distances are the key factors governing the properties of these complexes. To understand and manipulate the natural biochemical features, search is always on to isolate and characterize the natural molecules, to synthesize their analogs and to study their biochemical applications. Investigations in the field of metal-ligand interactions have proved that coordination of metal ions with synthetic organic and biomolecules may activate the ligand and/or metal ions. The metal-drug interaction studies have shown an increased efficacy and site specificity in many cases (Sorensen, 1976). The increased activity may be due to the altered transport across the lipid bilayer, change in its mechanism of action or the activation of the ligand molecule.

Change of substituents on various organic molecules in order to achieve more potent biodynamic agents is one of the thrust areas in synthetic chemistry. Various classes of compounds with varying substituents have been and are being synthesized and tried for their biological and industrial applications. Based on the differences in the mode of action, physiological deposition, metabolism and detoxification, it is possible to develop compounds with desirable characteristics like higher potency towards target organism and less toxicity to non-target organisms. The organic ligands containing nitrogen, oxygen or sulphur atoms are reported to possess a wide range of biological activities (Dey, 1974; Chaturvedi and Kansal, 1975 and Wilson et al., 1977) possibly due to the involvement of their donor sites for binding with biological receptors.

The compounds derived from hydrazine viz., the hydrazines, hydrozones and hydrazides having different substituents have been shown to exhibit a wide spectrum of biological activity in addition to industrial applications. Acid hydrazides possess antifungal (Luo et al. 1985; Sangwan et al., 1986 and Johri and Sharma, 1988), antibacterial (Romanenko et al., 1984; Bahadur et al., 1975 and Sengupta et al., 1984), antiinflammatory (Kulik et al., 1974), herbicidal (Crafts, 1964), antitumour (Haskar et al., 1971), antihypertensive (Arutyungyan et al., 1985) and nematicidal (Malik et al., 1989 and Cruickshank et al., 1982) activities. Maleic hydrazide has been used as a herbicide for the last three decades (Crafts, 1964) and it is known to inhibit the formation of RNA, decrease the protein level and change the auxin metabolism in plants (Nayler and Davis, 1950). Isonicotinic acid hydrazide is used as an antitubercular drug. Hydrazides of salicylic acid, phenoxyacetic acid, naphthalene-1-acetic acid

and benzylic acid have been reported to be potential antibacterial agents (Sengupta et al., 1984 and Aggarwal et al., 1987). Some naphthaloyal hydrazides have proved to be good herbicides (Takematru et al., 1986). Hydrazides of Meldrum's acid were evaluated for their antifungal efficacy by Luo et al., 1985 and some of these were found to be good antifungal agents. Arylsulfonylhydrazides of maleic and fumaric acids, their methyl esters, some substituted isobutyric acid hydrazides and hydrazides of (arylsulfonyl) succinamic acids exhibited antiinflammatory activity (Ramalingam and Sattur, 1989).

The presence of different substituents and varying side chain lengths have a marked effect on the biological activity of the acid hydrazides. The presence of pentadecyl side chain in the hydrazides of α-(3-pentadecylaryloxy) isobutyric acid rendered the compounds less antiinflammatory as compared to the compounds with smaller side chains (Ramalingam and Sattur, 1989). The nematicidal activity of substituted phenoxyacetic acid hydrazides was also found to be a function of functional groups on the aromatic nucleus (Malik et al., 1989).

The coordination of a metal ion with the organic ligands may alter the activity of the ligands and the resulting compounds may be more potential biodynamic agents with desirable characteristics. Herbicidal and fungicidal activities of benzoylhydrazide and salicylhydrazide were found to increase on metal coordination (Lakshmi et al., 1984). The herbicidal activity increased by 100 per cent in case of iron (II), copper (II) and manganese (II) complexes whereas, fungicidal activity improved by 80 per cent as a result of coordination.

The metal complexes of pyridine-2/4-carboxaldehyde thioisonicotinoylhydrazone proved to be better antibacterials than the ligands (Singh et al., 1984 and 1986). The copper (II), nickel (II) and cobalt (II) complexes of o-hydroxybenzaldehyde-N-salicyl/succinoyl hydrazone were better antimicrobial agents than their respective ligands (Sharma et al., 1991). Taking into consideration these and several other observations (Rainsford and Whitehouse, 1976; Pin and Xiaoping, 1989; Ghosh et al., 1984 and Parasher and Sharma, 1987), on the alteration of activity pattern of biomolecules and synthetic organic ligands on complexation with metal ions, it was considered of interest to develop some potential bioactive compounds from substituted acid hydrazides and their complexes.

The objectives of the present investigation were:

1. To synthesize some novel substituted acid hydrazides.
2. To prepare and characterize the coordination compounds of the above synthesized ligands with some first series transition metal ions.
3. To evaluate the comparative antimicrobial activity of the ligands and their complexes.

CHAPTER II

Review Of Literature

CHAPTER - II

REVIEW OF LITERATURE

Substituted acid hydrazides are promising biodynamic agents besides finding applications in industry and analytical chemistry. These compounds have potential donor sites and hence can be used as ligands for coordination with metal ions. The study of hydrazides and their coordination compounds for their physico-chemical, biochemical, biomedical and analytical applications constitutes an important area of chemistry. A brief review of literature on substituted acid hydrazides covering their diverse biological activities, effect of substitutions in the basic nucleus on their activity pattern and their coordination behaviour towards various metal ions has been presented in the following pages.

Maleic hydrazide has been used as a herbicide for the past more than three decades (Crafts, 1964). At molecular level, it has been found to inhibit the formation of RNA, decrease the protein level and change the auxin metabolism in plants as reported by Nayler and Davis (1950).

Lue et al. (1985) synthesized nineteen substituted hydrazides and observed that malonyl hydrazide was the most active hydrazide against Aspergillus and Penicillium species. In vitro antibacterial activity of several substituted phenoxyacetic acid hydrazides against Staphylococcus aureus was evaluated by Sengupta et al. (1984). The compound with substituent p-NO_2 was found to be more toxic than compounds with

substituents like o-, m- or p-Me, p-Cl and p-Br. Antimicrobial activity of hydrazides of salicylic acid, naphthalene acetic acid and benzylic acid was studied by Aggarwal et al. (1987). 8-Aminoxanthine propanoic acid hydrazides and their Schiff's bases with some aldehydes were screened for their antibacterial efficacy by Romanenko et al. (1984).

Nematicidal use of some substituted aryloxyacetic acid hydrazides was documented by Malik et al. (1989). A structure-activity relationship was established according to which the unsubstituted phenoxyacetic acid hydrazides and the acid hydrazides with chloro groups at 2- and 4-positions of the aromatic nucleus were found to be more active than those with other substituents against second stage juveniles of seed gall nematode (Anguina tritici), root knot nematode (Maloidogyne javanica) and pigeonpea cyst nematode (Heterodera cajani).

Cruickshank et al. (1982) observed a 95.80 per cent control of Tylenchorhynchus clayfoni, a nematode on corn seedling by the use of some hydrazine carboxamides. The substituted nephthoyl hydrazides were synthesized and screened for their herbicidal activity by Takematru et al. (1986). 1,4-dihydro-1-naphthoic acid phenyl hydrazide could control a wide variety of weeds in paddy fields.

Ramalingam and Sattur (1989) synthesized α-(3-pentadecylaryloxy)-isobutyric acids, their hydrazides and cyclic derivatives and evaluated these for antiinflammatory activity. The presence of pentadecyl side chain rendered the compounds less active. Arylsulfonyl hydrazides of maleic and fumaric acids were found to possess antiinflammatory, analgesic and

anticoagulant activities. 8-chlorodibenz [b,f] [1,4] oxazepine-10 (11H) - carboxylic acid hydrazides were prepared and patented as analgesics and prostaglandin antagonists by Mueller (1985). Konev et al. (1986) synthesized the hydrazide of (arylsulphonyl) succinic acid and these compounds exhibited neuroleptic, diuretic, antiinflammatory and antihypoxic activities. Synthesis and pharmacological studies of γ-hydroxycarboxylic acid hydrazides were carried out by Arutyunyan et al. (1985) who found that these compounds possessed spasmolytic and antihypertensive activity. Zhang and He (1984) synthesized some N-acyl-N-(2-indolylcarbonyl) hydrazides and evaluated these for antitubercular activity and observed that these compounds inhibited the growth of Mycobacterium tuberculosis. o-Ethyl-phenylmethanophosphonic hydrazide derivatives were found to possess better herbicidal and growth regulating properties as compared to diuron (Lachkova et al., 1985). The growth retardant activity of mono- and dihydrazides of dialiphatic dicarboxylic acids was correlated with fatty acid side chain by Aleksieva and Karanov (1987).

Gupta et al. (1983) synthesized some Schiff's base hydrazides derived from 7-hydroxycitronellal and the compounds exhibited a marginal activity as juvenile hormone for common Indian red cotton bug. The phthalic hydrazide salts were found to be plant growth regulators by Panea et al. (1984).

It is quite evident from the above studies that acid hydrazides exhibit a wide profile of biological activity which is a function of the substituents and the side chains associated with the main nucleus.

The coordination behaviour of variously substituted and biodynamically important acid hydrazides has been widely studied by several groups of researchers. Transition metal complexes of benzoyl hydrazide and salicyl hydrazide were studied for their herbicidal and fungicidal efficacy by Lakshmi et al. (1984). The study revealed growth inhibition of Cyprus tubers to the extent of 40-80 per cent at different concentration levels which may be due to the blocking of nucleic acid metabolism. The most significant observation in their study was that the inhibition was increased to around 100 per cent in case of metal complexes at 0.01 per cent concentration. The inhibition was maximum in case of Fe (II), and Cu (II) complexes of salicyl hydrazide. The complexes also exhibited fungicidal activity. Manganese (II) and cobalt (II) complexes of benzoyl hydrazide and cobalt (II), nickel (II) and copper (II) complexes of salicyl hydrazide were more potent antifungal agents than other complexes and their respective ligands. The metal complexes of maleic hydrazide have also been found to inhibit the DNA, RNA and protein synthesis in Yashid Sarcoma ascites cells under in vitro conditions (Fritz et al., 1977).

Mostafa et al. (1980, 1981 and 1985) synthesized and characterized the transition metal complexes of butyric acid hydrazide (BuH), isovelaric acid hydrazide (IvH) and isobutyric acid hydrazide (IBH). The proposed stereochemistries were assigned on the basis of magnetic and spectral data. In some cases, the ligands were found to be coordinating via carbonyl and $-NH_2$ groups, while in others, the ligands coordinated by deprotonation of the imidol form via azomethine group and the deprotonated enolic oxygen. The electronic spectral assignments and the calculation of Dq, B, β, and ν_2/ν_1 were used to predict the stereochemistry of the metal complexes.

The coordination number was found to decrease in the order BuH > IBH > IVH due to steric hinderance, while stability constants decreased in the opposite order i.e., IVH > IBH > BuH.

Rao et al. (1985) synthesized Mn (II), Co (II), Ni (II) and Cu (II) complexes of benzoylglycylhydrazide and assigned octahedral geometry for the non-ionic complexes on the basis of magnetic and spectral studies. ESR studies of copper complex indicated a very weak metal-metal interaction. Nickel (II) and cobalt (II) complexes of the hydrazide of 1-naphthylacetic acid were synthesized by Chundak et al. (1986). The physico-chemical analysis of the ligand and their complexes showed that the ligand behaved as neutral bidentate and coordinated through amido-nitrogen and the carbonyl oxygen. The complexes of general formula [$M(acac)_2$ L] [M=Co (II), Ni (II) and Zn (II) and L=2-3, 4-pyridine carboxylic acid hydrazide] were prepared and characterized by Aggarwal et al. (1984). They also calculated the ligand field parameters and assigned the high spin octahedral geometry to the complexes. Synthesis and IR spectral analysis of coordination compounds of lanthanoids with picolinic acid hydrazide were carried out by Tsintradze and Bazgadze (1986). A bidentate ligand behaviour was speculated by them.

Synthesis and structural studies of complexes of some first row transition metal ions with l-tyrosine hydrazide were undertaken by Rao et al. (1984). The complexes formed had the general formula $M(TH)_2Cl_2$, $M(TH)_2(OH)_2$ and (MTH-H) (OH). nH_2O [M=Mn (II), Co (II), Ni (II), Cu (II) and Zn (II), and n=0 or 2]. The complexes were characterized by molar conductance, magnetic susceptibility, electronic, IR and ESR spectral data.

The ligand behaved as neutral bidentate or uninegative tridentate in the complexes. Various ligand field parameters like Dq, B, β and ligand field stabilization energy were calculated to elucidate and support the proposed structures of the complexes. Copper (II) complexes were screened for antifungal activity against Rhizoctonia solani. The complex $Cu(TH)_2(OH)_2$ was more active while $Cu(TH)_2Cl_2$ and Cu (TH-H) (OH). $2H_2O$ were less active than the ligand.

Some other complexes of trivalent lanthanide ions with l-tyrosine hydrazide of the general formula $[M(TH)_3Cl_2]Cl$, where M=La (III), Pr (III) and Nd (III) were isolated and characterized by Rao and Khan (1987). The characterization of the complexes was done by elemental analysis, molar conductance, magnetic susceptibility, IR, electronic and ^1H NMR spectra. The nephelauxetic ratio, covalency and bonding parameters of $[Nd(TH)_3Cl_2]Cl$ were also calculated. The ligand was found to behave as neutral bidentate. Platinum (II) complexes of hydrazides of aspartic and glutamic acids were prepared and characterized on the basis of IR and electronic spectra, differential thermal analysis, elemental analysis and titration curves which suggested that the ligand coordinated through the amino and hydrazide carbonyl groups, the carboxylic group remaining deprotonated and uncoordinated (Bontchev et al., 1985).

The copper (II) complexes of cyclobutane-, cyclohexane- and cycloheptane carboxylic acid hydrazides, cyclopentane- and cyclohexane acetic acid hydrazide and cyclohexanebutyric acid hydrazide with the general formula $CuLSO_4.nH_2O$ (n=0-2) were prepared and characterized by

Ikekwere et al. (1989). A square planer geometry with bidentate ligand behaviour was proposed. There was no evidence to suggest the formation of polymeric species. Ali et al. (1989) investigated the complexes of phthalic hydrazide with chromium (III), manganese (II), iron (II) and copper (II). IR and electronic spectra and the magnetic data suggested an octahedral structure for all the complexes. Cobalt (II) complexes of thioacetic acid hydrazide were characterized by electronic and diffuse reflectance spectra, X-ray diffraction and thermogravimetric analysis by Saveleva and Larionov (1985). Cobalt (II), nickel (II) and copper (II) complexes of diphenylphosphonylacetic acid hydrazide were prepared and characterized by Zelentsov et al. (1986). The authors also calculated the crystal field parameters for cobalt (II) and nickel (II) complexes. An octahedral configuration was assigned to the complexes. Sallomi and Dawood (1984) synthesized complexes of indium (III) having general formulae $[In\ (LH)_3]\ X_3$, $[In\ (LH)_3X_3]$, $[In\ (LH)_2\ X_3]X$, $[In\ (LH)_2\ X_2]X$ and $[InL_3].\ 2H_2O$, where LH=R ($C_6H_4C(O)\ NHNH_2$, R=o-OH, p-MeO or p-NO_2, X=Cl, Br, NO_3 or 0.5 SO_4 and characterized by elemental analysis, IR spectra and molar conductance measurements.

Coordination behaviour of isonicotinic acid hydrazides has been reported by several workers. Rao et al. (1986) prepared the lanthanide complexes of general formula $[M(INH)_3X_3]$, where INH=isonicotinic hydrazide, X=Cl, SCN and M=La (III), Pr (III), Nd (III), Sm(III) and Gd (III). Characterization of the complexes was made on the basis of elemental analysis, molar conductance, magnetic susceptibility, IR and electronic spectral studies. The nephelauxetic ratio, covalency and bonding parameters were calculated from the electronic

spectra. IR spectral studies revealed that INH acted as a neutral bidentate chelating agent in all the complexes and thiocyanate was nitrogen coordinated. Thermochemical analysis of solid isonicotinic acid hydrazide transition metal complexes was reported by Sekkina et al. (1984). Ryakhovskikh et al. (1986) studied indium (III) complexes of nicotinic and isonicotinic acid hydrazides. The hydrazides behaved as bidentate ligands.

Azizov et al. (1986) studied the coordination compounds of manganese (II), cobalt (II) and nickel (II) formates and acetates with isonicotinic acid hydrazide and some of its derivatives. Bychkova et al. (1986) conducted a spectrophotometric study of coordination of copper (II) with hydrazides of benzoic acid and isonicotinic acid in aqueous DMF at pH 3-3.5. The investigation established the formation of deprotonated and protonated (for benzoic acid hydrazide) complexes. Stability constants of copper (II) complexes with aspartic, glutamic and isonicotinic acid hydrazides were determined by Tsvetanova et al. (1987) by pH metric titration at 25°C and ionic strength 0.1M (KNO_3). Both 1:1 and 1:2 copper (II)- ligand complexes were found to be formed. Preparation and IR absorption studies of lanthanide coordination compounds based on thiocynates and bromides with nicotinic acid hydrazides was reported by Tsintradze et al. (1985). The ligands behaved as bidentate in bromide complexes coordinating through the hydrazine nitrogen and carbonyl oxygen atoms and as monodentate in case of thiocynate complexes coordinating through the hydrazine nitrogen only. The presence of coordinated and uncoordinated water was also established. Tsintradze et al. (1986) studied the coordination compounds of iron (II)

and iron (III) with pyridine carboxylic acid hydrazides and derivatives of isonicotinic acid hydrazide.

Machkhoshvili et al. (1987) studied the cerium (III) bromide complexes of the general formula $CeL_4Br_3 . nH_2O$, where L=acetic-, capronic-, salicylic- and anisic acid hydrazides. The ligands were found to behave as bidentate coordinating through the primary amine nitrogen and carbonyl oxygen atoms. Coordination complexes of capric acid hydrazide with cobalt (II), nickel (II) and copper (II) were prepared by Chundak et al. (1987). The paramagnetic high spin bis-and tris- (ligand) chelates were assigned octahedral configuration based upon the bidentate coordination of three neutral hydrazine molecules.

Complexes of dihydrazides of various acids have also been extensively explored. Srivastava et al. (1987) studied the aliphatic acid dihydrazide derivatives of dicyclopentadienylzirconium (IV) dichloride and their reaction with β-diketones. The complexes had a general formula $[Cp_2Zr\ (L)]$ and $[Cp_2Zr\ (LH)_2]Cl_2$. The aliphatic acid dihydrazides used in the study were oxalic acid-, succinic acid- and adipic acid dihydrazides. The acid hydrazides behaved as bidentate chelating agents. All the complexes contained terminal amino or hydrazino nitrogen atoms with an unshared electron pair, enabling nucleophilic condensations. These complexes cyclised with β-diketones in the presence of glacial acetic acid to yield macrocyclic ligand complexes. Vardosanidze et al. (1985) studied the crystal and molecular structure of a manganese (II) sulphate complex with dihydrazide of malonic acid. The compound was found to be satisfying the orthorhombic space group conditions. The manganese atoms were in Archimedian antiprism coordinating with malonic acid dihydrazide acting as bis bidentate

bridges through their $-NH_2$ and O-groups at each end to form five membered rings. The sulphate ion and water molecules were uncoordinated. Bontchev et al. (1985) studied the palladium(II) complexes of dihydrazides of aspartic acid in 1:1 and 1:2 metal-ligand ratios. The cationic $[Pd_2L_2Cl_2]^{2+}$ complex contained bridging Cl groups. The ligand coordinated through the amino nitrogen atom adjacent to the carbonyl group and the oxygen of the carbonyl group forming a five membered ring.

X-ray structural analysis of α-and β- modifications of crystals of the manganese(II) malonic acid dihydrazide compounds was undertaken by Vardosanidze et al. (1985). The compounds satisfied the conditions for orthorhombic space groups. The manganese atom was dodecahedral with m m m m symmetry. Vardosanidze et al. (1985) synthesized the cobalt (II), manganese (II), iron (II), and nickel (II) complexes of malonic acid dihydrazide and characterized these by X-ray structural analysis. The compounds were found to be monoclinic. Coordination compounds of some 3d transition metal ions with a product of condensation of malonic dihydrazide with acetone were synthesized by Parpiev et al. (1985). The ligand behaved as tetradentate, bridging in the dimer with coordination through the two azomethine nitrogen atoms and two oxygen atoms.

Kumbhar (1986) prepared the polynuclear complexes of fumaric acid dihydrazide with copper (II), nickel (II) and cobalt (II). The octahedral complexes were obtained in which the ligand coordinated through carbonyl oxygen and amino nitrogen atoms. A polymeric octahedral structure for chloro complexes and a bridged quadricoordinate structure for sulphate

complexes were proposed. Thermogravimetric and differential thermal analysis results were also reported. Synthesis and X-ray structure analysis of the manganese (II) coordination compound of succinic acid dihydrazide was undertaken by Zhorzholiani et al. (1987). Narang and Singh (1987) synthesized some mercury (II) chloride, nitrate and thiocyanate complexes of benzoic acid hydrazide, acetonebenzoylhydrazone, oxalic acid hydrazide and oxalic acid bis (2-propylidine hydrazide), malonic acid dihydrazide and malonic acid bis (2-propylidine hydrazide). The complexes were characterized by IR spectral data, X-ray powder differaction and polarographic studies. Some of the complexes were screened for their antifungal and antibacterial activity and these were found to be more active than the ligands.

The Schiff's bases derived from acid hydrazides have good donor sites and act as potential ligands. Symal and Maurya (1986a) synthesized nickel (II), cobalt (II), copper (II), manganese (II), zinc (II), zirconium (II), oxomolybdenum (IV) and dioxouranium (VI) complexes of the Schiff's base derived from salicylaldehyde and thiophene-2-carboxylic acid hydrazide. The Schiff's base behaved as a dibasic tridentate ligand coordinating through an O, N, O donor system. The nickel (II), cobalt (II) and manganese (II) complexes exhibited normal magnetic moments at room temperature whereas, copper (II) and oxomolybdenum (IV) complexes exhibited interaction. The zinc (II), dioxouranium (VI) and zirconium (II) complexes were diamagnetic. The shifts of the ν(C=N), ν(C=O) and ν(C-O) phenolic and ν(N-N) strechings were followed to determine the donor sites of the ligand. Symal and Maurya (1986b) studied the dioxomolybdenum (VI) complexes of Schiff's bases prepared by the condensation of salicylaldehyde, 2-hydroxy-1-naphthaldehyde,

o-hydroxy acetophenone with o-cresotic acid hydrazide, thiophene-2-carboxylic acid hydrazide and 2-furoic acid hydrazide. The ligands were tridentate and dibasic and the complexes possessed a cis-MoO_2 structure.

Rao et al. (1986) carried out the synthesis and structural studies of some trivalent lanthanide complexes of o-hydroxy acetophenone isonicotinoylhydrazone. The complexes obtained had the general formula [MLX $(H_2O)_2$], where M=La (III), Pr (III), Nd (III), Sm (III), Gd (III) and Dy (III) and X=OH SCN. The nephelauxetic ratio β, covalency δ and bonding parameters of complexes were calculated. A coordination number six around the metal ion was proposed for all the complexes in which the ligands coordinated through azomethine nitrogen, phenolate oxygen and imidol oxygen. Thiocyanate was bonded through the nitrogen atom. Rao et al. (1985a and 1985b) studied the Mn (II), Co (II), Ni (II) and Zn (II) complexes of o-hydroxyacetophenone (N-benzoyl) glycylhydrazone and the Schiff's base derived from l-tyrosine hydrazide and o-hydroxyacetophenone and characterized these with the help of various physico-chemical techniques.

Sakamoto (1987) synthesized and characterized some lanthanoid (III) complexes with a pentadentate ligand derived from 2,6-diacetylpyridine and benzoylhydrazide. The complexes were classified in two groups based on IR spectral patterns of the nitrate ions. In one group all the three nitrate ions were bidentate while in the other nitrate ions were bidentate and unidentate. ^{13}C NMR studies revealed that the ligand formed more stable complexes with the heavier metal ions as compared to the lighter metal ions. Arora et al. (1985) studied the homobinuclear complexes of chromium (III), iron (III) and cobalt (III) with heptadentate (N_5O_2) donor Schiff's base derived from 2,6-dipicolinoyl dihydrazone. The structural elucidation of the complexes done

on the basis of molar conductance, magnetic moment, IR and electronic spectral data revealed that the two metal ions were present in different environments; one in octahedral field and the other in the five coordinated environment.

The antibacterial organosilicon and organotin complexes of phenyl glycylhydrazones were prepared and characterized by Aminabhavi et al. (1987). The ligands coordinate through the azomethine nitrogen and the ketonic oxygen atoms. The activity of the hydrazones was improved against the test organisms on coordination with the metal ion. Chauhan and Mishra (1985) studied the penta coordinated triorganotin (IV) complexes of isonicotinoyl hydrazone (LH) of various aldehydes and ketones with the general formula R_3Sn L (where R=Bu, Ph or Bz and L= anion of the hydrazone). The complexes were found to be monomeric and non-electrolytes and were assigned trigonal bipyramidal geometry. Srivastava et al. (1981) studied the molecular adducts (1:2) of tin (IV) chloride, mono- and diorganotin (IV) halides with salicylaldehyde hydrazone. The ligand was found to behave as neutral and monodentate. The triorganotin (IV) chlorides in the presence of sodium methoxide gave rise to pentacoordinated complexes in which ligand behaved as anionic bidentate chelating agent.

The complexes of general formula MLX_2, where M=Mn (II), Fe (II), Co(II), Ni(II), Cu(II) and Pt(IV), X=Cl; M=Zn(II) and X=OAc and L=2-pyridine-carboxaldehyde-2'-quinolylhydrazone and 2'-pyridylhydrazone were prepared and characterized by Mohan et al. (1988). The magnetic susceptibility data of the compounds were recorded down to liquid nitrogen temperature. The compounds were characterized by electronic, IR, ESR and Mossbauer spectra.

All MLX_2 complexes were monomeric, high spin and penta coordinated square pyramidal except for $Ni(PCPH)Cl_2$, which was polymeric, high spin and hexa coordinated. Each ligand behaved as a tridentate N,N,N donor via the pyridyl nitrogen, azomethine nitrogen and pyridine or quinoline nitrogen. One of the most active agent of this series $[Cu(PCPH)Cl_2]$ exhibited antitumour activity against a variety of tumours. This compound caused the inhibition of 3-H thymidine and 3-H uridine incorporation into DNA and RNA respectively of Sarcoma 180 ascites cells. Protein biosynthesis was relatively insensitive to the action of this compound. Mohan et al. (1987) prepared the complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Pt(IV) with 3-and 5-substituted salicylaldehyde-2-pyridinylhydrazones and screened these for their antitumour activity against P 338 lymphocytic leukemia cells in mice. The compounds were inactive at the dosages used.

Juneja et al. (1987) synthesized coordination polymers of $Mn^{(II)}$ Co(II), Ni(II), Cu(II) and Zn(II) with azelaic acid bis (phenylhydrazide) and azelaic acid 2,4-dinitrophenylhydrazide. Thermal study of each polymer was conducted by thermogravimetric analysis. Coordinating sites in the ligands were identified as carbonyl oxygen and amino nitrogen atoms. Heterocyclic 1:1 hydrazone-metal complex pigments of organic polymers were prepared and used by Cseh et al. (1990). The 2-hydroxypropiophenone was condensed with nicotinic acid hydrazide forming hydrazone which was complexed with nickel (II) acetate to form a yellow 1:1 metal-ligand complex. Starikova et al. (1987) prepared mono- and dinuclear copper (II) and nickel (II) complexes of aroylhydrazones based on acid dihydrazides and β-dicarbonyl compounds. Antiferromagnetic exchange interaction was observed in $[Cu_2L_2]$ complexes. Kogan et al. (1987) prepared and characterized trinuclear copper (II) complexes of aroylhydrazones

based on acid dihydrazide and nitromalonaldehyde. The structure of the compounds was such that the two copper atoms were out of the plane of N_2O_2 node by 0.2 Å and the third copper atom was out of the plane of O_4 node by 0.4Å . In this structure exchange was possible between the first and the third copper atoms as a result of folding over of the ligand.

Coordination polymers of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with glutaric acid bis (2,4-dinitrophenyl hydrazide) were prepared and characterized by elemental analysis, IR spectroscopy, magnetic susceptibility and thermal data by Munshi and Juneja (1987). Sharma (1987) studied the chemical behaviour of the complexes of the type $ML_2(H_2O)_2$ (M=Co(II), Ni(II); L=2-(acetylaminobenzoic and 2-(benzoylamino)benzoic acids), NiL'_2 [HL' =2-benzoylpyridine benzoylhydrazone] and $Co(HL')Cl_2$. Characterization of the complexes suggested a pseudoctahedral structure. Kapadia and Mehta (1986) studied some metal complexes of β-arylaminocinnamophenyl hydrazides and suggested a tetrahedral structure for Cd(II) and Hg(II) complexes of the general formula MLX_2.

Synthesis, characterization and antibacterial studies of iron (II), cobalt (II), nickel(II), copper (II) and zinc (II) complexes of pyridine-4-carboxaldehyde isonicotinoylhydrazone were carried out by Singh et al. (1984). An octahedral geometry was proposed for the complexes except for copper (II) complex which had a square planar geometry. ^1H NMR and IR spectral data suggested a uninegative bidentate behaviour of the ligand in $ML_2.nH_2O$ and a neutral bidentate behaviour in other complexes of the type $M(HL)SO_4.2H_2O$; M(HL)X and M(HL) (NCS). The donor sites identified were carbonyl/enolic oxygen and azomethine nitrogen atoms. The ligand and its cobalt (II),

nickel (II) and zinc (II) complexes exhibited good antibacterial activity against Klebsiella pneumoniae, Escherichia coli and Staphylococcus aureus. Singh et al. (1986) reported synthetic, structural and antibacterial studies of cobalt (II), zinc (II), nickel (II) and copper (II) complexes of pyridine-2-carboxaldehyde thioisonicotinoylhydrazone. Magnetic susceptibility and electronic and ESR spectral studies suggested high spin octahedral geometry for all the nickel (II) and cobalt (II) chloride and bromide adducts, tetrahedral geometry for cobalt (II) iodide and thiocyanate complexes and distorted octahedral geometry for copper (II) halide and thiocynate complexes. IR spectral analysis suggested a bidentate ligand behaviour except in $CuL(NCS)_2$ where it acted as uninegative bidentate. The bonding sites were thione/thiol sulphur and azomethine nitrogen atoms. ESR spectral studies suggested a monomeric nature for $Cu(HL)_2Cl_2$ and dimeric nature for CuL(NCS) and the presence of one unpaired electron in $d_{x^2-y^2}$ orbital of copper (II). Antibacterial activities of HL and its complexes were tested against Klebsiella pneuomoniae, Escherichia coli and Vibrio cholerae and revealed that the metal complexes were better antibacterial agents than the ligand.

Sharma et al. (1991) synthesized copper (II), nickel (II) and cobalt (II) complexes of o-hydroxybenzaldehyde-N-salicylhydrazone and o-hydroxybenzaldehyde-N-succinoylhydrazone and characterized the same on the basis of elemental analysis, molar conductance, molecular weight determination, magnetic measurements and IR and electronic spectral data. Different ligand field parameters, viz., Dq, B, β, ϑ_2/ϑ_1 and ligand field stabilization energy were also calculated to ascertain the geometry of the resulting complexes. Both the ligands and their metal

complexes were screened in vitro against two bacteria viz., Staphylococcus aureus and Escherichia coli and two fungi, viz., Aspergillus niger and Aspergillus flavus. The antimicrobial activity of the synthesized hydrazones against the test organisms under identical experimental conditions increased on coordination. Complexes of α-methyl-(2-thiophenomethylene)-acyloxyacetic acid hydrazides with copper (II) and zinc (II) were synthesized by Malhotra et al. (1991). The complexes were characterized on the basis of elemental analysis, molecular weight determination, molar conductance, magnetic moment and spectroscopic techniques. In the complexes, the ligands formed a conjugate O,N,S tridentate system coordinating through oxygen of the carbonyl group, nitrogen of the azomethine and sulphur of the thiophene moiety. Octahedral geometry was proposed for the complexes. The complexes were evaluated for their antimicrobial activity against the plant pathogenic fungi viz. Alternaria alternata, Rhizoctonia solani, Colletotrichum capsicum and Glomurella cingulata and two bacteria, viz., gram positive Bacillus subtilis and gram negative Escherichia coli . In some cases an increase in biocidal activity of the ligands was observed on coordination with the metal ion.

Ligational behaviour of aryloxyacetic acid hydrazides towards transition metals and their microbicidal activity was studied by Malhotra et al. (1992). From the physico-chemical data it was concluded that the ligands behaved as anionic bidentate, coordinating through oxygen of the carbonyl group and the hydrazinic nitrogen. In vitro growth inhibitory activity of the ligands and the metal complexes against Alternaria alternata, Colletotrichum capsicum, Fusarium oxysporum, Rhizoctonia solani, Bacillus

subtilis and Escherichia coli revealed that coordination of metal ions had pronounced effect on the microbicidal activity of the ligands. The general trend of growth inhibition in the complexes was found to be in the order Ni > Cu > Co > Zn.

D'Muhala et al. (1985) synthesized hydrazides of amino polyacetic acids like nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). These hydrazides were found useful as chelating agents and were used for the extraction of iron and calcium from the deposits.

It is evident from the review of literature that variously substituted acid hydrazides and their Schiff's bases with aldehydes and ketones behave as potential ligands for a variety of metal ions and form complexes of diverse stereochemistries and stoichiometries. The most common ligational behaviours of these ligands are neutral bidentate and anionic bidentate although sometimes they also behave as monodentate and tridentate ligands. Studies regarding effect of metal coordination on the biological activity of the ligands have firmly established that quite often it has a pronounced effect on activity.

CHAPTER III

Experimental

CHAPTER - III

EXPERIMENTAL

This section is divided into the following subtopics:

A. Chemicals and solvents

B. Physical methods

C. Preparation of the ligands and the complexes

D. Evaluation of the antimicrobial activity

A. Chemicals and the solvents

Thiophene-2-carboxaldehyde, 2-acetylthiophene and 5-chloro-2-acetyl thiophene were procured from the Aldrich Chemical Company, U.S.A. and used as such without further purification. Benzene (AR, Merck), toluene (AR, Merck) and p-xylene (rectified, Sarabhai M. Chemicals) were dried before use by dipping sodium wire in the organic liquids and then distilling at constant temperatures. Succinic anhydride prepared from succinic acid (LR, BDH), maleic anhydride (AR, CDH), anhydrous aluminium chloride (AR, Ranbaxy) manganese (II) chloride (AR, Merck), nickel (II) chloride tetrahydrate (AR, Ranbaxy), copper (II) chloride hexahydrate (AR, Merck), cobalt (II) chloride hexahydrate (AR, Merck), zinc (II) chloride (AR, Merck), sodium hydroxide pellets (BDH), hydrazine hydrate (LR, SD fine), acetic anhydride (AR, Merck) and thionyl chloride(for synthesis, Merck) were used as such without further purification.

The solvents viz., chloroform (AR, Merck), ethyl acetate (AR, Ranbaxy), hexane (AR, Ranbaxy), methylene chloride (AR, Ranbaxy), diethyl ether (LR, Merck), ethanol (Bengal Chemicals), dimethyl sulphoxide (LR, SD fine) and nitrobenzene (LR, SD fine) were used as such without further purification.

Sucrose (Qualigens), agar-agar (Qualigens), sodium nitrate (AR, Merck), potassium dihydrogen phosphate (AR, Merck), magnesium sulphate (AR, Merck), potassium chloride (AR, Merck), ferrous sulphate (AR, Ranbaxy), yeast extract (Polypharm), dextrose (SD fine) and peptone (bacteriological, Polypharm) were used for the preparation of growth medium for the evaluation of antimicrobial activity.

Double distilled water was used throughout the study for washings and for the preparation of growth medium for the antimicrobial studies.

B. Physical methods

The following physical techniques were employed for the characterization of the synthesized ligands and the complexes:

1. Infra-red spectra

The vibrational spectra of the ligands and the complexes are used to identify the ligating sites of the ligands as the IR spectral characteristics of the complexes differ significantly in position, magnitude or intensity due to the change in bond orders and electronic environment of the ligands on formation of metal-ligand coordination bonds. Some new absorptions appear in the spectra of complexes, whereas some peaks diminish. A careful comparative analysis of the spectra of the ligands and the complexes helps in the identification of the donor sites of the ligand molecules.

In the present study, the IR spectra of the compounds were recorded on a Perkin Elmer (Model 621, range 4000-200 cm^{-1}) Infra-red spectrophotometer and Beckmann Infra-red spectrophotometer (Acculab TM 2, range 4000-600 cm^{-1}). The spectra were either obtained as nujol mull on cesium iodide optics or by preparing potassium bromide pellets.

2. ^1H NMR spectra

^1H NMR spectra of the ligands were recorded on Varian EM 390-90 MHz spectrometer using TMS as an internal reference.

3. Magnetic studies

The magnetic susceptibility studies of the complexes were carried out on Magnetic Susceptibility Balance (Sherwood Scientific, England) at 25±1°C using tetrathiocyanatocobaltate (II) as a standard compound. The gram susceptibility of the samples was calculated using the formula:

$$\chi_g = \frac{C_{Bal} \; l \; (R-R_o)}{10^9 \; m}$$

where l = Sample length (cm)

m = Sample mass (g)

R = Reading for tube plus sample

R_o = Empty tube reading

C_{Bal} = Balance calibration consant

The gram susceptibility (χ_g) of the sample was converted into the molar susceptibility (χ_m) by multiplying with its molecular weight.

$\chi_m = \chi_g$ x Molecular weight of the compound.

The molar susceptibility was then corrected for diamagnetism of the atoms other than the metal ions.

Finally, the effective magnetic moment was calculated from the equation.

$$ueff = 2.828 \sqrt{\chi_m \text{ corr.} \times T}$$

where χ_m corr. is the corrected molar susceptibility and T is the absolute temperature at which measurements were made.

4. Elemental analysis

Carbon, hydrogen and sulphur were estimated on "CARLO ERBA STRUMENTHAZIONE (ITALY) Elemental Analyser-Model 1106" at Regional Sophisticated Instrumentation Centre, Chandigarh.

The metal content of the complexes was estimated by Atomic Absorption Spectrophotometer (Varian Techtran, Model AA 120) using the appropriate hollow cathode lamp.

5. Conductance Measurements

The molar conductance of 0.001 molar solution of each complex was measured at 25±0.5°C using Digital Conductivity Meter (Model NDC-732) with a cell having cell constant equal to one.

6. Electronic spectra

The study of electronic absorption spectra of transition metal complexes helps to characterize and understand the nature of the electronic structure and bonding in these compounds. Electronic transitions occur when electrons within the molecule or ion move from one energy level to another. The electronic transitions may take place between split d levels of the central atom, giving rise to d-d or the ligand field spectra. Secondly, the transitions may occur from molecular orbitals located primarily on the ligands or the metal-ligand bonding σ or π molecular orbitals to non-bonding or antibonding molecular orbitals located primarily on the metal atom. Such transitions are termed as ligand-to-metal charge transfer transitions. Other type of transitions arise from metal-to-ligand charge transfer and intraligand transitions.

The d^1 electron system gives rise to a single absorption maxima and can be assigned to the transition of the lone d electron from the $d\epsilon$ to the $d\gamma$ level. A similar but inverted situation holds good for d^9 system. But when we deal with ion systems having more than one but less than nine d electrons, the number of terms which arise in the free ion from inter-electronic repulsions complicate the picture. Some of the free ion terms which arise are : for d^2 or d^8 - ^3F, ^1D, ^3P, ^1S and ^1G; for d^3 or d^7 - ^4F, ^2G, ^4P, ^2P, ^2H ..... ; for d^4 and d^6 - ^5D, ^3H, ^3G, ^3D, ^3P ..... and for d^5 - ^6S, ^4G, ^4P, ^4D, ^4F ..... In addition, each of these terms is split further by various ligand fields.

The spectra of transition metal complexes may be found in certain energy level diagrams. In the extreme of weak ligand fields we employ Orgel diagrams and in the extreme of strong fields we employ Tanabe-Sugano diagrams. But for the more commonly found ligand fields of intermediate strength, we may employ either of the two.

Various ligand field parameters like ligand field splitting energy (Dq), Racah interelectronic parameter (B), nephelauxetic ratio (β), energy ratio (ν_2/ν_1) and ligand field stabilization energy (LFSE) are quite useful in understanding the effect of ligand environment on the splitting of various electronic states and magnitude of splitting.

In the present investigation, the electronic spectra of the complexes were recorded on Beckmann (DU) Spectrophotometer using DMSO as solvent.

C. Preparation of ligands and the complexes

I. Preparation of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)] propanoic acid hydrazides (HL_I - HL_{IX}).

The ligands (HL_I-HL_{IX}) were prepared by following a three step procedures. The methods of preparation of ligands are described as follows:

1. Preparation of 4-phenyl-4-oxo-1-[2-N-(2-thienylmethylene)] propanoic acid hydrazide (HL_I)

a) Preparation of 4-phenyl-4-oxo-1-propanoic acid (1a)

To a vigorously stirred solution of dry benzene (50 ml, excess) and succinic anhydride (10g, 0.1 mol) at 5-10°C was added anhydrous aluminium chloride (15g, 0.12 mol) slowly, in parts with continuous stirring. The reaction mixture was further stirred for 30 minutes, refluxed on a water bath for 2h, cooled to room temperature and hydrolysed with ice-cold 6N HCl. The solid thus obtained was filtred and dissolved in 5 per cent sodium carbonate solution, filtred and the filtrate was acidified with cold dil. HCl. The precipitate formed was filtred, washed with distilled water to remove the chloride ions present, dried and crystallized from benzene to yield 1a (14.4g, 81%).

b) Preparation of 4-phenyl-4-oxo-1-propanoic acid hydrazide (1b)

A mixture of 4-phenyl-4-oxo-1-propanoic acid (1a, 7.12g, 0.04 mol) and thionyl chloride (9.52 g, 0.08 mol) in benzene (100 ml) was refluxed on a steambath for 2 h. Benzene and excess thionyl-chloride were distilled off at reduced pressure. The viscous mass so

obtained was dissolved in ethanol Hydrazine hydrate (2.50g, 0.044 mol) was added to it and the reaction mixture was refluxed for 1 h, cooled to room temperature and poured over crushed ice. The solid thus separated was filtred, washed with water and crystallized from ethanol to furnish 1b (5.68g,74%).

c) **Preparation of HL_I**

4-phenyl-4-oxo-1-propanoic acid hydrazide (1b, 3.84g, 0.02 mol) was refluxed on a steambath with thiophene-2-carboxaldehyde (2.24g, 0.02 mol) in ethanol-for 2 h, concentrated and cooled. The solid thus obtained was filtered and crystallized from ethanol to yield HL_I (4.57g, 80%).

2. **Preparation of 4-(4-methylphenyl)-4-oxo-1-[2-N-(2-thienylmethylene)]-propanoic acid hydrazide (HL_{II})**

a) **Preparation of 4-(4-methylphenyl)-4-oxo-1-propanoic acid**

Toluene (9.2 g, 0.1 mol) was dissolved in dichloromethane (50 ml). Succinic anhydride (10g, 0.1 mol) was added to it and the reaction mixture was cooled to 5-10°C. Anhydrous aluminium chloride (15g, 0.12 mol) was added to it in parts with vigorous stirring. The stirring was further continued for 30 minutes and the reaction mixture was refluxed on a stembath for 1 h, cooled and hydrolysed with ice-cold 6N HCl. The solid thus separated was filtred, washed with water and dissolved in 5 per cent sodium carbonate solution, filtred and the filtrate was acidified with cold dil. HCl. The precipitate obtained was filtred, washed with distilled water, dried and crystallized from benzene to give 2a (16.1g, 84%).

b) Preparation of 4-(4-methylphenyl)-4-oxo-1-propanoic acid hydrazide (2b)

A mixture of 2a (7.68g, 0.04 mol), benzene (100 ml) and thionyl chloride (9.52g, 0.08 mol) was refluxed on a steambath for 2 h. The solvent and the excess of thionyl chloride were distilled off at reduced pressure. The viscous mass obtained was dissolved in ethanol and hydrazine hydrate (2.50g, 0.044 mol) was added to it. The mixture was refluxed for 1 h, cooled to room temperature and poured over crushed ice. The solid separated was filtred, washed repeatedly with water and crystallized from ethanol to yield 2b (6.24g, 76%).

c) Preparation of HL_{II}

Thiophene-2-carboxaldehyde (2.24g, 0.02 mol) and 2b (4.12g, 0.02 mol) were refluxed in ethanol for 2 h on a steambath. The reaction mixture was concentrated and cooled. The solid thus obtained was filtred and crystallised from ethanol to give HL_{II} (4.11g, 72%).

3. Preparation of 4-(2,5-dimethylphenyl)-4-oxo-1-[2-N-(thienyl-methylene)] propanoic acid hydrazide (HL_{III})

a) Preparation of 4-(2,5-dimethylphenyl)-4-oxo-1-propanoic acid (3a)

p-Xylene (10.6g, 0.1 mol) was dissolved in dichloromethane (50 ml). Succinic anhydride (10g, 0.1 mol) was added to it and the reaction mixture was cooled to 5-10°C. Anhydrous aluminium chloride

(15g, 0.12 mol) was added to it in lots with vigorous stirring and the stirring further continued for 30 minutes. It was then refluxed for 1 h, cooled and hydrolysed with ice-cold 6N HCl. The product was filtred, washed well with water and dissolved in 5 per cent sodium carbonate solution, filtred and the filtrate was acidified with cold dil. HCl. The solid separated was filtred, washed with water, dried and crystallized from benzene to yield 3a (16.5g, 80%).

b) Preparation of 4-(2,5-dimethylphenyl)-4-oxo-1-propanoic acid hydrazide (3b)

To a solution of 3a (8.24g, 0.04 mol) in benzene was added thionylchloride (9.52g, 0.08 mol) and the reaction mixture was refluxed on a steambath for 2 h. The solvent and excess of thionylchloride were removed at reduced pressure. The viscous mass thus obtained was dissolved in ethanol and hydrazine hydrate (2.50g, 0.044 mol) was added to it. The reaction mixture was relfuxed on a steambath for 1 h, cooled to room temperature and poured over crushed ice. The precipitate obtained was filtred and crystallized from ethanol to furnish 3b (7.92g, 72%).

c) Preparation of HL_{III}

An ethanolic solution of 3b (4.4g, 0.02 mol) was refluxed with thiophene-2-carboxaldehyde (2.24g, 0.02 mol) for 2 h, concentrated and cooled. The solid thus obtained was filtred and crystallized from ethanol to give HL_{III} (5.02g, 80%).

4. Preparation of 4-phenyl-4-oxo-1-[2-N-(2-thienylmethylmethylene)] propanoic acid hydrazide (HL_{IV})

4-Phenyl-4-oxo-1-propanoic acid hydrazide (1b, 3.84g, 0.02 mol) was refluxed with 2-acetylthiophene (2.52g, 0.02 mol) in ethanol for 2 h. The solution was concentrated and cooled. The precipitate obtained was filtred and crystallized from ethanol to yield HL_{IV} (4.2g, 70%).

5. Preparation of 4-(4-methylphenyl)-4-oxo-1-[2-N-(2-thienyl methylmethylene)] propanoic acid hydrazide (HL_V)

To a solution of 2b (4.12g, 0.02 mol) in ethanol was added 2-acetylthiophene (2.52g, 0.01 mol). The reaction mixture was refluxed on a steambath for 2 h, concentrated and cooled. The solid obtained was filtred and crystallized from ethanol to furnish HL_V (4.01g, 64%).

6. Preparation of 4-(2,5-dimethylphenyl)-4-oxo-1-[2-N-(2-thienylmethyl methylene)] propanoic acid hydrazide (HL_{VI})

An ethanolic solution of 3b (4.4g, 0.02 mol) prepared as above was treated with 2-acetylthiophene (2.52g, 0.02 mol), refluxed on a steambath for 2 h, concentrated and cooled. The product thus obtained was filtred and crystallized from ethanol to yield HL_{VI} (5.11g, 78%).

7. Preparation of 4-phenyl-4-oxo-1-[2-N-(5-chloro-2-thienylmethyl methylene)] propanoic acid hydrazide (HL_{VII})

4-Phenyl-4-oxo-1-propanoic acid hydrazide (1b, 3.84g, 0.02 mol) was dissolved in ethanol (100 ml). 5-chloro-2-acetylthiophene (3.20g, 0.02 mol) was added to it and the reaction mixture was refluxed on a steambath for 2 h. The solution was concentrated and cooled and the product obtained was filtred and crystallized from ethanol to yield HL_{VII} (4.54g, 68%).

8. Preparation of 4-(4-methylphenyl)-4-oxo-1-[2-N-(5-chloro-2-thienylmethylmethylene)] propanoic acid hydrazide (HL_{VIII})

To an ethanolic solution of 2b (4.12g, 0.02 mol) was added 5-chloro-2-acetylthiophene (3.20g, 0.01 mol) and the reaction mixture was refluxed for 2 h, concentrated and cooled. The solid separated was filtred and crystallized from ethanol to give HL_{VIII} (5.71g, 82%).

9. Preparation of 4-(2,5-dimethylphenyl)-4-oxo-1-[2-N-(5-chloro-2-thienylmethylmethylene)] propanoic acid hydrazide (IIL_{IX})

An ethanolic solution of 3b (4.4g, 0.02 mol) was refluxed with 5-chloro-2-acetylthiophene (3.20g, 0.02 mol) for 2h, concentrated and cooled. The product obtained was filtred and crystallized from ethanol to furnish (5.51g, 76%) of HL_{IX}.

II. Complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)] propanoic acid hydrazide

1. Manganese (II) complexes $[Mn(L_{I2})]$- $[Mn(L_{IX})_2]$

The respective ligand (10 mmol) was dissolved in ethanol and to it was added an aqueous solution of manganese (II) chloride (5 mmol) in minimum amount of water, slowly with continuous stirring. The pH of the system was raised slowly to $\simeq$9.0 and the solution was further stirred for 30 minutes. The precipitate formed was filtred, washed well with water, ethanol and diethylether and finally dried in vacuo over anhydrous calcium chloride.

2. **Cobalt (II) complexes $[CO(L_I)_2]$ - $[CO(L_{IX})_2]$**

To an ethanolic ligand solution (10 mmol) was added an ethanolic solution of cobalt (II) chloride hexahydrate (5 mmol) with stirring and the pH of the solution was raised gradually to $\simeq$9.0 by the addition of sodium hydroxide solution. The stirring was further continued for 30 minutes and the resulting solid was filtred, washed well with water, ethanol and diethylether and dried *in vacuo over anhydrous calcium chloride.*

3. **Nickel (II) complexes $[Ni(L_I)_2]$ - $[Ni(L_{IX})_2]$**

Nickel (II) chloride tetrahydrate (5 mmol) was dissolved in minimum amount of water and added slowly with vigorous stirring to an alkaline ethanolic ligand (10 mmol) solution (pH$\simeq$10). Stirring was further continued for 30 minutes and the precipitated complex was filtred. Washed well with water, ethanol and diethylether and finally dried over anhydrous calcium chloride in vacuo.

4. **Copper (II) complexes $[Cu(L_I)_2]$ - $[Cu(L_{IX})_2]$**

To an ethanolic solution of the respective ligand (10 mmol) was added an aqueous solution of copper (II) chloride hexahydrate (5 mmol) in minimum amount of water with continuous stirring. The pH of the solution was gradually raised to 7.5 with stirring and the stirring was further continued for 30 minutes. The precipitate obtained was filtred, washed with water, ethanol and diethylether and dried in vacuo over anhydrous calcium chloride.

5. **Zinc (II) complexes[$(Zn(L_I)_2$] - $(Zn(L_{IX})_2$]**

To an ethanolic solution of the ligand (10 mmol) was added an ethanolic solution of zinc (II) chloride (5 mmol) slowly with stirring. The pH of the system was slowly raised to 8.0 and the stirring continued further for 30 minutes. The solid thus separated was filtred washed well with water, ethanol and diethylether and dried over anhydrous calcium chloride in vacuo.

III. Preparation of 4-substituted phenyl-1-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides(HL_X- HL_{XVIII})

1. Preparation of 4-phenyl-4-oxo-1-[2-N-(thienylmethylene)]-prop-2-en-1-oic acid hydrazide (HL_X)

a) Preparation of 4-phenyl-4-oxo-2-propen-1-oic acid (11a)

Maleic anhydride (9.8 g, 0.1 mol) was added to dry benzene (50 ml, excess). It was cooled to 5-10°C and anhydrous aluminium chloride (15g, 0.12 mol) was added to it in parts with vigorous stirring. Stirring was further continued for 30 minutes and the reaction mixture was refluxed on a steambath for 2 h. It was cooled to room temperature and hydrolysed with ice-cold 6N HCl. The solid obtained was filtred and washed with distilled water. It was then dissolved in 5 per cent sodium carbonate solution, filtred and the filtrate was acidified with cold dil. HCl. The precipitate thus formed was filtred, washed, dried and crystallized from benzene to yield 14.78 g (84%) of 11a.

b) **Preparation of 4-phenyl-4-oxo-2-propen-1-oic acid hydrazide (11b)**

A solution of 11a (7.04, 0.04 mol) in benzene (20 ml) was refluxed with thionyl chloride (9.52g, 0.08 mol) for 2 h. Benzene and the excess thionylchloride were distilled off at reduced pressure. The viscous mass obtained was dissolved in ethanol and hydrazine hydrate (2.50g, 0.044 mol) was added to it. The reaction mixture was refluxed on a steambath for 1 h, cooled to room temperature and poured over crushed ice. The solid thus obtained was filtred, washed and crystallized from ethanol to furnish 11b (5.76g, 76%).

c) **Preparation of HL_X**

To an ethanolic solution of 11b (3.8g, 0.02 mol) was added thiophene-2-carboxaldehyde (2.24g, 0.02 mol). The reaction mixture was refluxed on a steambath for 2 h, concentrated and cooled. The product obtained was filtred and crystallized from ethanol to yield HL_X (3.97g, 70%).

2. **Preparation of 4-(4-methylphenyl)-4-oxo-1-[2-N-(2-thienylmethylene)]-prop-2-en-1-oic acid hydrazide (HL_{XI})**

a) **Preparation of 4-(4-methylphenyl)-4-oxo-2-propen-1-oic acid (12a)**

Toluene (9.2g, 0.1 mol) was dissolved in dichloromethane (50 ml) and maleic anhydride (9.8 g, 0.1 mol) was added to it. The reaction mixture was cooled to 5-10°C and anhydrous aluminium chloride (15g, 0.12 mol) was added to it slowly, in parts with vigorous stirring. The stirring was further continued for 30 minutes and the

reaction mixture was refluxed on a steambath for 2 h, cooled and hydrolysed with ice-cold 6 N HCl. The solid separated was filtred, washed with water and dissolved in 5 per cent sodium carbonate solution and filtred. The filtrate was acidified with cold dil. HCl and the precipitate obtained was filtred, washed well with distilled water, dried and crystallized from benzene to give (15.3g, 80.5%) of 12a.

b) Preparation of 4-(4-methylphenyl)-4-oxo-2-propen-1-oic acid hydrazide (12b)

4-(4-Methylphenyl)-4-oxo-2-propen-1-oic acid (12a, 7.6g, 0.04 mol) was dissolved in benzene (100 ml) and thionyl chloride (9.52, 0.08 mol) was added to it and the reaction mixture was refluxed on a steambath for 2 h. Benzene and excess of thionylchloride were removed at reduced pressure. The viscous mass obtained was dissolved in ethanol and hydrazine hydrate (2.50g, 0.044 mol) was added to it. The reaction mixture was refluxed for 1 h on a steambath, cooled to room temperature and poured over crushed ice. The solid so obtained was filtred, washed and crystallized from ethanol to yield 12b (6.04g, 74%).

c) Preparation of HL_{XI}

An ethanolic solution of 12b (4.12g, 0.02 mol) was refluxed with thiophene-2-carboxaldehyde (2.24g, 0.02 mol), concentrated and cooled. The precipitate obtained was filtred and crystallized from ethanol to give HL_{XI} (4.47g, 75%).

3. **Preparation of 4-(2,5-dimethylphenyl)-4-oxo-1-[2-N-(2-thienyl methylene)]-prop-2-en-1-oic acid hydrazide (HL_{XII})**

a) Preparation of 4-(2,5-dimethylphenyl)-4-oxo-2-propen-1-oic acid hydrazide (13a)

Xylene (10.6g, 0.1 mol) and maleic anhydride (9.8g, 0.1 mol) were taken in dichloromethane (50 ml) and the contents were cooled to 5-10°C. Anhydrous aluminium chloride (15g, 0.12 mol) was added to it in lots with continuous stirring. It was further stirred for 30 minutes and then refluxed on a steambath for 2 h. It was then hydrolysed with ice-cold 6N HCl. The product obtained was filtred, washed well with distilled water and dissolved in 5 per cent sodium carbonate solution and filtred. The filtrate was acidified with cold dil. HCl and the precipitate formed was filtred, washed, dried and crystallized from benzene to yield 13a (16.5g, 81%).

b) Preparation of 4-(2,5-dimethylphenyl)-4-oxo-2-propen-1-oic acid hydrazide (13b)

Thionyl chloride (9.52g, 0.08 mol) was added to a solution of 13a (8.16g, 0.04 mol) in benzene (20 ml). It was refluxed on a steambath for 2 h. Benzene and excess thionylchloride were removed at reduced pressure. The viscous mass so obtained was dissolved in ethanol, and hydrazine hydrate (2.50g, 0.044 mol) was added to it. The reaction mixture was refluxed on a steambath for 1 h, cooled to room temperature and poured over crushed ice. The product obtained was filtred, washed with water and crystallized from ethanol to yield 13b (6.24g, 74%).

c) Preparation of HL_{XII}

A solution of 13b (4.36g, 0.02 mol) in ethanol was refluxed with thiophene-2-carboxaldehyde (2.24g, 0.02 mol) for 2 h, concentrated and cooled. The solid separated was filtred and crystallized from ethanol to yield HL_{XII} (4.24g, 68%).

4. **Preparation of 4-phenyl-4-oxo-1-[2-N-(2-thienylmethylmethylene)]-prop-2-en-1-oic acid hydrazide (HL_{XIII})**

An ethanolic solution of 11b (3.8g, 0.02 mol) was refluxed with 2-acetylthiophene (2.52g, 0.02 mol)on a steambath for 2 h, concentrated and cooled. The product obtained was filtred and crystallized from ethanol to give HL_{XIII} (3.81g, 64%).

5. **Preparation of 4-(4-methylphenyl)-4-oxo-1-[2-N-(2-thienylmethyl-methylene)]-prop-2-en-1-oic acid hydrazide (HL_{XIV})**

A solution of 12b (4.08g, 0.02 ml) in ethanol was treated with 2-acetylthiophene (2.52g, 0.02 mol). The reaction mixture was refluxed on a waterbath for 2 h, concentrated and cooled. The solid separated was filtred and crystallized from ethanol to yield(4.43g, 71%) of HL_{XIV}.

6. **Preparation of 4-(2,5-dimethylphenyl)-4-oxo-1-[2-N-(thienylmethyl-methylene)]-prop-2-en-1-oic acid hydrazide (HL_{XV})**

To an ethanolic solution of 13b (4.36g, 0.02 mol) was added 2-acetylthiophene (2.52g, 0.02 mol) and the reaction mixture was refluxed on a steambath for 2 h. It was then concentrated and cooled. The solid thus obtained was filtred and crystallized from ethanol to give HL_{XV} (4.17g, 64%).

7. Preparation of 4-phenyl-4-oxo-1-[2-N-(5-chloro-2-thienylmethyl-methylene)]-prop-2-en-1-oic acid hydrazide (HL_{XVI})

4-Phenyl-4-oxo-2-propen-1-oic acid hydrazide (11b, 3.8g, 0.02 mol) was refluxed with 5-chloro-2-acetylthiophene (3.20g, 0.02 mol) in ethanol for 1 h. The contents were concentrated and cooled. The product obtained was filtred and crystallized from ethanol to give HL_{XVI} (4.09g, 60%).

8. Preparation of 4-(4-methylphenyl)-4-oxo-1-[2-N-(5-chloro-2-thienylmethylmethylene)]-prop-2-en-1-oic acid hydrazide (HL_{XVII})

An ethanolic solution of 12b (4.08g, 0.02 mol) was refluxed with 5-chloro-2-acetylthiophene (3.20g, 0.02 mol) for 1h, concentrated and cooled. The product obtained was filtred and crystallized from ethanol to yield HL_{XVII} (4.50g, 65%).

9. Preparation of 4-(2,5-dimethylphenyl)-4-oxo-1-[2-N(5-chloro-2-thienylmethylmethylene)]-prop-2-en-1-oic acid hydrazide (HL_{XVIII})

A solution of 13b (4.36g, 0.02 mol) and 5-chloro-2-acetylthiophene (3.20g, 0.01 mol) in ethanol was refluxed for 1 h on a steambath. It was then concentrated and cooled. The solid separated was filtred and crystallized from ethanol to yield HL_{XVIII} (4.47g, 62%).

IV. Complexes of 4-substituted phenyl-4-oxo-1-(2-N(substituted-2-thienylmethylene/methylmethylene)-prop-2-en-1-oic acid hydrazides

1. Manganese (II) complexes $[Mn(L_X)_2]$ - $[Mn(L_{XVIII})_2]$

The respective ligand (10 mmol) in ethanol was mixed with an aqueous solution of manganese (II) chloride (5 mmol) and the pH of the solution was gradually raised to $\simeq$9.0 with continuous stirring. Stirring

was further continued for 30 minutes and the precipitated solid was filtred, washed repeatedly with water, alcohol and diethylether and dried in vacuo over anhydrous calcium chloride.

2. **Cobalt(II) complexes $[Co(L_X)_2]$ - $[Co\ (L_{XVIII})_2]$**

Cobalt (II) chloride hexahydrate (5 mmol) was dissolved in ethanol and was added slowly to an ethanolic solution of the respective ligand (10 mmol). pH of the system was slowly raised to $\simeq$ 9.0 by the addition of dil. sodium hydroxide solution with stirring and stirring continued for 30 minutes. The solid separated was filtred, washed with water, ethanol and diethyl ether and finally dried in vacuo over anhydrous calcium chloride.

3. **Nickel (II) complexes $[Ni\ (L_X)_2]$ - $[Ni\ (L_{XVIII})_2]$**

Nickel (II) chloride (5 mmol) was dissolved in minimum amount of water and added slowly with stirring to an alkaline ethanolic solution of the ligand (10 mmol) (pH $\simeq$ 10). Stirring was further continued for half an hour and the resulting complex was filtred, washed with water, ethanol and diethylether and dried over anhydrous calcium chloride in vacuo.

4. **Copper (II) complexes $[Cu(L_X)_2]$ - $[Cu\ (L_{XVIII})_2]$**

To an ethanolic ligand solution (10 mmol) was added an ethanolic solution of copper (II) chloride hexahydrate (5 mmol) and the pH of the medium was raised gradually to 7.5 by the addition of sodium hydroxide solution. It was then stirred for 30 minutes and the precipitated complex was filtred, washed with water, ethanol and diethylether and dried over anhydrous calcium chloride.

5. Zinc (II) complexes [Zn $(L_X)_2$] - [Zn $(L_{XVIII})_2$]

An ethanolic ligand solution (10 mmol) was mixed with an ethanolic zinc chloride (5 mmol) solution with stirring and the pH of the solution was very slowly raised to$\simeq$8.0. Stirring was further continued for about 30 minutes and the precipitate obtained was filtred, washed repeatedly with water, ethanol and diethylether and dried over anhydrous calcium chloride in vacuo.

D. Evaluation of Antimicrobial Activity

The antimicrobial activity of the compounds was evaluated against the following phytopathogenic fungi and bacteria:

FUNGI
1. Alternaria alternata
2. Fusarium oxysporum
3. Colletotrichum capsicum and
4. Rhizoctonia solani

BACTERIA
1. Escherichia coli and
2. Bacillus subtilis

Czapek's Dox agar medium (Tuite, 1969) was used for growing culture of fungi and dextrose agar medium for bacteria. The following steps were involved in the evaluation of antimicrobial activity:

1. Sterlization of the apparatus

All the glass apparatus was cleaned with chromic acid followed by double distilled water and then sterlized at 180°C in an hot air oven for about four hours.

2. Preparation of the medium :

Constituents of Czapek's Dox agar medium

1.	Sucrose	30g
2.	Agar-agar	20g
3.	Sodium nitrite	3g
4.	Potassium dihdyrogen phosphate	1g
5.	Magnesium sulphate	0.6g
6.	Potassium chloride	0.5g
7.	Ferrous sulphate	10mg
8.	Streptopenicillin	50mg

All the constituents were dissolved in double distilled water and the total volume made to 1000 ml. The medium was autoclaved at 15 lbs. pressure for 15 minutes.

Constituents of the dextrose agar medium

1.	Yeast extract	5g
2.	Glucose	5g
3.	Peptone	5g
4.	Agar-agar	18g

All the constituents were dissolved in double distilled water and the final volume made to 1000 ml. The medium was autoclaved for 15 minutes at 15 lbs. pressure.

Stock solutions of the compounds were prepared in dimethyl sulphoxide.

3. Testing of antimicrobial activity

Two fold serial dilution technique was used to determine the minimum inhibitory concentration (MIC) values.

A loopful of the fungal/bacterial culture from the slant was incubated aseptically into broth which was incubated for 48 h for fungi and 24 h for bacteria at 30±1°C and was used for testing of compounds. A stock solution of 1000 $\mu g\ ml^{-1}$ concentration was prepared by dissolving the test compound in DMSO. 0.2 ml of it was added to 1.8 ml of the seeded broth to form the first dilution (conc. 100 $\mu g\ ml^{-1}$). Second dilution was made by further diluting 1 ml of the solution from first dilution with 1 ml of the seeded broth. Same process was repeated until a set of six dilutions with test compound concentrations of 100, 50, 25, 12.5, 6.25 and 3.12 $\mu g\ ml^{-1}$ was obtained. A set of tubes containing seeded broth only was kept as control. The tubes were incubated at 30±1°C in case of fungi and 35±1°C in case of bacteria. The last tube without any growth was taken to represent minimum inhibitory concentration (MIC) expressed in $\mu g\ ml^{-1}$.

Bavistin, 2-(methoxycarbamoyl) benzimidazole, was used as a standard fungicide to compare the results and streptopenicillin was used as a reference to compare the antibacterial activity.

CHAPTER IV

Results & Discussion

CHAPTER - IV

RESULTS AND DISCUSSION

This chapter is subdivided into three sections. Section "A" deals with synthesis and characterization of the Schiff's bases derived from 4-substituted phenyl-4-oxo-1-propanoic acid hydrazides (substituted benzoyl-propanoic acid hydrazides) and substituted-2-acetylthiophene or thiophene-2-carboxaldehyde, and their complexes with some first row transition metal ions viz., manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II).

Synthesis and characterization of the ligands derived from 4-substituted phenyl-4-oxo-2-propen-1-oic acid hydrazides and substituted 2-acetylthiophene/thiophene-2-carboxaldehyde and their complexes with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) are discussed in Section "B".

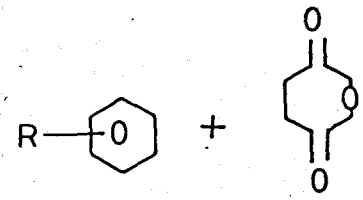
In Section "C" the comparative antimicrobial activity of the ligands and their complexes against four phytopathogenic fungi, viz., Alternaria alternata, Fusarium oxysporum, Colletotrichum capsicum and Rhizoctonia solani and two bacteria viz., Escherichia coli (gram negative) and Bacillus subtilis (gram positive) is described.

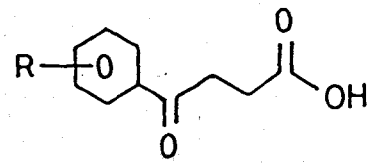
SECTION "A"

I. Synthesis and characterization of 4-substituted phenyl-4-oxo-1-(2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides (HL_I-HL_{IX})

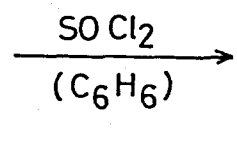
Friedel Craft's acylation of substituted benzene with succinic anhydride in presence of anhydrous aluminium chloride resulted in the formation of substituted benzoylpropanoic acids (1). These acids on reaction with thionyl chloride gave the corresponding acid chlorides (2). In situ reaction of (2) with hydrazine hydrate in equimolar ratio yielded the corresponding 4- substituted-phenyl-4-oxo-1-propanoic acid hydrazide (3). These acid hydrazides on reaction with substituted-2-acetyl/carboxaldehyde thiophene gave the title ligands (HL_I-HL_{IX}) in good yields. The scheme for the preparation of these ligands is represented in Fig. 1.

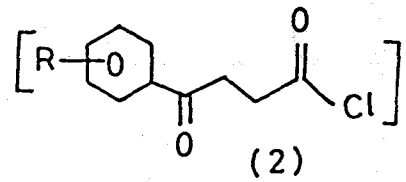
The synthesized ligands were characterized by their elemental analysis and IR and ^{1}H NMR spectra. The ^{1}H NMR spectra of the ligands gave a multiplet in the region 2.0-2.5 ppm which was assigned to the ethylene-protons. A multiplet in the region 6.7-7.7 ppm corresponds to aromatic protons of phenyl and thienyl moieties. A singlet in the region 8.8-8.9 ppm was assigned to -N=C<u>H</u> proton and the singlets appearing around 2.6 ppm and 2.9-3.1 ppm were assigned to C<u>H</u>$_3$ group attached to thienyl and phenyl rings respectively. The integral proton ratios of various groups in the spectrum of each ligand were well in agreement with the proposed structures. Some prominent absorption frequencies in the IR spectra of these ligands in the regions 3100-3170, 1670-1680, 1645-1650, 1610-1615 and 940-950 cm^{-1} were assigned to ν(N-H), (NHC=O), ν(C=O), ν(C=N) and ν(N-N) vibrations



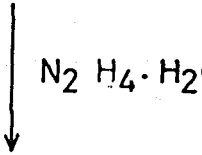


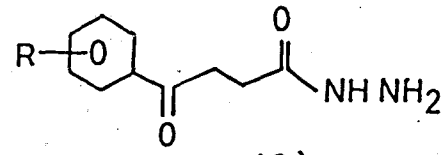
(1)



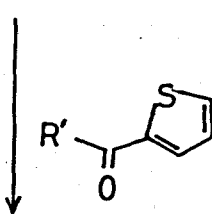


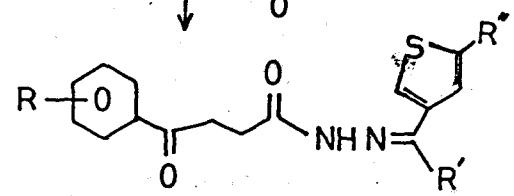
(2)





(3)





$HL_I - HL_{IX}$

Ligand	R	R'	R''
HL_I	H	H	H
HL_{II}	4-CH_3	H	H
HL_{III}	2,5-$(CH_3)_2$	H	h
HL_{IV}	H	CH_3	H
HL_V	4-CH_3	CH_3	H
HL_{VI}	2.5-$(CH_3)_2$	CH_3	H
HL_{VII}	H	CH_3	Cl
HL_{VIII}	4-CH_3	CH_3	Cl
HL_{IX}	2,5$(CH_3)_2$	CH_3	Cl

respectively confirming the presence of these functional groups in the proposed structure. The stretching vibrations for thienyl C-S appeared in the regions 570-590 and 490-500 cm^{-1} (Socrates, 1980). The elemental analysis of the compounds also agreed well with the proposed molecular formulae. The physical and analytical data of the compounds (HL_I-HL_{IX}) are given in table 1 and the IR and ^1H NMR spectral data alongwith the proposed assignments are given in tables 2 and 3 respectively.

II. Complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides (HL_I-HL_{IX})

The complexes of the ligands (HL_I-HL_{IX}) with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) were prepared by reacting the corresponding metal chloride and the ligand in 1:2 molar ratios in ethanolic solution with pH maintained at 8-10. The isolated complexes were characterized on the basis of their elemental analysis, conductance measurements, magnetic susceptibility and infra-red and electronic absorption spectral data. The complexes were assigned the general formula ML_2 [M=Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); HL=ligands HL_I-HL_{IX}]. The complexes were insoluble in water, ethanol, diethyl ether and acetone but were soluble in dimethyl-sulphoxide, dimethylformamide and nitrobenzene. The low molar conductance values (0.5-15 $ohm^{-1}.\ cm^2.\ mol^{-1}$) indicated the non-electrolytic nature of the complexes. The other physico-chemical characteristics of the complexes are discussed in the following pages.

1. Manganese(II) complexes

The microanalytical data (Table 4) and the conductance studies indicated the formation of non-ionic 1:2 manganese(II)-ligand complexes. The spectral

Table 1. Physical and analytical data of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienyl-methylene/methylmethylene)]-propanoic acid hydrazides(HL_I-HL_{IX}).

Compound	M.P.(°C)	Yield (%)	Molecular formula	Analytical data(%) observed (Calcd.)		
				C	H	N
HL_I	187	80	$C_{15}H_{14}N_2O_2S$	62.4 (62.9)	4.5 (4.9)	9.3 (9.8)
HL_{II}	210	72	$C_{16}H_{16}N_2O_2S$	63.7 (64.0)	5.0 (5.3)	8.8 (9.3)
HL_{III}	188	80	$C_{17}H_{18}N_2O_2S$	64.5 (64.9)	5.4 (5.7)	8.5 (8.9)
HL_{IV}	135	70	$C_{16}H_{16}N_2O_2S$	63.4 (64.0)	5.1 (5.3)	8.9 (9.3)
HL_V	182	64	$C_{17}H_{18}N_2O_2S$	64.4 (64.9)	5.4 (5.7)	8.5 (8.9)
HL_{VI}	195	78	$C_{18}H_{20}N_2O_2S$	65.6 (65.8)	5.8 (6.0)	8.4 (8.5)
HL_{VII}	183	68	$C_{16}ClH_{15}N_2O_2S$	57.0 (57.4)	4.1 (4.5)	8.1 (8.3)
HL_{VIII}	197	82	$C_{17}ClH_{17}N_2O_2S$	58.0 (58.2)	4.7 (4.8)	7.8 (8.0)
HL_{IX}	194	76	$C_{18}ClH_{19}N_2O_2S$	59.2 (59.5)	5.0 (5.2)	7.4 (7.7)

Table 2. IR spectral chracteristics of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienyl-methylene/methylmethylene)]-propanoic acid hydrazides

Compound	IR (cm^{-1})						
	ν(N-H)	ν(NHC=O)	ν(C=O)	ν(C=N)	ν(C=C)	ν(N-N)	ν(C-S) thienyl
HL_I	3160	1670	1650	1610	1590, 1550	1075	570, 490
HL_{II}	3150	1680	1650	1610	1600, 1550	1080	570, 500
HL_{III}	3160	1675	1650	1612	1595, 1550	1080	570, 495
HL_{IV}	3150	1675	1645	1615	1590, 1540	1090	580, 490
HL_V	3150	1680	1650	1615	1600, 1550	1080	575, 490
HL_{VI}	3150	1680	1645	1610	1590, 1560	1070	570, 500
HL_{VII}	3170	1675	1650	1615	1600, 1550	1080	570, 490
HL_{VIII}	3100	1680	1650	1610	1595, 1550	1090	590, 500
HL_{IX}	3160	1670	1645	1615	1600, 1560	1082	570, 495

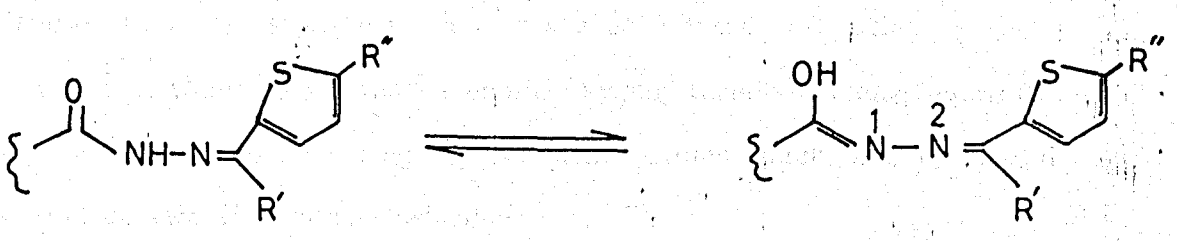
Table 3. ^{1}H NMR data of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides.

Compound	^{1}H NMR (ppm)				
	$-CH_2-CH_2-$	$Ph-CH_3$	Thienyl-CH_3	Arom-H & thienyl-H	N=CH
HL_I	2.0-2.5 (m,4H)	-	-	6.7-7.6 (m,8H)	8.8 (s,1H)
HL_{II}	2.1-2.5 (m,4H)	2.9 (s,3H)	-	6.6-7.7 (m,7H)	8.9 (s,1H)
HL_{III}	2.1-2.4 (m,4H)	3.1 (s,6H)	-	6.9-7.5 (m,6H)	8.8 (s,1H)
HL_{IV}	2.1-2.4 (m,4H)	-	2.6 (s,3H)	6.8-7.6 (m,8H)	-
HL_V	2.1-2.4 (m,4H)	2.9 (s,3H)	2.6 (s,3H)	6.8-7.5 (m,7H)	-
HL_{VI}	2.1-2.4 (m,4H)	3.0 (s,6H)	2.6 (s,3H)	6.8-7.5 (m,6H)	-
HL_{VII}	2.4-2.4 (m,4H)	-	2.6 (s,3H)	6.8-7.7 (m,6H)	-
HL_{VIII}	2.1-2.4 (m,4H)	2.9 (s,3H)	2.6 (s,3H)	6.8-7.6 (m,6H)	-
HL_{IX}	2.1-2.4 (m,4H)	3.0 (s,3H)	2.6 (s,3H)	6.8-7.4 (m,5H)	-

and magnetic data have been used to elucidate and explain the stereochemistry of the complexes.

a) Infra-red spectra

The IR spectra of the free ligands (HL_I-HL_{IX}) exhibited absorption bands in the region 3100-3160 cm^{-1} due to the N-H stretching vibrations which were absent in the complexes suggesting thereby, the enolization of the keto group followed by deprotonation during the formation of metal-ligand bonds. Since all the complexes were non-ionic in nature and were prepared at higher pH values, the ligands possibly existed in enolic form in which deprotonation can easily take place (Sacconi, 1952). Enolization and deprotonation of the carbonyl group were further substantiated by the absence of ν(NHC=O) absorption frequency which was observed in the region 1670-1680 cm^{-1} in the spectra of the parent ligands and the appearance of ν(C-O) band at 1110-1130 cm^{-1} in the spectra of complexes. The free ligands existed in the ketonic form (I) as there was no evidence of the presence of ν(O-H) frequency in the region 3300-3600 cm^{-1}. However, in solution or in the presence of metal ions the ligands may form an equilibrium mixture of tautomeric forms I and II (Fig. 2).



I II

FIG.2 TAUTOMERIC FORMS I AND II

A sharp band diagnostic of the azine chromophore (-C=N-N=C-) underwent a negative spectral shift of ν(C=N) vibration from 1610-1615 cm^{-1} in the free ligands to 1590-1600 cm^{-1} in the complexes (Birader and Kulkarni, 1971). The participation of nitrogen in coordination was further confirmed by shifting of N-N stretchings from 1070-1090 cm^{-1} to 1040-1060 cm^{-1} (Mohan et al., 1985). Of the two azomethine nitrogen atoms (Fig. 2), coordination through the terminal nitrogen 2 has been suggested because the geometry of the Schiff's bases derived from substituted benzoylpropionic acid hydrazide and substituted-2-acetyl/carboxaldehyde thiophene does not permit the involvement of both the nitrogen atoms in coordination with the same metal ion. On coordination through the nitrogen 2, a five membered ring (Fig. 3) is formed which has lesser ring strain as compared to that in a four membered ring (Chauhan and Mishra, 1985). Splitting and hypsochromic shift of the ring frequencies of thiophene observed at 570-590 cm^{-1} indicated the coordination of sulphur of the thiophene ring to the metal ion (Socrates, 1980). In the far infra-red region the bands observed at 450-460 cm^{-1}, 390-410 cm^{-1} and 280-300 cm^{-1} were assigned to the ν(M-O), ν(M-N) and ν(M-S) vibrations respectively (Ferraro, 1971).

These observations suggest a tridentate conjugated ONS donor system of the ligand in which deprotonated enolic oxygen, terminal azomethine nitrogen and sulphur of the thiophene ring are the donor atoms which bind the metal ion to produce two five membered rings.

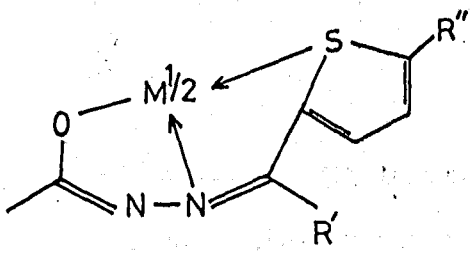


FIG. 3

The detailed IR spectral characteristics of the complexes, $[M(L_I)_2]$-$[M(L_{IX})_2]$ are given in Table 4.

b) Magnetic moment and electronic spectra

The symmetrical d^5 Mn(II) ion forms quite stable complexes due to the exceptional stability of the ion on account of the presence of half filled 3d orbitals. However, the high spin configuration provides no crystal field stabilization energy. Consequently, the stability constants of these complexes are comparatively lower than those of the corresponding complexes of neighbouring Mn(II) ions and these complexes are quite labile (Cotton and Wilkinson, 1988). In this configuration the complexes of Mn(II) exhibit magnetic moment values corresponding to the presence of five unpaired electrons with little or no orbital contribution. The electronic spectra of these complexes are quite complicated having many absorption bands and that too of lower intensities. The d-d electronic transitions in a d^5 configuration may involve the pairing of some electron spins and these transitions are both spin forbidden and orbitally forbidden. Theoretically possible bands near 19400, 22600, 25200, 28200 and 29900 cm^{-1} can be attributed to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$,

$^6A_{1g} \rightarrow {}^4E_g$, $^6A_{1g} \rightarrow {}^4A_{1g}$ and $^6A_{1g} \rightarrow {}^4t_{2g}$ (D) transitions respectively. Apart from these bands, many charge transfer bands are also observed in the UV region which can be explained from the Tanabe-Sugano energy diagram (Fig. 4) (Greenwood and Earnshaw, 1990).

In the present investigation the observed magnetic moment values of the complexes $[Mn(L_I)_2]$-$[Mn(L_{IX})_2]$ ranged from 5.94-6.15 B.M. which were consistent with the theoretically calculated and experimentally obtained values for various spin free Mn(II) complexes (Cotton and Wilkinson, 1988; Rao et al., 1984 and Sharma and Parasher, 1988). The electronic spectra of the complexes exhibited bands in the regions, 16900-17500, 22000-22200, 23800-24400 and 27500-28000 cm^{-1} (Table 6) which were assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$ (G), $^6A_{1g} \rightarrow {}^4T_{2g}$(D) transitions respectively confirming an octahedral geometry for the complexes. The assignments are in conformity with the observations made by Heidt et al. (1958) and Sharma and Parasher (1988).

Based on the elemental analysis and physico-chemical data, a coordination number six with octahedral geometry is proposed for the metal ion in all the complexes in which each of the two uninegative tridentate ligands coordinated through the oxygen of carbonyl group (enolic form after deprotonation), terminal azomethine nitrogen and sulphur of the thiophene nucleus.

2. Cobalt(II) complexes

The ligational behaviour of the Schiff's bases and the stereochemistry of the non-ionic, 1:2 cobalt(II)– ligand complexes has been elucidated on the basis of IR spectral data, magnetic moments and electronic absorption studies.

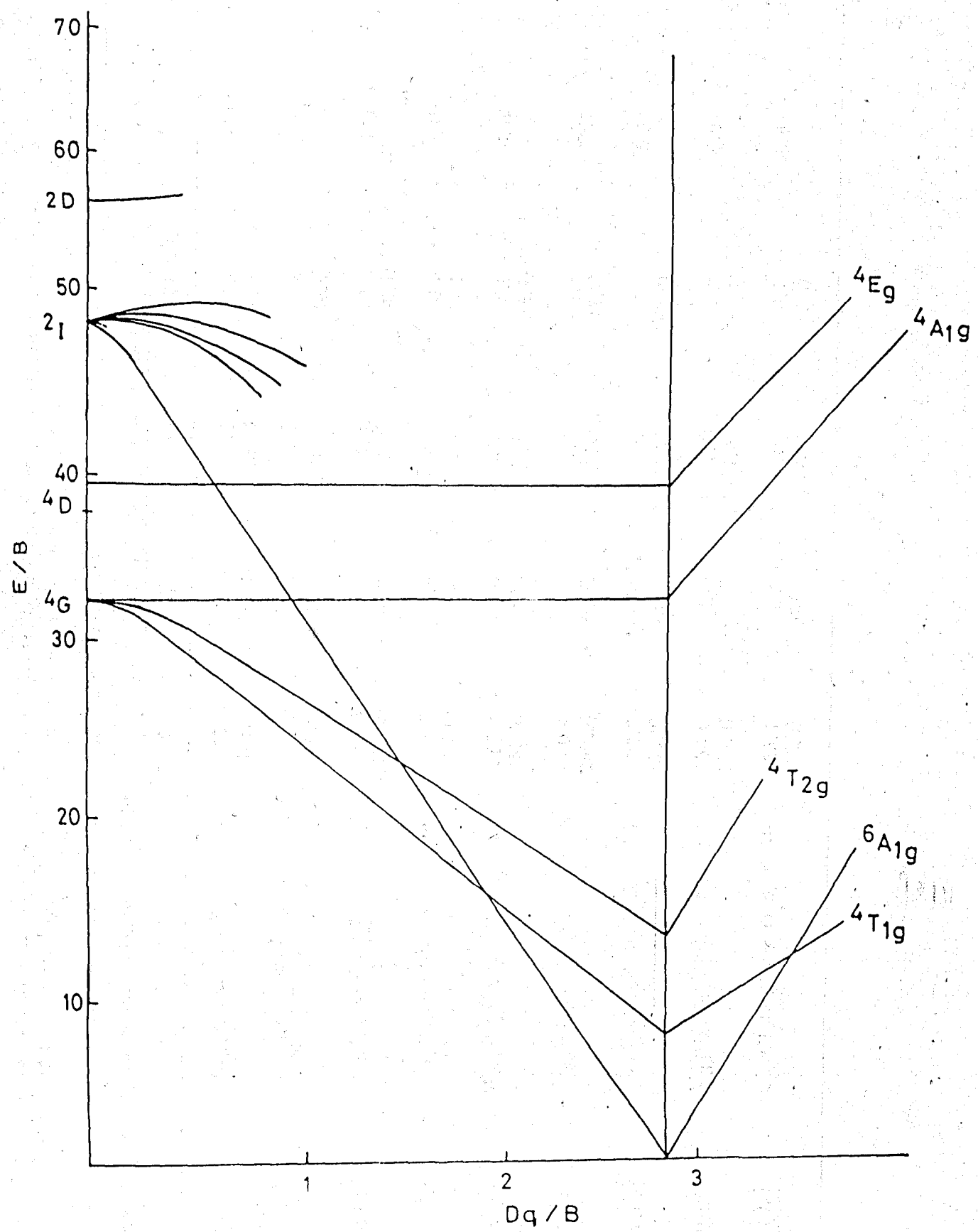


FIG.4 TANABE-SUGANO DIAGRAM FOR Mn(II) IN AN OCTAHEDRAL FIELD.

Table 4. Physical analytical and magnetic data of manganese(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides

Compound	Molecular formula	Yield (%)	Analytical data % observed (calcd.)				ueff. (B.M.)
			C	H	N	Metal	
$[Mn(L_I)_2]$	$C_{30}H_{26}MnN_4O_4S_2$	61	57.4 (57.6)	4.0 (4.2)	8.4 (8.9)	8.4 (8.8)	6.08
$[Mn(L_{II})_2]$	$C_{32}H_{30}MnN_4O_4S_2$	58	58.3 (58.8)	3.7 (3.9)	8.3 (8.6)	8.2 (8.4)	5.95
$[Mn(L_{III})_2]$	$C_{34}H_{34}MnN_4O_4S_2$	54	59.5 (59.9)	4.7 (4.9)	7.9 (8.2)	7.8 (8.1)	5.80
$[Mn(L_{IV})_2]$	$C_{32}H_{30}MnN_4O_4S_2$	60	58.5 (58.8)	3.6 (3.9)	8.4 (8.6)	8.0 (8.4)	6.15
$[Mn(L_V)_2]$	$C_{34}H_{34}MnN_4O_4S_2$	57	59.8 (59.9)	4.6 (4.9)	8.0 (8.2)	8.0 (8.1)	6.10
$[Mn(L_{VI})_2]$	$C_{36}H_{38}MnN_4O_4S_2$	58	60.4 (60.9)	5.2 (5.4)	7.7 (7.9)	7.4 (7.7)	5.82
$[Mn(L_{VII})_2]$	$C_{32}Cl_2H_{28}MnN_4O_4S_2$	54	52.8 (53.2)	3.6 (3.9)	7.5 (7.7)	7.2 (7.6)	5.94
$[Mn(L_{VIII})_2]$	$C_{34}Cl_2H_{32}MnN_4O_4S_2$	61	54.0 (54.4)	4.0 (4.3)	7.1 (7.5)	7.0 (7.3)	6.04
$[Mn(L_{IX})_2]$	$C_{36}Cl_2H_{36}MnN_4O_4S_2$	60	55.1 (55.5)	4.2 (4.6)	7.0 (7.2)	6.7 (7.1)	5.98

Table 5. IR spectral characteristics of manganese(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides.

Compound	IR (cm^{-1})							
	ν(C=N)	ν(C=O)	ν(C-O)	ν(N-N)	ν(C-S) thioph.	ν(M-O)	ν(M-N)	ν(M-S)
$[Mn(L_I)_2]$	1590	1645	1120	1040	570	460	400	280
$[Mn(L_{II})_2]$	1590	1645	1120	1050	570	455	410	280
$[Mn(L_{III})_2]$	1600	1640	1110	1040	575	450	405	285
$[Mn(L_{IV})_2]$	1590	1650	1120	1050	560	450	395	300
$[Mn(L_V)_2]$	1600	1650	1115	1060	560	400	400	290
$[Mn(L_{VI})_2]$	1595	1645	1120	1060	570	460	410	290
$[Mn(L_{VII})_2]$	1595	1640	1110	1050	580	450	410	300
$[Mn(L_{VIII})_2]$	1600	1640	1110	1040	560	450	390	300
$[Mn(L_{IX})_2]$	1590	1650	1120	1060	575	455	400	280

Table 6. Electronic spectral assignments for manganese(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides.

Compound	$^6A_{1g} \rightarrow {}^4T_{1g}$ (cm^{-1})	$^6A_{1g} \rightarrow {}^4T_{2g}$ (cm^{-1})	$^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ (cm^{-1})	$^6A_{1g} \rightarrow {}^4T_{2g}(D)$ (cm^{-1})
$[Mn(L_I)_2]$	17300	22050	23800	27850
$[Mn(L_{II})_2]$	17100	22200	24200	28000
$[Mn(L_{III})_2]$	16900	22100	23900	27500
$[Mn(L_{IV})_2]$	17000	22000	24250	27500
$[Mn(L_V)_2]$	17500	22100	24400	27550
$[Mn(L_{VI})_2]$	17500	22180	23950	27950
$[Mn(L_{VII})_2]$	17200	22150	24200	26600
$[Mn(L_{VIII})_2]$	17350	22080	23800	28000
$[Mn(L_{IX})_2]$	17400	22200	24200	27700

a) Infra-red spectra

The IR spectral characteristics (Table 8) of the ligands and the complexes suggested a tridentate behaviour of the ligands (HL_I-HL_{IX}) in the cobalt(II) complexes. The ligand molecules were found to coordinate through the terminal azomethine nitrogen, deprotonated enolic oxygen and the sulphur of thiophene ring.

The ν(N-H) absorption frequency observed at 3100-3170 cm^{-1} in the spectra of the ligands was absent in the spectra of the complexes suggesting the involvment of azomethine nitrogen in coordination. The ligands did not exhibit any absorption frequency in the region 3300-3600 cm^{-1} which suggested that the ligands existed in the ketonic form in the solid state, but during coordination under alkaline conditions the enolisation of the keto group, and subsequent deprotonation led to the formation of a non-ionic complex by neutralization of the charge on the metal ion. This hypotheses is further supported by the absence of ν(NHC=O) absorption in the region 1670-1680 cm^{-1} in the spectra of the complexes and appearance of new band at 1110-1130 cm^{-1} diagnostic of ν(C-O) vibration in the spectra of the complexes.

A negative spectral shift of 10-15 cm^{-1} in the absorption frequency of the azine chromophore and hypsochromic shifting of N-N stretching frequency from 1070-90 to 1050-75 cm^{-1} clearly pointed to the participation of azomethine nitrogen in coordination with the metal ion.

The involvement of thiophene ring sulphur in coordination with the metal ion was evident from the splitting and shifting of the thiophene ring

stretching vibrations at 570-590 cm^{-1} and 490-500 cm^{-1} to lower regions (Socrates, 1980). The new bands at 460-470, 400-415 and 290-300 cm^{-1} in the spectra of complexes were assigned to the M-O, M-N and M-S stretching vibrations respectively (Ferraro, 1971).

b) Magnetic moment and electronic spectra

The magnetic moment values for spin free octahedral and tetragonally distorted cobalt(II) complexes are in excess of the spin only value for three unpaired electrons (3.89 B.M.) by 0.8-1.3 B.M., the excess arising from the unquenched orbital contribution of both the ground state $t_{2g}^5 e_g^2$ and the first excited state $t_{2g}^4 e_g^3$ (Figgis, 1976). The exact excess magnitude, however, depends upon the ligand field strength. The magnetic moments of low spin cobalt(II) complexes correspond to single unpaired electron (1.73 B.M.) with slight orbital contribution and these complexes are formed with the ligands of higher field strength only. The observed effective magnetic moment values for cobalt(II) complexes of the ligands (HL_I-HL_{IX}) ranged from 4.24-4.80 B.M. which correspond to the presence of three unpaired electrons with significant orbital contribution.

Cobalt(II) is the most important d^7 species and in an octahedral field three spin allowed d-d transitions are generally anticipated due to the splitting of the free ion, ground ^4F term and the accompanying ^4P term (Carlin, 1965). The Tanabe-Sugano diagram for cobalt(II) in an octahedral field is shown in fig. 5. The three electronic transitions generally observed in such complexes

originate from the ground term $^4T_{1g}(F)$:

$$^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F) \qquad (\nu_1)$$

$$^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F) \qquad (\nu_2)$$

$$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P) \qquad (\nu_3)$$

In the complexes under present investigation, the absorption frequencies observed in the region 8400-9100 cm^{-1}, 16000-17980 cm^{-1} and 21730-24100 cm^{-1} (Table 9) were assigned to $^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ (ν_1) ; $^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ (ν_3) transitions respectively (Lever, 1968). The observed magnetic moment values and the electronic absorptions were characteristic of the octahedral geometry.

Various ligand field parameters like energy ratio (ν_2/ν_1), ligand field splitting energy (10 Dq), Racah interelectronic parameter (B), nephelauxetic ratio (β) and ligand field stabilization energy (LFSE) were also calculated from this data and are presented in table 9. The energy ratios (1.89-2.01) were consistent with the proposed octahedral geometry (Ferguson et al., 1963 and Goodgame and Cotton, 1951). The 10 Dq values (7600-8930 cm^{-1}), B (896.9-961.3 cm^{-1}), the values of nephelauxetic ratio (0.918-0.981) and the LFSE values (13.03-15.27 K cal mol^{-1}) for the complexes $[Co(L_I)_2]$-$[Co(L_{IX})_2]$ agreed well with the those reported for octahedral complexes (Eilbeck, 1967 and Carlin, 1965). The less than one values for β and the lower B values than the free ion value (971 cm^{-1}) suggested a considerable

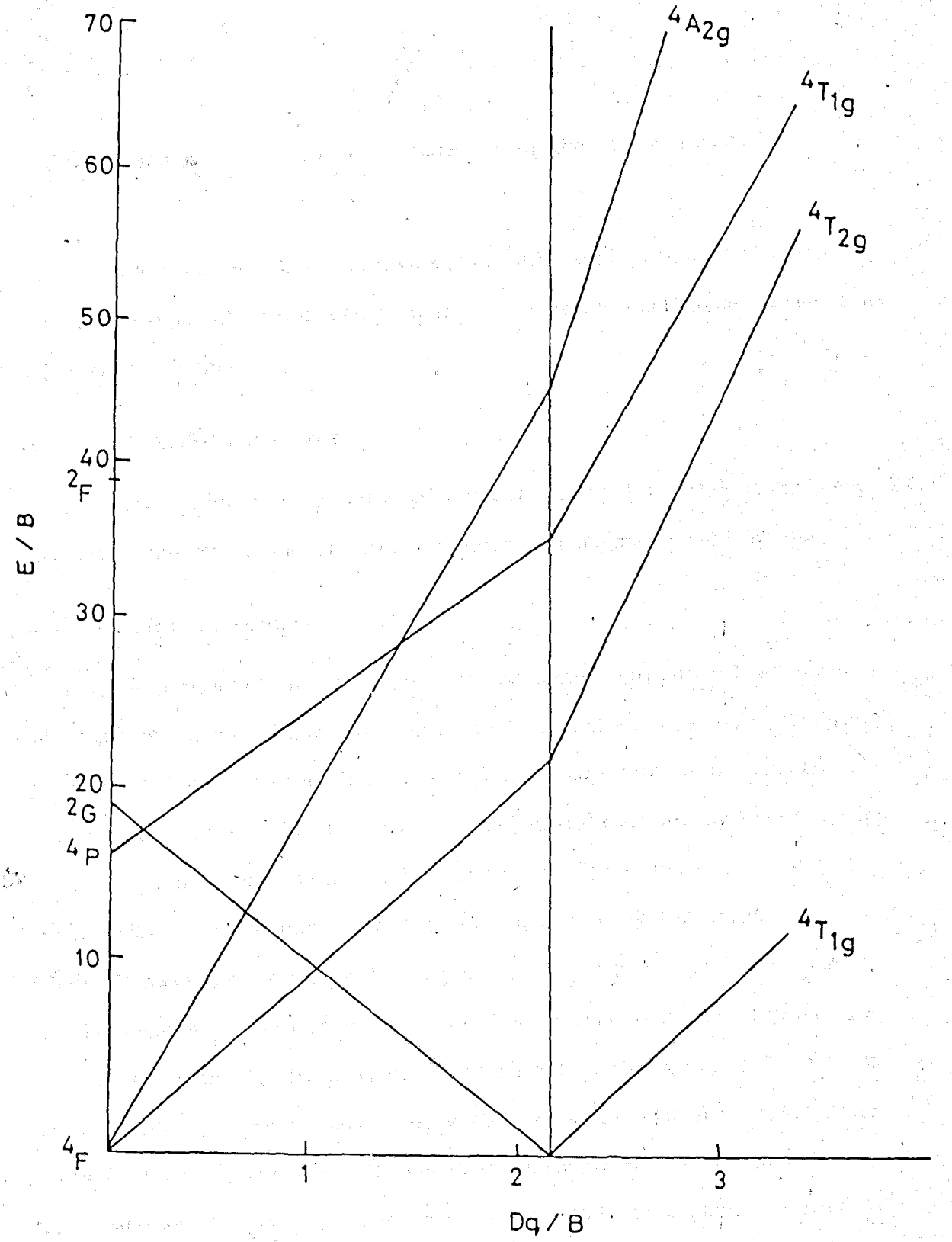


FIG. 5 TANABE-SUGANO DIAGRAM FOR Co (II) IN AN OCTAHEDRAL FIELD.

orbital overlap and some covalent character of the metal ligand bonds.

Based on the above discussion, an octahedral geometry is assigned to the non-ionic 1:2 metal-ligand complexes in which each ligand behaved as uninegative tridentate.

3. Nickel(II) complexes

The structure elucidation of non-conducting 1:2 metal-ligand complexes has been done by IR and electronic spectra and magnetic moment data.

a) Infra-red spectra

A perusal of the IR spectra of the ligands (HL_I-HL_{IX}) and their nickel(II) complexes (Table 11)revealed that the ν(N-H) absorption frequency at 3100-3170 cm^{-1} in the spectra of ligands was absent in the spectra of the complexes suggesting thereby, the enolisation followed by deprotonation of the carbonyl group during metal-ligand bond formation (Aggarwal and Rao, 1973). This conclusion was further supported by the absence of ν(NHC=0) stretching vibrational frequency and appearance of ν(C-0) band in the spectra of the complexes. The ligands existed in keto form in the solid state as the ν(0-H) absorption was absent in the region 3300-3600 cm^{-1} in the spectra of the ligands. The complexes were formed by reacting the metal salt and ligand in alkaline medium under which enolisation of the keto group and subsequently its deprotonation can easily take place resulting in the formation of non-ionic complexes (Sacconi, 1952).

Table 7. Physical, analytical and magnetic data of cobalt(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides.

Compound	Molecular formula	Yield (%)	Analytical data % observed (calcd.)				μ_{eff} (B.M.)
			C	H	N	Metal	
$[Co(L_I)_2]$	$C_{30}CoH_{26}N_4O_4S_2$	54	57.0 (57.2)	4.0 (4.1)	8.4 (8.9)	8.9 (9.4)	4.71
$[Co(L_{II})_2]$	$C_{32}CoH_{30}N_4O_4S_2$	56	58.0 (58.4)	4.2 (4.5)	8.2 (8.5)	8.7 (9.0)	4.34
$[Co(L_{III})_2]$	$C_{34}CoH_{34}N_4O_4S_2$	53	59.4 (59.6)	4.6 (4.9)	8.0 (8.2)	8.2 (8.6)	4.68
$[Co(L_{IV})_2]$	$C_{32}CoH_{30}N_4O_4S_2$	58	58.4 (58.4)	4.1 (4.5)	8.1 (8.5)	8.6 (9.0)	4.56
$[Co(L_V)_2]$	$C_{34}CoH_{34}N_4O_4S_2$	55	59.2 (59.6)	4.7 (4.9)	7.8 (8.2)	8.2 (8.6)	4.24
$[Co(L_{VI})_2]$	$C_{36}CoH_{38}N_4O_4S_2$	51	60.1 (60.6)	5.0 (5.3)	7.4 (7.8)	8.1 (8.3)	4.38
$[Co(L_{VII})_2]$	$C_{32}Cl_2CoH_{28}N_4O_4S_2$	48	52.5 (52.9)	3.4 (3.8)	7.3 (7.7)	8.0 (8.1)	4.80
$[Co(L_{VIII})_2]$	$C_{34}Cl_2CoH_{32}N_4O_4S_2$	53	54.0 (54.1)	4.0 (4.2)	7.1 (7.4)	7.4 (7.8)	4.64
$[Co(L_{IX})_2]$	$C_{36}Cl_2CoH_{36}N_4O_4S_2$	57	54.8 (55.2)	4.2 (4.6)	7.0 (7.2)	7.1 (7.5)	4.71

Table 8. IR spectral characteristics of cobalt(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides.

Compound	IR (cm^{-1})							
	ν(C=N)	ν(C=O)	ν(C-O)	ν(N-N)	ν(C-S) thioph.	ν(M-O)	ν(M-N)	ν(M-S)
$[Co(L_I)_2]$	1595	1640	1120	1060	570	460	410	300
$[Co(L_{II})_2]$	1595	1645	1115	1050	550	460	400	300
$[Co(L_{III})_2]$	1600	1645	1115	1070	575	470	415	290
$[Co(L_{IV})_2]$	1600	1640	1110	1075	560	460	400	295
$[Co(L_V)_2]$	1595	1650	1120	1050	570	470	410	290
$[Co(L_{VI})_2]$	1600	1650	1110	1060	550	470	415	300
$[Co(L_{VII})_2]$	1600	1645	1115	1065	560	465	410	290
$[Co(L_{VIII})_2]$	1595	1650	1120	1075	570	465	410	300
$[Co(L_{IX})_2]$	1595	1645	1120	1070	560	470	415	290

Table 9. Electronic spectral data and ligand field parameters for the cobalt(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides.

Compound	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (cm^{-1})	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (cm^{-1})	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (cm^{-1})	Dq(cm^{-1})	ν_2/ν_1	B(cm^{-1})	β	LFSE (Kcal mol^{-1})
$[Co(L_I)_2$	8400	16000	22860	760	1.90	910.6	0.932	13.03
$[Co(L_{II})_2]$	9100	17560	24100	846	1.92	957.6	0.981	14.50
$[Co(L_{III})_2]$	8860	16800	23200	794	1.89	961.3	0.984	13.61
$[Co(L_{IV})_2]$	8230	16600	21730	837	2.01	908.6	0.930	14.31
$[Co(L_V)_2]$	9050	17980	23000	893	1.98	922	0.944	15.27
$[Co(L_{VI})_2]$	8570	17100	22660	853	1.99	936	0.959	14.57
$[Co(L_{VII})_2]$	8910	17500	23100	859	1.96	923.7	0.946	14.71
$[Co(L_{VIII})_2]$	8530	17100	22800	857	2.00	953.4	0.976	14.68
$[Co(L_{IX})_2]$	8470	16760	22000	829	1.97	896.9	0.918	14.22

The involvement of azomethine nitrogen in coordination with the metal ion was confirmed by the hypsochromic shift (15-20 cm^{-1}) of the characteristic absorption frequency of azine chromophore. It was further supported by the shifting of $\bar{\nu}$(N-N) absorption frequency to lower regions i.e. from 1070-90 cm^{-1} to 1050-1065 cm^{-1} (Mohan et al., 1985). The other donor atom of the ligands was sulphur of the thiophene nucleus as the thiophene ring stretching vibrations observed in the ligand spectra at 570-590 and 490-500 cm^{-1} underwent shifting to lower regions by 10-15 cm^{-1} in the spectra of the complexes (Socrates, 1980). Participation of N, O and S in the coordination was further confirmed by the appearance of new absorption bands in the far infra-red region at 440-460, 380-410, and 290-300 cm^{-1} which were assigned to the M-O, M-N and M-S stretching vibrations respectively (Ferraro, 1971 and Nakamoto, 1978).

b) Magnetic moment and electronic spectral data

The observed effective magnetic moment values (μ_{eff}) and the electronic spectral absorption frequency values along with the calculated ligand field parameters are listed in tables 10 & 12. Nickel(II), the most common and comparatively stable oxidation state of nickel, forms a large number of complexes with different stoichiometries and of stereochemical types such as octahedral, square planar and tetrahedral beside some complicated equilibria of the above stereochemical types. The octahedral complexes involve $sp^3d_z2d_{x^2-y^2}$ (outer orbital) hybridization and the tetrahedral complexes have sp^3 hybridization. Both the types have magnetic moment values which correspond to the presence of two unpaired electrons. The square planar complexes involve $d_{x^2-y^2}$ sp_xp_y

hybridization and are invariably diamagnetic. The spin only magnetic moment value for two unpaired electrons is 2.83 B.M. but in practice the complexes usually exhibit higher values due to varying degrees of orbital contribution. In some polymeric forms the adjacent nickel atoms also experience weak ferromagnetic interactions. The orbital contribution to the spin only values is often determined by the stereochemistry of the complex. The T ground term of the tetrahedral ion is expected to lead to a temperature independent orbital contribution to the magnetic moment, whereas there is no such contribution in the A ground term of the octahedral ion. Further, the mixing of excited $^3T_{2g}$ (F) term into $^3A_{2g}$(F) ground term may raise its magnetic moment. These increments in magnetic moment result in the values 3.2-4.1 B.M. for tetrahedral complexes and 2.9-3.3 B.M. for octahedral complexes (Greenwood and Earnshaw, 1990).

The octahedral and tetrahedral complexes have the configuration $t_{2g}^6 e_g^2$ and $e_g^4 t_{2g}^4$ respectively. The relative ease of formation and abundance of octahedral complexes can be explained by the crystal field stabilization energy of the d^8 configuration. The John-Teller effect leading to distortion of the symmetry is practically inoperative in a $t_{2g}^6 e_g^2$ geometry. On the other hand, the square planar configuration is favoured in strong ligand fields leading to the pairing of all the eight 3d electrons.

The complexes under observation exhibited effective magnetic moment values in the range 3.10-3.32 B.M. indicating the presence of two unpaired electrons with relatively low orbital contribution to the spin only magnetic moment values, suggesting thereby, an octahedral configuration of the complexes.

Magnetic moment of octahedral Ni(II) having a $^3A_{2g}$ ground state is given by the relation.

$$\mu_{eff.} = 2.83 \left(1 + \frac{2\rho}{10\ Dq}\right)$$

and should be relatively insensitive to temperature and small departures from octahedral symmetry. Using the free ion value of $\rho = 650\ cm^{-1}$, Jesson et al. (1967) calculated 10 Dq = 9400 cm^{-1}. In the present investigation, the 10 Dq values ranged from 10500-11310 cm^{-1} (Table 12) which is fairly close to the theoretical value. The variation observed may be due to the approximations involved in the formula for calculation of effective magnetic moment and the ligand influences (Jesson et al., 1967). The effective magnetic moment values of 3.10 to 3.32 B.M for the complexes $[Ni(L_I)_2]$ - $[Ni(L_{IX})_2]$ are consistent with the postulated octahedral geometry.

The Tanabe-Sugano diagram representing the splitting patterns for the ground term ^3F and the excited state ^3P in an octahedral field is shown in fig. 6. The electronic spectra of Ni(II) complexes usually exhibit three bands ν_1, ν_2 and ν_3, apart from some weak spin forbidden transitions which appear as shoulders on these major absorptions. The ν_1 band represents the transition $^3T_{2g}(F) \longrightarrow {}^3A_{2g}(F)$ and its energy is equal to the crystal field splitting energy, Δ or 10 Dq. ν_2 is a band for the transition $^3T_{1g}(F) \longrightarrow {}^3A_{2g}(F)$ and ν_3 represents the $^3T_{1g}(P) \longrightarrow {}^3A_{2g}(F)$ transition (Greenwood and Earnshaw, 1990). The absorption spectra of the complexes, $[Ni(L_I)_2]$ - $[Ni(L_{IX})_2]$ exhibited absorptions in the regions 10500-11310, 17135-18130 and 27700-30000 cm^{-1} (Table 12) which were assigned to the $^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$

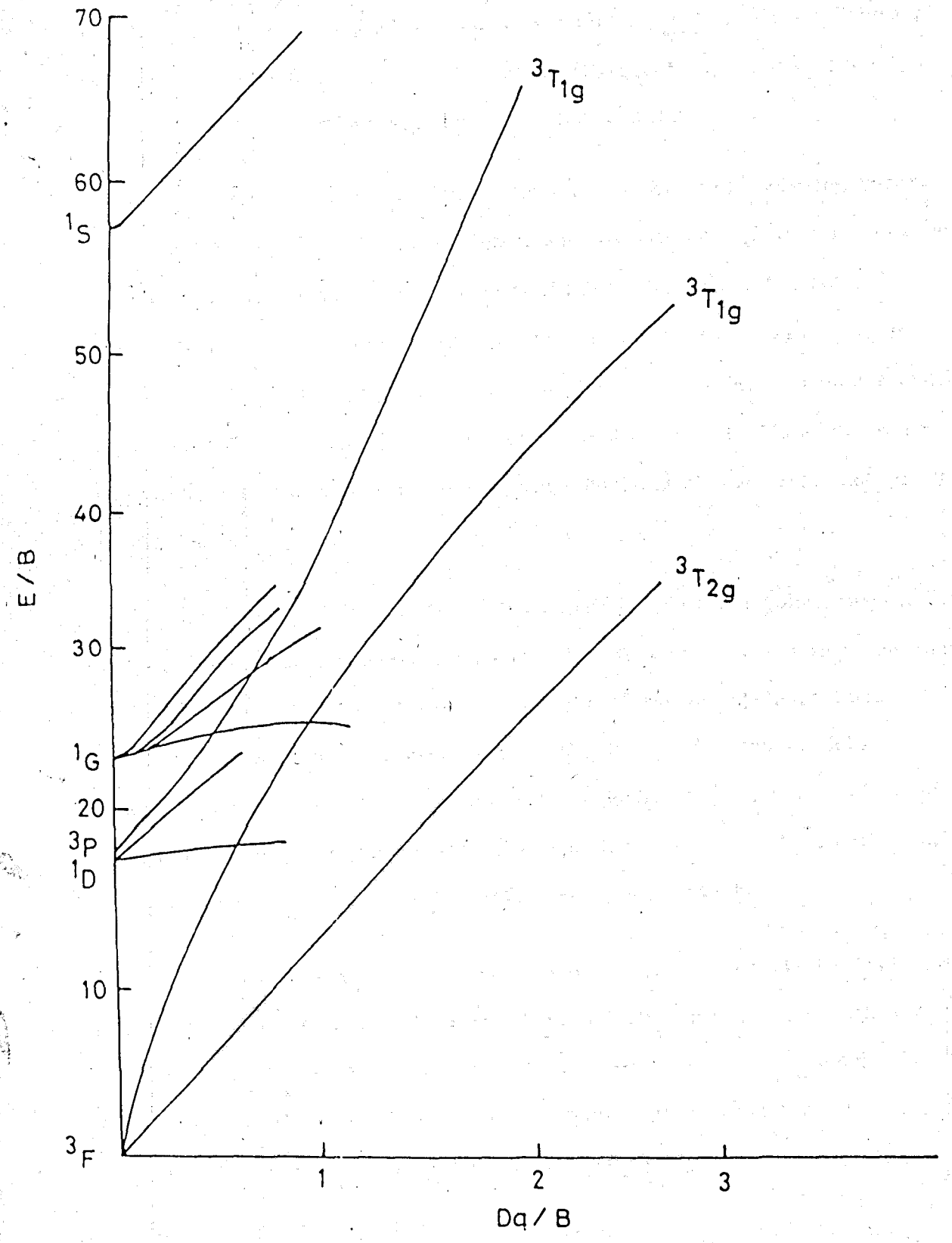


FIG. 6 TANABE-SUGANO DIAGRAM FOR Ni(II) IN AN OCTAHEDRAL FIELD.

and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transitions respectively (Jesson et al., 1967). Values of ν_2 transition calculated by Drago's method (Drago, 1971) were in good agreement with the values obtained from the spectra.

The various ligand field parameters like ligand field splitting energy , energy ratio (ν_2/ ν_1), Racah interelectronic parameter (B), nephelauxetic ratio (β) and ligand field stabilization energy (LFSE) were calculated from the electronic absorption spectral data (Drago, 1965). The calculated energy ratios (1.58-1.67), 10 Dq values (1050-1131 cm^{-1}), the interelectronic Racah parameters (829-946 cm^{-1}) and the nephelauxetic ratios (0.797-0.909) were consistent with the values for octahedral complexes (Lever, 1984 and Goodgame et al., 1961).

The values of B and β were less than the free ion values because of the decreased interelectronic repulsion from electron delocalisation resulting in appreciable amount of covalent character of the metal-ligand bonds (Rana and Shah, 1986 and Prabhakar et al., 1989). The ligand field stabilization energies for the complexes ranged from 36.00-38.79 K cal mol^{-1} and were in good agreement with the reported values for octahedral complexes [Lever et al. (1965), Ellis et al. (1975) and Sacconi (1968)].

The magnitude of 10 Dq for a given metal ion determines the position of a ligand in the spectrochemical series, which represents the variation of the value of 10 Dq as a function of central atom and of the ligand. To the first approximation, 10 Dq may be represented as a product of two factors, one for the ligand and the other for the central ion (Jorgensen, 1958).

10 Dq = f (ligand) x g(central ion)

The function f has been fixed at 1.00 for the hexaaquo ions and the ligands have been arranged accordingly as per their f values. The f values calculated from the spectroscopic data for the ligands in the complexes $[Ni(L_I)_2]$ - $[Ni(L_{IX})_2$ varied from 1.22-1.29 (Table 12) suggesting that the ligands lie in vicinity of ethylenediamine ($H_2NCH_2CH_2NH_2$) (f=1.28) in the spectrochemical series.

Based on the above discussion, the Ni(II) complexes of the title ligands were assigned octahedral geometry with a 1:2 stoichiometric ratio in which each ligand acted as uninegative tridentate, coordinating through the deprontonated enolic oxygen, terminal azomethine nitrogen and sulphur of the thiophene moiety. The various ligand field parameters coupled with magnetic data supported the assigned geometry.

4. Copper(II) complexes

The elemental analysis (Table 13) and the conductance studies indicated the formation of non-ionic 1:2 Ni(II)-ligand complexes. The structure elucidation of the compounds was done on the basis of spectral and magnetic studies.

a) Infra-red spectra

The spectra of free ligands (HL_I-HL_{IX}) exhibited strong absorption bands in the region 3100-3160 cm^{-1} and 1670-80 cm^{-1} which were assigned to the ν(N-H) and ν(NHC=O) modes of vibrations respectively. These bands were altogether absent in the spectra of the complexes suggesting thereby, the participation of the deprotonated enolised carbonyl oxygen in coordination. This was further confirmed by the appearance of ν(C-O) band at 1110-1130 cm^{-1}

Table 10. Physical, analytical and magnetic moment data of nickel(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazide.

Compound	Molecular formula	Yield (%)	Analytical data % observed (Calcd.) C	H	N	Metal	μ_{eff} (B.M.)
$[Ni(L_I)_2]$	$C_{30}H_{26}N_4NiO_4S_2$	55	56.9 (57.2)	4.1 (4.4)	8.6 (8.9)	9.0 (9.4)	3.27
$[Ni(L_{II})_2]$	$C_{32}H_{30}N_4NiO_4S_2$	64	58.0 (58.4)	4.4 (4.5)	8.1 (8.5)	8.7 (9.0)	3.11
$[Ni(L_{III})_2]$	$C_{34}H_{34}N_4NiO_4S_2$	58	59.2 (59.6)	4.7 (4.9)	8.0 (8.2)	8.2 (8.6)	3.31
$[Ni(L_{IV})_2]$	$C_{32}H_{30}N_4NiO_4S_2$	60	58.1 (58.4)	4.4 (4.5)	8.1 (8.5)	8.6 (9.0)	3.10
$[Ni(L_V)_2]$	$C_{34}H_{34}N_4NiO_4S_2$	65	59.3 (59.6)	4.6 (4.9)	7.8 (8.2)	8.1 (8.6)	3.30
$[Ni(L_{VI})_2]$	$C_{36}H_{38}N_4NiO_4S_2$	61	60.2 (60.6)	5.0 (5.3)	7.3 (7.8)	8.1 (8.3)	3.32
$[Ni(L_{VII})_2]$	$C_{32}Cl_2H_{28}N_4NiO_4S_2$	49	52.5 (52.9)	3.3 (3.9)	7.4 (7.7)	8.0 (8.1)	3.18
$[Ni(L_{VIII})_2]$	$C_{34}Cl_2H_{32}N_4NiO_4S_2$	53	54.0 (54.1)	4.0 (4.2)	7.1 (7.4)	7.4 (7.8)	3.14
$[Ni(L_{IX})_2]$	$C_{36}H_{36}Cl_2N_4NiO_4S_2$	55	55.0 (55.2)	4.2 (4.6)	7.0 (7.2)	7.1 (7.5)	3.17

Table 11. IR spectral characteristics of nickel(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides.

Compound	IR (cm^{-1})							
	ν(C=N)	ν(C=O)	ν(C-O)	ν(N-N)	ν(C-S) thioph.	ν(M-O)	ν(M-N)	ν(M-S)
$[Ni(L_I)_2]$	1590	1640	1115	1060	575	450	410	290
$[Ni(L_{II})_2]$	1590	1640	1110	1065	570	450	400	290
$[Ni(L_{III})_2]$	1600	1640	1110	1065	570	440	380	300
$[Ni(L_{IV})_2]$	1590	1650	1120	1050	575	450	390	290
$[Ni(L_V)_2]$	1595	1640	1120	1060	560	460	390	300
$[Ni(L_V)_2]$	1595	1650	1110	1060	575	450	380	290
$[Ni(L_{VII})_2]$	1600	1650	1115	1065	560	440	400	290
$[Ni(L_{VIII})_2]$	1600	1645	1110	1065	575	445	410	300
$[Ni(L_{IX})_2]$	1590	1640	1120	1050	570	460	410	300

Table 12. Electronic spectral data and ligand field parameters for the nickel(II) complexes of 4-substituted-4-oxo-1-[2-N-substituted-2-thienylmethylene/methylmethylene]-propanoic acid hydrazides.

Compound	$^3A_{2g} \longrightarrow {}^3T_{2g}$ (cm^{-1})	$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$ (cm^{-1})	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$ (cm^{-1})	Dq (cm^{-1})	ν_2/ν_1	B(cm^{-1})	β	LFSE (Kcal mol^{-1})	f
$[Ni(L_I)_2$	10800	17135	27700	1080	1.58	829	0.797	37.03	1.24
$[Ni(L_{II})_2]$	10860	17700	28000	1086	1.62	874	0.840	37.23	1.24
$[Ni(L_{III})_2]$	10900	17880	28340	1090	1.64	901	0.866	37.37	1.25
$[Ni(L_{IV})_2]$	11100	18000	29000	1110	1.62	913	0.877	38.06	1.27
$[Ni(L_V)_2]$	10800	17920	27590	1080	1.67	903	0.909	37.03	1.24
$[Ni(L_{VI})_2]$	10500	17330	27800	1050	1.65	908	0.873	36.00	1.20
$[Ni(L_{VII})_2]$	11270	18130	29000	1127	1.60	888	0.853	38.64	1.28
$[Ni(L_{VIII})_2]$	11310	18000	30000	1131	1.59	937	0.900	38.79	1.29
$[Ni(L_{IX})_2]$	10730	17790	28640	1073	1.64	936	0.900	36.99	1.22

in the spectra of complexes. Another sharp absorption diagnostic of the azine chromophore (-C=N-N=C-) underwent a negative spectral shift from 1610-15 cm^{-1} in the free ligands to 1590-1600 cm^{-1} in the complexes establishing, thereby, the involvement of azomethine nitrogen in coordination. The participation of nitrogen was further confirmed by the shifting of (N-N) stretching frequency from 1070-90 to 1040-60 cm^{-1}. Of the two azomethine nitrogens, coordination with the proximal nitrogen was suggested as it would result in the formation of a stable five membered ring with lesser ring strain as compared to a four membered ring resulting through coordination of N1 (Chauhan and Mishra, 1985). Splitting and shifting of the thiophene ring stretching vibrational frequencies observed at 570-80 and 490-505 cm^{-1} to lower regions indicated the involvement of thiophene ring sulphur in coordination with the metal ion. In the far infra-red region, the new bands appearing in the spectra of complexes at 450-60, 390-410 and 280-300 cm^{-1} were assigned to the $\bar{\nu}$(M-O), $\bar{\nu}$(M-N) and $\bar{\nu}$(M-S) vibrations respectively.

Some important absorptions in the infra-red spectra of the complexes $[Cu(L_I)_2]$ - $[Cu(L_{IX})_2]$ are listed in table 14.

b) Magnetic moment and electronic spectra

The magnetic moment values for copper(II) complexes normally range from 1.7-2.2 B.M. which correspond to the presence of one unpaired electron with variable degrees of orbital contributions to the spin only value depending upon the electronic environment around the central metal ion. In the present investigation, the observed effective magnetic moment ($\mu_{eff.}$) values for

the complexes $[Cu(L_I)_2]$ - $Cu(L_{IX})_2]$ ranged from 1.72 B.M. to 1.86 B.M. confirming the presence of a single unpaird electron.

Copper(II) has the configuration (Ar) $3d^9$ and is the equivalent of d^1 with inverted energy levels. Consequently, a simple spectrum is expected for the copper(II) complexes. But, due to considerable distortion from the octahedral symmetry as a result of Jahn-Teller effect, the free ion ground term ^2D is expected to split in a crystal field in the same way as the ^5D term of the ^4D ion and renders the spectra more complex. The energy level diagram for the six fold coordinated copper (II) ion can be represented as follows:

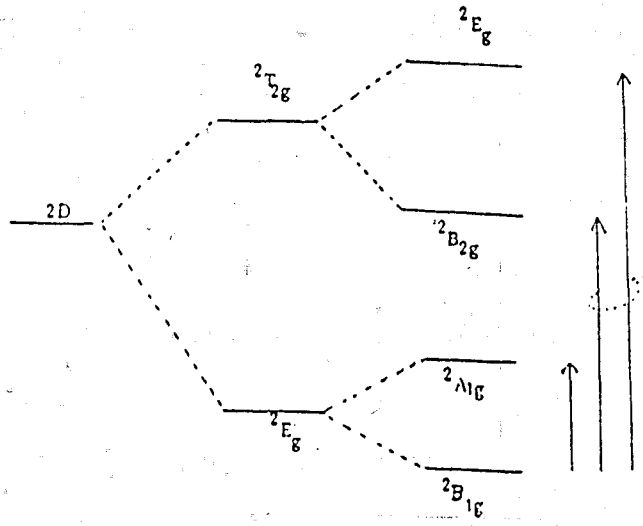


Fig.7. CRYSTAL FIELD SPLITTING DIAGRAM FOR Cu(II) ION

On the basis of the above diagram, three transitions are expected when the symmetry is square planar or distorted octahedral. But a fairly large number of distorted octahedral copper(II) complexes display only a single broad band in the region 11000-16000 cm^{-1} (Hathaway, 1971). This single absorption band is broadened due to distortion as well as by the spin orbital coupling. In the present investigation, the copper(II) complexes

exhibited a single broad absorption band in the region 14100-16600 cm^{-1} (Table 15) which was assigned to $^2E_g \longrightarrow {}^2T_{2g}$ electronic transition and is characteristic of the distorted octahedral geometry.

The Dq values (1418-1460 cm^{-1}) and the ligand field stabilization energies (24.31 - 25.02 K cal mol^{-1}) for the complexes $[Cu(L_I)_2$ - $[Cu(L_{IX})_2]$ were also consistent with the distorted octahedral geometry proposed for them.

5. Zinc(II) complexes

The 1:2 stoichiometry of the complexes was confirmed by elemental analysis (Table 33). The complexes were non-ionic and diamagnetic as evidenced by molar conductance and magnetic susceptibility studies.

Infra-red spectra

The absorption bands diagnostic of the ν(N-H) and ν(NHC=0) modes of vibrations observed at 3300-3260 cm^{-1} and 1640-30 cm^{-1} in the spectra of free ligands were absent in the spectra of complexes suggesting thereby the enolization of the carbonyl oxygen. The appearance of ν(C-O) absorption band at 1125-10 cm^{-1} in the spectra of complexes and the absence of ν(NH) and ν(NHC=0) bands affirmed the participation of deprotonated enolic oxygen in coordination with the metal ion. The involvement of azomethine nitrogen in coordination was evidenced by the hypsochromic shifting of C=N stretching vibrational frequency from 1620-10 to 1610-1590 cm^{-1} as well as by the shifting of ν(N-N) from 1070-60 to 1050-40 cm^{-1}. Splitting and shifting of ring stretching frequency of thiophene from 590-80 cm^{-1} in the

Table 13. Physical and analytical data of copper(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazide.

Compound	Molecular formula	Yield (%)	Analytical data % observed (Calcd.)				$\mu_{eff.}$(B.M)
			C	H	N	Metal	
$[Cu(L_I)_2]$	$C_{30}CuH_{26}N_4O_4S_2$	63	56.4 (56.8)	4.0 (4.1)	8.3 (8.8)	9.8 (10.0)	1.72
$[Cu(L_{II})_2]$	$C_{32}CuH_{30}N_4O_4S_2$	62	57.5 (58.0)	4.2 (4.5)	8.2 (8.5)	9.5 (9.8)	1.78
$[Cu(L_{III})_2]$	$C_{34}CuH_{34}N_4O_4S_2$	60	59.0 (59.1)	4.7 (4.9)	7.6 (8.1)	9.0 (9.2)	1.84
$[Cu(L_{IV})_2]$	$C_{32}CuH_{30}N_4O_4S_2$	61	57.6 (58.0)	4.2 (4.5)	8.2 (8.5)	9.4 (9.8)	1.75
$[Cu(L_V)_2]$	$C_{34}CuH_{34}N_4O_4S_2$	58	58.7 (59.1)	4.7 (4.9)	7.9 (8.1)	9.0 (9.2)	1.74
$[Cu(L_{VI})_2]$	$C_{36}CuH_{38}N_4O_4S_2$	65	59.7 (60.2)	5.1 (5.3)	7.4 (7.8)	8.4 (8.8)	1.72
$[Cu(L_{VII})_2]$	$C_{32}Cl_2CuH_{28}N_4O_4S_2$	54	52.7 (52.5)	4.0 (3.8)	7.2 (7.6)	8.6 (8.7)	1.74
$[Cu(L_{VIII})_2]$	$C_{34}Cl_2CuH_{32}N_4O_4S_2$	59	53.0 (53.5)	4.0 (4.2)	7.0 (7.3)	8.0 (8.3)	1.82
$[Cu(L_{IX})_2]$	$C_{36}Cl_2CuH_{36}N_4O_4S_2$	61	54.6 (54.9)	4.3 (4.6)	6.8 (7.1)	7.7 (8.1)	1.86

Table 14. IR spectral characteristics of copper(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides.

Compound	IR (cm^{-1})							
	$\bar{\nu}$(C=N)	$\bar{\nu}$(C=0)	$\bar{\nu}$(C-0)	$\bar{\nu}$(N-N)	$\bar{\nu}$(C-S) thioph.	$\bar{\nu}$(M-0)	$\bar{\nu}$(M-N)	$\bar{\nu}$(M-S)
$[Cu(L_I)_2]$	1600	1650	1120	1040	560	450	400	290
$[Cu(L_{II})_2]$	1590	1645	1110	1040	565	440	380	285
$[Cu(L_{III})_2]$	1590	1645	1110	1050	560	445	400	280
$[Cu(L_{IV})_2]$	1595	1645	1115	1050	560	450	410	290
$[Cu(L_V)_2]$	1600	1640	1120	1060	570	450	390	295
$[Cu(L_{VI})_2]$	1590	1650	1110	1040	565	460	400	300
$[Cu(L_{VII})_2]$	1600	1650	1120	1045	565	450	405	290
$[Cu(L_{VIII})_2]$	1590	1645	1115	1040	570	460	390	280
$[Cu(L_{IX})_2]$	1595	1645	1120	1050	565	445	405	300

Table 15. Electronic spectral assignments Dq and ligand field stabilization energies of copper(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides.

Compound	ν_1 (cm^{-1})	Assignment	Dq (cm^{-1})	LFSE (Kcal mol^{-1})
$[Cu(L_I)_2]$	14600	$^2E_g \rightarrow {}^2T_{2g}$	1460	25.02
$[Cu(L_{II})_2]$	14490	$^2E_g \rightarrow {}^2T_{2g}$	1449	24.84
$[Cu(L_{III})_2]$	14660	$^2E_g \rightarrow {}^2T_{2g}$	1466	25.13
$[Cu(L_{IV})_2]$	14200	$^2E_g \rightarrow {}^2T_{2g}$	1420	24.35
$[Cu(L_V)_2]$	14380	$^2E_g \rightarrow {}^2T_{2g}$	1438	24.66
$[Cu(L_{VI})_2]$	14490	$^2E_g \rightarrow {}^2T_{2g}$	1449	24.84
$[Cu(L_{VII})_2]$	14180	$^2E_g \rightarrow {}^2T_{2g}$	1418	24.31
$[Cu(L_{VIII})_2]$	14380	$^2E_g \rightarrow {}^2T_{2g}$	1438	24.66
$[Cu(L_{IX})_2]$	14450	$^2E_g \rightarrow {}^2T_{2g}$	1445	24.77

spectra of ligands to 580-560 cm^{-1} in the spectra of complexes suggested the coordination through thiophene sulphur. The new bands at 460-440, 425-410 and 300-290 cm^{-1} in the spectra of complexes were assigned to the ν(M-O),ν(M-N) and ν(M-S) vibrational modes respectively confirming the tridentate nature of the ligands.

On the basis of the elemental analysis and the tridentate ligand behaviour as proved by the infra-red spectral characteristics, an octahedral geometry was assigned to the non-ionic zinc(II) complexes.

Table 16. Physical, analytical and magnetic data of zinc(II) complexes of 4-substituted phenyl-4-oxo-1-(2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides.

Compound	Molecular formula	Yield (%)	Analytical data % observed (Calcd.)				$\mu_{eff.}$ (B.M.)
			C	H	N	Metal	
$[Zn(L_I)_2]$	$C_{30}H_{26}N_4O_4S_2Zn$	53	56.3 (56.6)	3.9 (4.1)	8.4 (8.8)	10.1 (10.3)	-
$[Zn(L_{II})_2]$	$C_{32}H_{30}N_4O_4S_2Zn$	48	57.5 (57.8)	4.2 (4.5)	8.0 (8.4)	9.3 (9.5)	-
$[Zn(L_{III})_2]$	$C_{34}H_{34}N_4O_4S_2Zn$	51	58.6 (59.0)	4.4 (4.9)	7.9 (8.1)	9.0 (9.4)	-
$[Zn(L_{IV})_2]$	$C_{32}H_{30}N_4O_4S_2Zn$	55	57.4 (57.8)	4.1 (4.5)	8.0 (8.4)	9.0 (9.5)	-
$[Zn(L_V)_2]$	$C_{34}H_{34}N_4O_4S_2Zn$	53	58.8 (59.0)	4.6 (4.9)	7.9 (8.1)	9.1 (9.4)	-
$[Zn(L_{VI})_2]$	$C_{32}H_{38}N_4O_4S_2Zn$	55	59.4 (60.0)	5.1 (5.3)	7.5 (7.8)	8.7 (9.1)	-
$[Zn(L_{VII})_2]$	$C_{32}Cl_2H_{28}N_4O_4S_2Zn$	52	52.0 (52.4)	3.3 (3.8)	7.3 (7.7)	9.0 (8.9)	-
$[Zn(L_{VIII})_2]$	$C_{34}Cl_2H_{32}N_4O_4S_2Zn$	49	53.4 (53.7)	4.0 (4.2)	7.0 (7.4)	8.3 (8.6)	-
$[Zn(L_{IX})_2]$	$C_{36}Cl_2H_{36}N_4O_4S_2Zn$	47	54.4 (54.8)	4.2 (4.6)	7.0 (7.1)	7.8 (8.2)	-

Table 17. IR spectral characteristics of zinc(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienyl-methylene/methylmethylene)]-propanoic acid hydrazides.

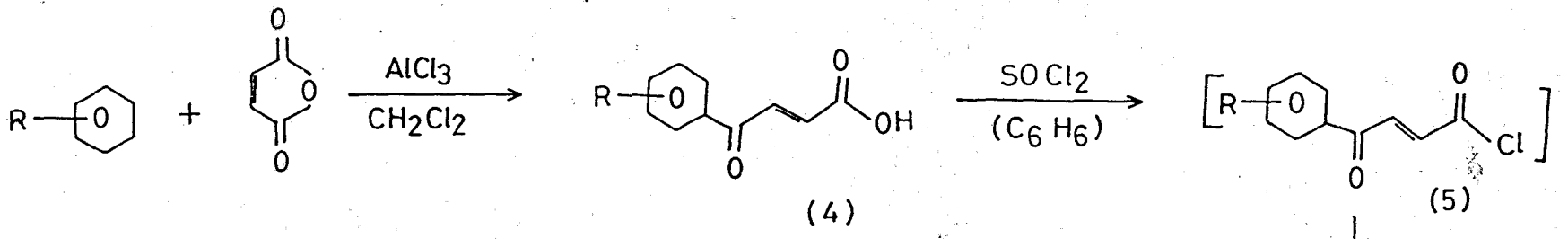
Compound	IR (cm^{-1})							
	ν(C=N)	ν(C=O)	ν(C-O)	ν(N-N)	ν(C-S) thioph.	ν(M-O)	ν(M-N)	ν(M-S)
$Zn(L_I)_2$	1610	1640	1110	1070	560	470	420	300
$Zn(L_{II})_2$	1600	1650	1110	1040	560	470	400	300
$Zn(L_{III})_2$	1600	1645	1120	1040	570	450	400	320
$Zn(L_{IV})_2$	1600	1640	1110	1060	570	470	420	300
$Zn(L_V)_2$	1610	1640	1120	1050	560	450	420	300
$Zn(L_{VI})_2$	1610	1650	1110	1050	570	470	410	320
$Zn(L_{VII})_2$	1600	1650	1110	1060	565	440	420	320
$Zn(L_{VIII})_2$	1600	1640	1110	1060	570	470	400	300
$Zn(L_{IX})_2$	1610	1650	1120	1070	560	460	410	310

SECTION "B"

I. Synthesis and characterization of 4-substituted phenyl-4-oxo-1-(2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides (HL_X-HL_{XVIII})

Substituted benzene on condensation with maleic anhydride resulted in the formation of 4-substituted phenyl-4-oxo-prop-2-en-1-oic acids (benzoyl-propenoic acid) (4) which on reaction with thionylchloride yielded the corresponding substituted acid chlorides (5). The acid chlorides on treatment with hydrazine hydrate in equimolar ratios gave the corresponding acid hydrazides (6). The reaction of (6) with substituted 2-acetyl/carboxaldehyde thiophene in ethanol resulted in the formation of title ligands in good yields (60-75%). The schematic representation for the preparation of the ligands HL_X-HL_{XVIII} is given in fig. 8.

The ligands (HL_X-HL_{XVIII}) were characterized by spectroscopic techniques, viz., ^1H NMR and IR spectroscopy and elemental analysis. The ligands were assigned trans configuration on the basis of coupling constant (16 Hz) between two downfield olefinic protons, which appeared in the region 6.8-6.9 (H_A) and 8.1-8.2 (H_B) ppm as doublets. The aromatic protons of thiophene and phenyl moieties appeared as multiplets between 6.9 and 8.0 ppm. The methyl groups attached to thiophene or phenyl groups appeared as a singlet at 2.7 and 2.3-2.4 ppm respectively. The integral proton ratios of various groups in the spectrum of each ligand were also in agreement with the proposed structure. The IR spectral absorptions for the ligands in the regions 3260-3300 cm^{-1} and 1640-1630 cm^{-1} were assigned to $\tilde{\nu}$(N-H) and $\tilde{\nu}$(NHC=O) vibrations respectively.



Ligand	R	R'	R''
HL_X	H	H	H
HL_{XI}	4-CH_3	H	H
HL_{XII}	2,5-$(CH_3)_2$	H	H
HL_{XIII}	H	CH_3	H
HL_{XIV}	4-CH_3	CH_3	H
HL_{XV}	2,5-$(CH_3)_2$	CH_3	H
HL_{XVI}	H	CH_3	Cl
HL_{XVII}	4-CH_3	CH_3	Cl
HL_{XVIII}	2,5$(CH_3)_2$	CH_3	Cl

FIG.8 : SCHEME-B

The strong band at 1610-1620 cm^{-1} was assigned to the combination of ν(C=N) and ν(C=C) mode. The physical and analytical data, IR characteristics and ^{1}H NMR data for the ligands HL_X-HL_{XVIII} are given in tables 18, 19 and 20 respectively.

II. Complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides

Manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of the title ligands (HL_X-HL_{XVIII}) were prepared by reacting the respective metal chloride and ligand in 1:2 molar ratios in ethanolic solution at pH 7.5-10. The synthesized complexes were characterized on the basis of their elemental analysis, conductance measurements, magnetic susceptibility and infra-red and electronic spectral data. The complexes were assigned the general formula ML_2, where HL=ligand (HL_X-HL_{XVIII}). The complexes were non-ionic in nature (Molar conductance values 0.5-20 ohm^{-1} cm^2 mol^{-1}) and were soluble in nitrobenzene, dimethylformamide and dimethylsulphoxide but insoluble in water, ethanol, diethylether and acetone.

1. Manganese (II) complexes

The non-ionic 1:2 metal-ligand complexes were characterized by their magnetic and spectral data.

a) Infra-red spectra

The ν(N-H) and ν(NHC=O) absorption bands observed at 3300-3260 cm^{-1} and 1640-30 cm^{-1} in the spectra of ligands were absent in the spectra of complexes suggesting thereby the enolization of the carbonyl group followed by its deprotonation

Table 18. Physical and analytical data of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazide (HL_X-HL_{XVIII}).

Compound	M.P (°C)	Yield (%)	Molecular formula	Analytical data % observed (Calcd.)		
				C	H	N
HL_X	149	70	$C_{15}H_{12}N_2O_2S$	63.0 (63.4)	4.3 (4.2)	10.1 (9.8)
HL_{XI}	220	75	$C_{16}H_{14}N_2O_2S$	64.1 (64.4)	5.0 (4.7)	9.4 (9.4)
HL_{XII}	182	68	$C_{17}H_{16}N_2O_2S$	65.1 (65.4)	5.1 (5.1)	8.7 (8.9)
HL_{XIII}	142	64	$C_{16}H_{14}N_2O_2S$	64.1 (64.4)	4.5 (4.7)	9.2 (9.4)
HL_{XIV}	140	71	$C_{17}H_{16}N_2O_2S$	65.8 (65.4)	4.7 (5.1)	9.2 (8.9)
HL_{XV}	123	64	$C_{18}H_{18}N_2O_2S$	65.9 (66.2)	5.9 (6.1)	8.9 (8.6)
HL_{XVI}	138	60	$C_{16}ClH_{13}N_2O_2S$	57.5 (57.7)	4.2 (3.9)	8.1 (8.4)
HL_{XVII}	122	65	$C_{17}ClH_{15}N_2O_2S$	59.2 (58.9)	4.4 (4.3)	7.8 (8.1)
HL_{XVIII}	130	62	$C_{18}ClH_{17}N_2O_2S$	60.2 (59.9)	4.9 (5.2)	8.0 (7.8)

Table 19. IR spectral characteristics of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	IR (cm^{-1})						
	ν(N-H)	ν(NHC=O)	ν(C=O)	ν(C=N)+(C=C)	ν(C=C)	ν(N-N)	ν(C-S) thienyl
HL_X	3250	1635	1650	1620	1590, 1545	1060	590, 510
HL_{XI}	3300	1640	1650	1620	1600, 1550	1070	585, 500
HL_{XII}	3260	1630	1640	1610	1595, 1550	1070	590, 510
HL_{XIII}	3280	1630	1640	1615	1600, 1545	1060	580, 510
HL_{XIV}	3260	1640	1650	1620	1590, 1540	1060	580, 510
HL_{XV}	3280	1635	1650	1610	1600, 1550	1070	585, 500
HL_{XVI}	3250	1635	1650	1620	1600, 1545	1070	580, 510
HL_{XVII}	3300	1630	1650	1620	1600 1550	1065	590, 510
HL_{XVIII}	3260	1640	1640	1615	1590 1540	1070	590, 500

Table 20. ^{1}H NMR data of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	^{1}H NMR data (ppm)					
	Ph-C<u>H</u>$_3$	Thienyl-C<u>H</u>$_3$	-C<u>H</u>$_A$=C<u>H</u>$_B$-	Arom-<u>H</u> and Thienyl-<u>H</u>	-CH$_A$=C<u>H</u>$_B$-	-N=C<u>H</u>
HL_X	-	-	6.8(d,1H) (J=16Hz)	7.0-8.0(m,8H)	8.1(d,1H) (J=16Hz)	8.8(s,1H)
HL_{XI}	2.3(s,3H)	-	6.8(d,1H) (J=16Hz)	7.0-8.0(m,7H)	8.1(d,1H) (J=16Hz)	8.8(s,1H)
HL_{XII}	2.4(s,6H)	-	6.8(d,1H) (J=16Hz)	6.9-7.6(m,6H)	8.1(d,1H) (J=16Hz)	8.8(s,1H)
HL_{XIII}	-	2.7(s,3H)	6.8(d,1H) (J=16Hz)	7.0-7.9(m,7H)	8.1(d,1H) (J=16Hz)	-
HL_{XIV}	2.4(s,3H)	2.7(s,3H)	6.9(d,1H) (J=16Hz)	7.2-8.0(m,6H)	8.2(d,1H) (J=16Hz)	-
HL_{XV}	2.4(s,6H)	2.7(s,3H)	6.9(d,1H) (J=16Hz)	7.0-7.9(m,6H)	8.2(d,1H) (J=16Hz)	-
HL_{XVI}	-	2.7(s,3H)	6.8(d,1H) (J=16Hz)	7.0-8.0(m,6H)	8.1(d,1H) (J=16Hz)	-
HL_{XVII}	2.4(s,3H)	2.7(s,3H)	6.9(d,1H) (J=16Hz)	7.2-8.0(m,6H)	8.2(d,1H) (J=16Hz)	-
HL_{XVIII}	2.4(s,6H)	2.7(s,3H)	6.9(d,1H) (J=16Hz)	7.2-8.0(m,5H)	8.2(d,1H) (J=16Hz)	-

before the metal-oxygen bond formation as evident from the appearance of ν(C-O) band at 1120-1110 cm^{-1}. The participation of azomethine nitrogen in coordination was confirmed by the shifting of C=N stretching band from 1620-10 to 1600-1590 cm^{-1} as well as by the hypsochromic shift of ν(N-N) from 1070-60 to 1040-30 cm^{-1} (Mohan and Sharma, 1985). Splitting and shifting of ring frequency of thiophene moiety observed at 590-80 cm^{-1} in the spectra of free ligands indicated the coordination of sulphur of thiophene ring with the metal ion. The new bands at 450-430, 410-390 and 300-280 cm^{-1} in the spectra of the complexes were assigned to M-O, M-N and M-S stretching vibrations respectively (Ferraro, 1971).

b) Magnetic moment and electronic spectra

The observed effective magnetic moment values for the complexes $[Mn(L_X)_2]$ - $[Mn(L_{XVIII})_2]$ ranged from 5.82 to 6.10 B.M. which suggested the presence of five unpaired electrons expected for a symmetrical d^5 configuration in which the orbital contribution is quite low due to the absence of spin-orbit mixing of the excited states. The electronic spectra of the complexes exhibited absorption bands in the regions 16500-17500, 22000-22500, 23800-24000 and 27000-28000 cm^{-1} (Table 23) which were assigned to the $^6A_{1g} \longrightarrow {}^4T_{1g}$ (G), $^6A_{1g} \longrightarrow {}^4T_{2g}$(G), $^6A_{1g} \longrightarrow {}^4E_g$, $^4A_{1g}$ and $^6A_{1g} \longrightarrow {}^4T_{2g}$ (D) transitions respectively (Heidt et al., 1958) and are characteristic of an octahedral geometry around the central metal ion.

On the basis of electronic spectra and magnetic moment values coupled with IR spectral characteristics and elemental analysis an octahedral geometry was assigned to the complexes $[Mn(L_X)_2]$ — $[Mn(L_{XVIII})_2]$ in which each ligand showed uninegative tridentate behaviour.

Table 21. Physical, analytical and magnetic data of manganese(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	Molecular formula	Yield (%)	Analytical data % observed (Calcd.)				$\mu_{eff.}$(B.M.)
			C	H	N	Metal	
$[Mn(L_X)_2]$	$C_{30}H_{22}MnN_4O_4S_2$	52	57.5 (57.9)	3.4 (3.5)	8.5 (9.0)	8.5 (8.9)	5.84
$[Mn(L_{XI})_2]$	$C_{32}H_{26}MnN_4O_4S_2$	54	59.0 (59.2)	3.7 (4.0)	8.3 (8.6)	8.1 (8.5)	6.03
$[Mn(L_{XII})_2]$	$C_{34}H_{30}MnN_4O_4S_2$	55	59.8 (60.2)	3.9 (4.4)	8.0 (8.3)	7.7 (8.1)	5.94
$[Mn(L_{XIII})_2]$	$C_{32}H_{26}MnN_4O_4S_2$	51	58.9 (59.2)	3.6 (4.0)	8.2 (8.6)	8.1 (8.5)	5.80
$[Mn(L_{XIV})_2]$	$C_{34}H_{30}MnN_4O_4S_2$	50	59.9 (60.2)	4.0 (4.4)	8.1 (8.3)	7.8 (8.1)	5.84
$[Mn(L_{XV})_2]$	$C_{36}H_{34}MnN_4O_4S_2$	55	61.0 (61.3)	4.5 (4.8)	7.6 (7.9)	7.4 (7.8)	6.10
$[Mn(L_{XVI})_2]$	$C_{32}Cl_2H_{24}MnN_4O_4S_2$	52	53.0 (53.5)	3.0 (3.3)	7.7 (7.8)	7.4 (7.7)	5.97
$[Mn(L_{XVII})_2]$	$C_{34}Cl_2H_{28}MnN_4O_4S_2$	54	54.5 (54.7)	3.4 (3.7)	7.0 (7.5)	7.0 (7.4)	5.82
$[Mn(L_{XVIII})_2]$	$C_{36}Cl_2H_{32}MnN_4O_4S_2$	48	55.4 (55.8)	4.0 (4.1)	7.0 (7.2)	6.8 (7.1)	5.95

Table 22. IR spectral characteristics of manganese(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-enoic acid hydrazides.

Compound	IR (cm^{-1})								
	ν(C=N)	ν(C=C)	ν(C=O)	ν(C-O)	ν(N-N)	ν(C-S) thioph.	ν(M-O)	ν(M-N)	ν(M-S)
$[Mn(L_X)_2]$	1600	1600	1650	1120	1030	570	430	390	280
$[Mn(L_{XI})_2]$	1590	1610	1640	1115	1040	575	430	400	280
$[Mn(L_{XII})_2]$	1600	1610	1640	1115	1030	575	440	410	300
$[Mn(L_{XIII})_2]$	1590	1620	1640	1120	1030	570	440	410	290
$[Mn(L_{XIV})_2]$	1595	1620	1645	1110	1035	570	450	410	300
$[Mn(L_{XV})_2]$	1590	1610	1642	1110	1030	560	445	400	290
$[Mn(L_{XVI})_2]$	1600	1600	1642	1120	1040	570	450	390	300
$[Mn(L_{XVII})_2]$	1590	1620	1650	1115	1040	575	430	410	280
$[Mn(L_{XVIII})_2]$	1595	1620	1640	1110	1030	575	450	390	280

Table 23. Electronic spectral assignments for manganese(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	$^6A_{1g} \rightarrow {}^4T_{1g}$ (cm^{-1})	$^6A_{1g} \rightarrow {}^4T_{2g}$ (cm^{-1})	$^6A_{1g} \rightarrow {}^4E_g, {}^4A_{1g}$ (cm^{-1})	$^6A_{1g} \rightarrow {}^4T_{2g(D)}$ (cm^{-1})
$[Mn(L_X)_2]$	17200	22500	23800	27500
$[Mn(L_{XI})_2]$	17500	22100	24000	27200
$[Mn(L_{XII})_2]$	17000	22200	24000	27000
$[Mn(L_{XIII})_2]$	16500	22200	23850	27000
$[Mn(L_{XIV})_2]$	16850	22000	23800	27400
$[Mn(X_V)_2]$	17200	22100	24000	28000
$[Mn(L_{XVI})_2$	17000	22500	23900	27000
$[Mn(L_{XVII})_2$	17350	22500	24000	27800
$[Mn(L_{XVIII})_2]$	17300	12400	24000	27500

2. Cobalt(II) complexes

A 1:2 stoichiometric ratio was confirmed by the elemental analysis (Table 24) for the non-conducting complexes $[Co(L_X)_2]$ - $[Co(L_{XVIII})_2]$. The structure elucidation was done by spectral and magnetic moment data.

a) Infra-red spectra

A perusal of the IR spectra of the free ligands and their cobalt(II) complexes revealed that the addends acted as tridentate and the metal-ligand bonds were formed through the carbonyl oxygen (deprotonated enolic form), proximal azomethine nitrogen (N2) and the sulphur of the thiophene moiety. The absorption frequencies characteristic of tne ν(N-H) and ν(NH C=0) modes of vibrations observed at 3300-3260 cm^{-1} and 1640-30 cm^{-1} in the spectra of ligands were absent in the spectra of complexes. These observations along with the appearance of ν(C-0) absorption band at 1120-1110 cm^{-1} affirmed firmly the deprotonation of the enolised carbonyl group during coordination with the metal ion. Shifting of the sharp band at 1620-1595 cm^{-1} diagnostic of the azine chromophore (Biradar and Kulkarni, 1971) to lower frequencies by 15-20 cm^{-1} and hypsochromic shifting of ν(N-N) band by 25-30 cm^{-1} from 1070-60 cm^{-1} confirmed the coordination through azomethine nitrogen. The stretching band at 590-70 cm^{-1} in the spectra of free ligands were shifted to lower regions on complexation which indicated the involvement of thiophene sulphur in coordination. The participation of oxygen, nitrogen and sulphur in coordination was further confirmed by the appearance of new bands in the far infra-red region at 450-430, 410-400 and 300-270 cm^{-1} due to ν(M-0), ν(M-N) and ν(M-S) modes.

b) Magnetic moment and electronic spectra

The magnetic moment values of cobalt(II) complexes for octahedral and tetrahedral environments correspond to the presence of three unpaired electrons. However, there is considerable orbital contribution to the magnetic moment in the octahedral configuration because of intrinsic orbital angular momentum and thus the effective magnetic moments for such complexes are around 4.2-5.2 B.M. In the present investigation the observed effective magnetic moment of cobalt(II) complexes at 25°C (μ_{eff}) ranged from 4.10 to 4.72 B.M. suggesting an octahedral geometry for the complexes.

The ground term ^4F of cobalt(II) ion splits into three spin allowed transitions in an octahedral environment giving rise to three major transitions viz. $^4T_{1g} \longrightarrow {}^4T_{2g}$ (F), $^4T_{1g} \longrightarrow {}^4A_{2g}$ (F) and $^4T_{1g} \longrightarrow {}^4T_{1g}$ (P). The electronic spectra of the cobalt(II) complexes, $[Co(L_X)_2]$ - $[Co(L_{XVIII})_2]$, exhibited three bands in the regions 7500-8300 (ν_1), 14400-16000 (ν_2) and 19400-21000 (ν_3) cm^{-1} which were assigned to $^4T_{1g} \longrightarrow {}^4T_{2g}$ (F), $^4T_{1g} \longrightarrow {}^4A_{2g}$ (F) and $^4T_{1g} \longrightarrow {}^4T_{1g}$(P) transitions respectively (Table 26) confirming the octahedral geometry for the complexes. The energy ratio (ν_2/ν_1) for the complexes ranged from 1.89 to 2.00 which were diagnostic of the octahedral complexes (Goodgame and Cotton, 1961).

Various ligand field parameters like ligand field splitting energy, 10 Dq (6850-8000 cm^{-1}), Racah interelectronic repulsion parameter, B (736.6 - 840.0 cm^{-1}), nephelauxetic ratio, β (0.758-0.865) and the LFSE (11.83 - 13.37 K cal mol^{-1}) were also consistent with the octahedral nature of these cobalt(II) complexes (Eilbeck, 1967). The less than one values for β and the lower values of B than the free ion value suggested a considerable degree of orbital overlap and partial covalent character of the metal ligand bonds (Maki, 1959).

Table 24. Physical, analytical and magnetic data of cobalt(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	Molecular formula	Yield (%)	Analytical data % observed (Calcd.)				$\mu_{eff.}$ (B.M.)
			C	H	N	Metal	
$[Co(L_X)_2$	$C_{30}CoH_{22}N_4O_4S_2$	59	57.2 (57.6)	3.6 (3.5)	8.7 (9.0)	9.1 (9.4)	4.72
$[Co(L_{XI})_2]$	$C_{32}CoH_{26}N_4O_4S_2$	64	58.6 (58.8)	4.2 (4.0)	8.3 (8.6)	8.9 (9.0)	4.10
$[Co(L_{XII})_2]$	$C_{34}CoH_{30}N_4O_4S_2$	58	60.0 (59.9)	4.2 (4.4)	8.4 (8.2)	8.4 (8.6)	4.50
$[Co(L_{XIII})_2]$	$C_{32}CoH_{26}N_4O_4S_2$	62	59.1 (58.8)	3.8 (4.0)	8.8 (8.6)	9.3 (9.0)	4.60
$[Co(L_{XIV})_2]$	$C_{34}CoH_{30}N_4O_4S_2$	55	60.2 (59.9)	4.6 (4.4)	8.0 (8.2)	8.7 (8.6)	4.52
$[Co(L_{XV})_2]$	$C_{36}CoH_{34}N_4O_4S_2$	58	61.1 (60.9)	5.0 (4.8)	8.1 (7.9)	8.6 (8.3)	4.20
$[Co(L_{XVI})_2]$	$C_{32}Cl_2CoH_{24}N_4O_4S_2$	62	52.9 (53.2)	3.2 (3.3)	7.9 (7.7)	7.9 (8.2)	4.35
$[Co(L_{XVII})_2]$	$C_{34}Cl_2CoH_{28}N_4O_4S_2$	59	54.4 (54.4)	3.5 (3.7)	7.6 (7.4)	8.2 (7.8)	4.12
$[Co(L_{XVIII})_2]$	$C_{36}Cl_2CoH_{32}N_4O_4S_2$	60	55.2 (55.5)	3.9 (4.1)	6.9 (7.2)	7.9 (7.6)	4.20

Table 25. IR spectral characteristics of cobalt(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	IR (cm^{-1})								
	ν(C=N)	ν(C=C)	ν(C=O)	ν(C-O)	ν(N-N)	ν(C-S) thioph.	ν(M-O)	ν(M-N)	ν(M-S)
$[Co(L_X)_2]$	1595	1610	1645	1120	1030	570	440	400	280
$[Co(L_{XI})_2]$	1600	1600	1640	1120	1020	570	450	400	300
$[Co(L_{XII})_2]$	1600	1600	1650	1120	1030	560	430	400	270
$[Co(L_{XIII})_2]$	1580	1620	1640	1110	1020	580	435	410	270
$[Co(L_{XIV})_2]$	1590	1620	1650	1110	1020	575	450	405	300
$[Co(L_{XV})_2]$	1590	1610	1640	1120	1040	570	440	410	280
$[Co(L_{XVI})_2]$	1600	1620	1645	1110	1030	570	435	410	285
$[Co(L_{XVII})_2]$	1595	1620	1645	1120	1030	570	430	400	285
$[Co(L_{XVIII})_2]$	1590	1620	1640	1120	1040	580	450	410	300

Table 26. Electronic spectral data and ligand field parameters for cobalt(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	$^4T_{1g} \longrightarrow {}^4T_{2g}(F)$ (cm^{-1})	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (cm^{-1})	$^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ (cm^{-1})	$Dq(cm^{-1})$	ν_2/ν_1	$B(cm^{-1})$	β	LFSE (Kcal mol^{-1})
$[Co(L_X)_2]$	8100	15900	21000	780	1.96	840.0	0.865	13.37
$[Co(L_{XI})_2]$	7900	15700	20200	780	1.98	813.3	0.837	13.37
$[Co(L_{XII})_2]$	8300	16000	20400	770	1.92	766.6	0.789	13.20
$[Co(L_{XIII})_2]$	7650	14500	19500	685	1.89	736.6	0.758	11.74
$[Co(L_{XIV})_2]$	7500	14400	19400	690	1.92	753.3	0.775	11.83
$[Co(L_{XV})_2]$	8200	15500	21000	730	1.89	793.3	0.816	12.51
$[Co(L_{XVI})_2]$	8000	16000	20000	800	2.00	800.0	0.823	13.71
$[Co(L_{XVII})_2]$	8300	15900	20800	760	1.91	786.6	0.810	13.03
$[Co(L_{XVIII})_2]$	7700	14600	19500	690	1.89	800.0	0.823	11.83

3. Nickel(II) complexes

The stoichiometry of the complexes $[Ni(L_X)_2]$ - $[Ni(L_{XVIII})_2]$ was confirmed by their elemental analysis (Table27). The conductance measurements suggested non-ionic nature of these 1:2 metal-ligand complexes.

a) Infra-red spectra

The $\bar{\nu}$(N-H) band at 3300-3260 cm^{-1} and the $\bar{\nu}$(NHC=0) band at 1640-30 cm^{-1} observed in the IR spectra of ligands were absent in the spectra of the corresponding complexes suggesting thereby the involvement of deprotonated enolic oxygen in coordination with the metal ion which was further evident from appearance of $\bar{\nu}$ (C-0) band at 1120-10 cm^{-1} in the spectra of complexes. A sharp band diagnostic of the azine chromophore (-C=N-N=C-) observed at 1620-1610 cm^{-1} in the spectra of the ligands underwent a negative spectral shift indicating the involvement of sulphur in coordination. In the far infra-red region, the new bands appearing at 450-420, 410-390 cm^{-1} and 300-270 cm^{-1} in the spectra of the complexes were assigned to M-0, M-N and M-S stretching vibrations respectively.

b) Magnetic moment and electronic spectra

The magnetic moment values ($\mu_{eff.}$) for the complexes $[Ni(L_X)_2]$ - $[Ni(L_{XVIII})_2]$ ranged from 3.12 to 3.30 B.M. which correspond to the paramagnetism due to the presence of two unpaired electrons. The electronic spectra of the nickel(II) complexes exhibited three intense bands in the regions 10500-11300 ($\bar{\nu}_1$), 17300-19200 ($\bar{\nu}_2$) and 26500-27700 ($\bar{\nu}_3$) cm^{-1} which were assigned to the three spin allowed transitions namely,

$^3A_{2g} \longrightarrow {}^3T_{2g}$, $^3A_{2g} \longrightarrow {}^3t_{1g}$ and $^3A_{2g} \longrightarrow {}^3T_{1g}$ respectively. The energy ratio (ν_2/ν_1) for the complexes ranged from 1.56 to 1.77 which was characteristic of the octahedral complexes. The ν_2 frequencies calculated by employing Drago's method (Drago, 1965) agreed fairly with the practically observed values.

The ligand field parameters (Dq, B, β and LFSE) calculated for these complexes by using standard equations (Huheey, 1983) are given in table 29. The values of Racah interelectronic repulsion parameter (773.3-900.0 cm^{-1}) were lower than the free ion values indicating thereby the orbital overlap and delocalization of d-orbitals (Lever, 1966). The β values (0.750-0.873) obtained were less than unity suggesting considerable amount of covalent character of the metal-ligand bonds (Rana and Shah, 1986). The Dq values (1050-1130 cm^{-1}) and LFSE (36.00-38.40 K cal mol^{-1}) also confirmed the octahedral geometry of the complexes.

The position of the ligands in the spectrochemical series was determined by calculating their f values using Jorgensen equation (Jorgensen, 1958).

10 Dq = f (ligands) X g (central ion)

The f values (1.20-1.30) for the ligands suggested that these occupy a position near ethylene-diamine in the spectrochemical series.

4. Copper(II) complexes

The 1:2 stoichiometry for the non-ionic copper(II) complexes was confirmed by elemental analysis (Table 30). The structure elucidation of the compounds was done on the basis of spectral and magnetic studies as described below.

Table 27. Physical, analytical and magnetic data of nickel(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	Molecular formula	Yield (%)	Analytical data % observed (Calcd.)				$\mu_{eff.}$ (B.M.)
			C	H	N	Metal	
$[Ni(L_X)_2]$	$C_{30}H_{22}N_4NiO_4S_2$	60	58.0 (57.6)	3.3 (3.5)	9.1 (9.0)	9.0 (9.4)	3.18
$[Ni(L_{XI})_2]$	$C_{32}H_{26}N_4NiO_4S_2$	58	59.2 (58.8)	3.8 (4.0)	8.7 (8.6)	8.9 (9.0)	3.26
$[Ni(L_{XII})_2]$	$C_{34}H_{30}N_4NiO_4S_2$	62	60.3 (59.9)	4.6 (4.4)	8.4 (8.2)	8.4 (8.6)	3.24
$[Ni(L_{XIII})_2]$	$C_{32}H_{26}N_4NiO_4S_2$	55	58.6 (58.8)	4.2 (4.0)	8.3 (8.6)	8.8 (9.0)	3.15
$[Ni(L_{XIV})_2]$	$C_{34}H_{30}N_4NiO_4S_2$	61	59.6 (59.9)	4.2 (4.4)	8.0 (8.2)	8.4 (8.6)	3.30
$[Ni(L_{XV})_2]$	$C_{36}H_{34}N_4NiO_4S_2$	62	61.2 (60.9)	4.9 (4.9)	8.2 (7.9)	8.3 (8.3)	3.22
$[Ni(L_{XVI})_2]$	$C_{32}Cl_2H_{24}N_4NiO_4S_2$	55	53.4 (53.2)	3.6 (3.3)	7.4 (7.7)	8.0 (8.2)	3.12
$[Ni(L_{XVII})_2]$	$C_{34}Cl_2H_{28}N_4NiO_4S_2$	51	54.2 (54.4)	3.9 (3.7)	7.1 (7.4)	7.4 (7.8)	3.14
$[Ni(L_{XVIII})_2]$	$C_{36}Cl_2H_{32}N_4NiO_4S_2$	53	55.3 (55.5)	4.4 (4.1)	7.0 (7.2)	7.2 (7.6)	3.17

Table 28. IR spectral characteristics of nickel(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	IR (cm^{-1})								
	ν(C=N)	ν(C=C)	ν(C=O)	ν(C-O)	ν(N-N)	ν(C-S) thienyl	ν(M-O)	ν(M-N)	ν(M-S)
$[Ni(L_X)_2]$	1590	1610	1650	1110	1020	570	420	400	280
$[Ni(L_{XI})_2]$	1605	1600	1650	1120	1020	570	450	390	280
$[Ni(L_{XII})_2]$	1600	1600	1640	1110	1030	560	440	410	270
$[Ni(L_{XIII})_2]$	1600	1620	1650	1110	1025	580	440	410	300
$[Ni(L_{XIV})_2]$	1605	1620	1640	1120	1025	575	430	400	300
$[Ni(L_{XV})_2]$	1590	1600	1642	1115	1030	580	450	400	290
$[Ni(L_{XVI})_2]$	1600	1600	1642	1110	1020	570	450	400	300
$[Ni(L_{XVII})_2]$	1605	1620	1650	1120	1030	580	440	390	270
$[Ni(L_{XVIII})_2]$	1600	1600	1640	1110	1030	570	420	390	280

Table 29. Electronic spectral data and ligand field parameters for nickel(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	$^3A_{2g} \rightarrow {}^3T_{2g}$ (cm^{-1})	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (cm^{-1})	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (cm^{-1})	Dq	ν_2/ν_1	B(cm^{-1})	β	LFSF (Kcal mol^{-1})	f
$[Ni(L_X)_2]$	10500	17900	27000	1050	1.70	893.3	0.867	36.00	1.20
$[Ni(L_{XI})_2]$	11200	17500	27700	1120	1.56	773.3	0.750	38.40	1.28
$[Ni(L_{XII})_2]$	10600	18800	26500	1060	1.77	900.0	0.873	36.34	1.22
$[Ni(L_{XIII})_2]$	10900	17800	26850	1090	1.63	796.6	0.773	37.37	1.25
$[Ni(L_{XIV})_2]$	10850	18400	26500	1085	1.69	827.3	0.803	37.20	1.25
$[Ni(L_{XV})_2]$	11300	19200	27000	1130	1.69	820.0	0.796	38.74	1.30
$[Ni(L_{XVI})_2]$	11000	19000	26900	1100	1.72	860.0	0.834	37.71	1.26
$[Ni(L_{XVII})_2]$	10750	18200	27200	1075	1.69	876.6	0.851	36.86	1.24
$[Ni(L_{XVIII})_2]$	10900	17900	26800	1090	1.64	800.0	0.776	37.37	1.25

a) **Infra-red spectra**

The absorption bands at 3300-3260 cm^{-1} and 1640-30 cm^{-1} diagnostic of the $\tilde{\nu}$(N-H) and $\tilde{\nu}$(NHC=O) respectively in the free ligands were absent in the spectra of the complexes indicating the involvement of deprotonated enolised carbonyl oxygen in coordination. The shifting of $\tilde{\nu}$(C=N) from 1610-1615 to 1590-1600 cm^{-1} and the positional change of $\tilde{\nu}$(N-N) from 1070-60 to 1040-30 cm^{-1} in the spectra of complexes affirmed the coordination through the azomethine nitrogen. The third coordination site in the ligands was the thiophene ring sulphur as evidenced by the splitting and shifting of the ring stretching band observed at 590-70 cm^{-1} in the free ligands. The new absorptions appearing in the spectra of complexes at 450-440, 410-400 and 300-280 cm^{-1} were assigned to M-O, M-N and M-S stretching vibrations respectively (Ferraro, 1971).

b) **Magnetic moment and electronic spectra**

The magnetic moment values ($\mu_{eff.}$) for these complexes $[Cu(L_X)_2]$-$[Cu(L_{XVIII})_2]$ were in the range 1.74-1.86 B.M. indicating spin only value for single electron. The electronic spectra of these complexes exhibited a single broad absorption band in the region 13000 to 14000 cm^{-1} which was due to $^2E_g \longrightarrow {}^2T_{2g}$ transition suggesting the distorted octahedral geometry (Lever, 1984). The Dq values (1300-1400 cm^{-1}) and the LFSE values (22.28-24.00 K cal mol^{-1}) (Table 32) were also consistent with the proposed octahedral geometry (Ravinder et al., 1984).

5. **Zinc(II) complexes**

The 1:2 stoichiometry of the complexes was confirmed by elemental analysis (Table 16). The complexes were non-ionic and diamagnetic as evidenced by molar conductance and magnetic susceptibility studies.

Table 30. Physical, analytical and magnetic data of copper(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	Molecular formula	Yield (%)	Analytical data % observed (Calcd.)				$\mu_{eff.}$ (B.M.)
			C	H	N	Metal	
$[Cu(L_X)_2]$	$C_{30}CuH_{22}N_4O_4S_2$	67	56.9 (57.2)	3.7 (3.5)	8.0 (8.9)	9.8 (10.1)	1.76
$[Cu(L_{XI})_2]$	$C_{32}CuH_{26}N_4O_4S_2$	64	58.2 (58.4)	3.6 (3.9)	8.9 (8.5)	9.6 (9.7)	1.74
$[Cu(L_{XII})_2]$	$C_{34}CuH_{30}N_4O_4S_2$	65	59.2 (59.5)	4.8 (4.4)	8.0 (8.2)	9.0 (9.3)	1.74
$[Cu(L_{XIII})_2]$	$C_{32}CuH_{26}N_4O_4S_2$	59	58.8 (58.4)	4.2 (3.9)	8.3 (8.5)	9.6 (9.7)	1.74
$[Cu(L_{XIV})_2]$	$C_{34}CuH_{30}N_4O_4S_2$	61	59.5 (59.5)	4.6 (4.4)	8.6 (8.2)	9.6 (9.3)	1.84
$[Cu(L_{XV})_2]$	$C_{36}CuH_{34}N_4O_4S_2$	65	60.4 (60.5)	4.6 (4.7)	7.4 (7.8)	9.1 (8.9)	1.86
$[Cu(L_{XVI})_2]$	$C_{32}Cl_2CuH_{24}N_4O_4S_2$	63	53.1 (52.8)	3.0 (3.3)	7.8 (7.7)	8.9 (8.7)	1.81
$[Cu(L_{XVII})_2$	$C_{34}Cl_2CuH_{28}N_4O_4S_2$	67	53.8 (54.1)	3.7 (3.7)	7.0 (7.4)	8.4 (8.4)	1.77
$[Cu(L_{XVIII})_2$	$C_{36}Cl_2CuH_{32}N_4O_4S_2$	58	54.9 (55.2)	3.8 (4.1)	7.4 (7.1)	7.8 (8.1)	1.79

Table 31. IR spectral characteristics of copper(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	IR (cm^{-1})								
	ν (C=N)	ν (C=C)	ν (C=O)	ν(C-O)	ν (N-N)	ν(C-S) thioph.	ν (M-O)	ν (M-N)	ν(M-S)
$[Cu(L_X)_2]$	1595	1610	1645	1110	1030	560	440	410	300
$[Cu(L_{XI})_2]$	1590	1610	1645	1110	1030	570	440	410	280
$[Cu(L_{XII})_2]$	1590	1612	1640	1120	1040	570	450	410	300
$[Cu(L_{XIII})_2]$	1600	1610	1650	1120	1040	570	440	400	300
$[Cu(L_{XIV})_2]$	1590	1615	1650	1112	1040	560	450	400	290
$[Cu(L_{XV})_2]$	1600	1610	1645	1115	1035	560	445	410	290
$[Cu(L_{XVI})_2]$	1600	1610	1642	1120	1035	575	445	400	280
$[Cu(L_{XVII})_2]$	1595	1615	1640	1120	1030	575	450	400	300
$[Cu(L_{XVIII})_2]$	1595	1610	1642	1110	1040	570	440	410	290

Table 32. Electronic spectral assignments, Dq and ligand field stabilization energies of copper(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	ν_1 (cm^{-1})	Assignment	Dq (cm^{-1})	LFSE (Kcal mol^{-1})
$[Cu(L_X)_2]$	14000	$^2E_g \rightarrow {}^2T_{2g}$	1400	24.00
$[Cu(L_{XI})_2]$	13800	$^2E_g \rightarrow {}^2T_{2g}$	1380	23.65
$[Cu(L_{XII})_2]$	13800	$^2E_g \rightarrow {}^2T_{2g}$	1380	23.65
$[Cu(L_{XIII})_2]$	13500	$^2E_g \rightarrow {}^2T_{2g}$	1350	23.14
$[Cu(L_{XIV})_2]$	13000	$^2E_g \rightarrow {}^2T_{2g}$	1300	22.28
$[Cu(L_{XV})_2]$	14000	$^2E_g \rightarrow {}^2T_{2g}$	1400	24.00
$[Cu(L_{XVI})_2]$	13800	$^2E_g \rightarrow {}^2T_{2g}$	1380	23.65
$[Cu(L_{XVII})_2$	13500	$^2E_g \rightarrow {}^2T_{2g}$	1350	23.14
$[Cu(L_{XVIII})_2]$	13200	$^2E_g \rightarrow {}^2T_{2g}$	1320	22.62

Infra-red spectra

The absorption bands diagnostic of the ν(N-H) and ν(NHC=0) modes of vibrations observed at 3300-3160 cm^{-1} and 1640-30 cm^{-1} in the spectra of free ligands were absent in the spectra of complexes suggesting thereby the enolization of the carbonyl oxygen. The appearance of ν(C-0) absorption band at 1125-10 cm^{-1} in the spectra of complexes and the absence of ν(NH) and ν(NHC=0) bands affirmed the participation of deprotonated enolic oxygen in coordination with the metal ion. The involvement of azomethine nitrogen in coordination was evidenced by the hypsochromic shifting of C=N stretching vibrational frequency from 1620-10 to 1610-1590 cm^{-1} as well as by the shifting of ν(N-N) from 1070-60 to 1050-40 cm^{-1}. Splitting and shifting of ring stretching frequency of thiophene from 590-80 cm^{-1} in the spectra of ligands to 580-560 cm^{-1} in the spectra of complexes suggested the coordination through thiophene sulphur. The new bands at 460-440, 425-410 and 300-290 cm^{-1} in the spectra of complexes were assigned to the ν(M-O), ν(M-N) and ν(M-S) vibrational modes respectively confirming the tridentate nature of the ligands.

On the basis of the elemental analysis and the tridentate ligand behaviour as proved by the infra-red spectral characteristics, an octahedral geometry was assigned to the non-ionic zinc(II) complexes.

Table 33. Physical, analytical and magnetic data of zinc(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	Molecular formula	Yield (%)	Analytical data % observed (Calcd.)				ueff.(B.M)
			C	H	N	Metal	
$[Zn(L_X)_2]$	$C_{30}H_{22}N_4O_4S_2Zn$	54	56.7 (57.0)	3.2 (3.5)	8.6 (8.9)	10.1 (10.3)	-
$[Zn(L_{XI})_2$	$C_{32}H_{26}N_4O_4S_2Zn$	57	57.8 (58.2)	3.7 (3.9)	8.3 (8.5)	9.4 (9.9)	-
$[Zn(L_{XII})_2]$	$C_{34}H_{30}N_4O_4S_2Zn$	49	59.1 (59.4)	4.2 (4.4)	7.8 (8.1)	9.2 (9.5)	-
$[Zn(L_{XIII})_2]$	$C_{32}H_{26}N_4O_4S_2Zn$	58	58.0 (58.2)	3.5 (3.9)	8.0 (8.5)	9.3 (9.9)	-
$[Zn(L_{XIV})_2]$	$C_{34}H_{30}N_4O_4S_2Zn$	55	58.9 (59.4)	4.2 (4.4)	8.0 (8.1)	9.2 (9.5)	-
$[Zn(L_{XV})_2]$	$C_{36}H_{34}N_4O_4S_2Zn$	56	60.1 (60.4)	4.3 (4.7)	7.3 (7.8)	9.0 (9.1)	-
$[Zn(L_{XVI})_2]$	$C_{32}Cl_2H_{24}N_4O_4S_2Zn$	49	52.4 (52.7)	3.4 (3.3)	8.1 (7.7)	9.5 (8.9)	-
$[Zn(L_{XVII})_2]$	$C_{34}Cl_2H_{28}N_4O_4S_2Zn$	52	53.5 (53.9)	3.8 (3.7)	7.1 (7.4)	8.1 (8.6)	-
$[Zn(L_{XVIII})_2]$	$C_{36}Cl_2H_{32}N_4O_4S_2Zn$	48	54.7 (55.1)	4.1 (4.1)	6.7 (7.1)	8.0 (8.3)	-

Table 34. IR spectral characteristics of zinc(II) complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides.

Compound	IR (cm^{-1})								
	ν(C=N)	ν(C=C)	ν(C=O)	ν(C-O)	ν(N-N)	ν(C-S) thioph.	ν(M-O)	ν(M-N)	ν(M-S)
$[Zn(L_X)_2]$	1600	1600	1640	1115	1040	580	460	410	290
$[Zn(L_{XI})_2]$	1590	1610	1640	1110	1040	580	440	420	300
$[Zn(L_{XII})_2]$	1600	1620	1645	1120	1050	575	450	415	295
$[Zn(L_{XIII})_2]$	1600	1620	1640	1115	1045	580	440	410	300
$[Zn(L_{XIV})_2]$	1595	1620	1650	1125	1050	570	450	415	290
$[Zn(L_{XV})_2]$	1610	1610	1650	1120	1040	570	460	420	290
$[Zn(L_{XVI})_2]$	1600	1620	1640	1120	1045	560	445	425	300
$[Zn(L_{XVII})_2]$	1595	1610	1650	1110	1040	570	445	420	300
$[Zn(L_{XVIII})_2]$	1600	1600	1640	1110	1050	580	450	410	290

SECTION "C"

Antimicrobial activity

The ligands and the complexes were screened for their antimicrobial activity against some phytopathogenic fungi of economic significance viz., Alternaria alternata, Fusarium oxysporum, Colletotrichum capsicum and Rhizoctonia solani and two bacteria viz., gram positive Bacillus subtilis and gram negative Escherichia coli. Two fold serial dilution technique (Spooner and Sykes, 1972) was employed to evaluate the antimicrobial activity and the results obtained were expressed in terms of the minimum inhibitory concentration (MIC) values. The minimum concentration at which a complete growth inhibition of the test organism was observed was taken as the MIC value expressed in $\mu g\ ml^{-1}$. The results were plotted (concentration Vs compounds) for comparing the activity pattern of different ligands and their complexes and are given in figures 9-20.

The substituted benzoylpropanoic acid hydrazides (HL_I-HL_{IX}) exhibited promising activity against the test organisms. Out of the four fungi, the ligands were most active against Alternaria alternata in which, the minimum inhibitory concentration values were 12.5 $\mu g\ ml^{-1}$ for the ligand HL_{VIII}, 25 $\mu g\ ml^{-1}$ for the ligands HL_I, HL_{II}, HL_{IV}, HL_{VIII} and HL_{IX}, 50 $\mu g\ ml^{-1}$ for the ligands HL_V and HL_{VI} and 100 $\mu g\ ml^{-1}$ for HL_{III}. The MIC values against Fusarium oxysporum were 50 $\mu g\ ml^{-1}$ for almost all the ligands. The ligands HL_{III} and HL_{IV} exhibited complete growth inhibition of Colletotrichum capsicum at a concentration of 25 $\mu g\ ml^{-1}$ whereas others had MIC value of

50 $\mu g\ ml^{-1}$. Rhizoctonia solani was the least affected test fungi (MIC values 50-100 $\mu g\ ml^{-1}$). The ligands exhibited more activity against the fungi than the bacteria with MIC values varying from 50 to 100 $\mu g\ ml^{-1}$ for the latter. Among the bacteria, Bacillus subtilis was more affected on treatment with the compounds. Investigating the mode of action of some acid hydrazides Nyler and Davis (1950) established that the acid hydrazides, at molecular level, inhibit the formation of RNA, decrease the protein level and also result in fragmentation of the chromosomal DNA and dissipation of the nuclei affecting thereby the normal cellular processes of growth and division resulting in growth inhibition of various organisms.

The side chain length and the presence of various substituents on the main nucleus and on the side chain(s) have pronounced impact on the nature and the magnitude of the biological activities. Consequently, substituting various nuclei of biological importance has emerged as one of the important aspects in the development of novel compounds with potential antimicrobial activity. In the present investigation the benzoylpropanoic acid hydrazides was substituted at two sites, the phenyl and hydrazide moieties, with various groups. The phenyl ring was substituted with methyl at position 4- in one case and with two methyl groups at 2- and 5- positions in the other. The proximal nitrogen atom of the hydrazide was also substituted with thienyl moiety, thus creating a conjugate ONS donor system and simultaneously altering the molecules with lipophilic $-CH_3$ groups. As an outcome, the ligands proved to be quite promising antimicrobials. On a comparative account, the substitutions in these nuclei did not exhibit any significant alteration in the biological

activity of the series of ligands (HL_I-HL_{IX}) and no definite structure-activity relationship could be established for these compounds.

The metal coordination, in general, alters the activity of the ligands due to the activation of the ligand and/or metal ion as the ligand molecule may prove to be a vehicle for the activation of the metal ion or vice-versa. The effect on the activity may be due to the changed mechanism of action, change in the transport across the lipid bilayer of the ligand molecule and/or the metal ion and their combined effect on the cellular metabolism. The polarity of the metal ion is considerably reduced on chelation mainly due to sharing of its positive charge with the donor atoms and possibly π-electron delocalization over the whole chelate ring (Srivastava, 1981). Such chelation increase the lipophilic character of the metal complex which probably leads to the breakdown of permeability barrier of the cells affecting thereby the normal cell processes. Furthermore, the activity of the coordination compounds is a function of the stereochemical manifestations and the stability and lability of the molecule so formed.

In the present investigation, the activity of the ligands, 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides (HL_I-HL_{IX}), was found to be altered on coordination with some biologically significant first series transition metal ions. The present investigation aimed at preparing and screening the antimicrobial activity of the ligands and their complexes with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) followed by their screening for antimicrobial activity. In all the

cases, in general, the activity was found to be enhanced significantly on coordination of the ligands with Co(II), Ni(II) and Cu(II), but no significant alteration was observed in case of Mn(II) and Zn(II) (not in plotted figures) complexes against all the test organisms. Thus while the ligands had the minimum inhibitory concentration values in the range 25-100 $\mu g\ ml^{-1}$ against Alternaria alternata. The copper(II) complexes exhibited the MIC values ranging from 6.25-25 $\mu g\ ml^{-1}$ and the plotted curve (Fig. 9) is continuously above the curve for the ligands. The activity curves of cobalt(II) and nickel(II) are either above the curve obtained for the ligand or are contiguous with these. The ligands showed MIC values 50-100 $\mu g\ ml^{-1}$ against Fusarium oxysporum. The copper(II) complexes had the MIC values in the range 12.5-25 $\mu g\ ml^{-1}$, whereas the cobalt(II) and nickel(II) complexes showed lower activity than the corresponding copper(II) complexes (Fig. 10). A similar activity relationship was obtained for the ligands and their complexes against Colletotrichum capsicum and Rhizoctonia solani (Fig. 11 and 12). The ligands HL_I-HL_{IX} exhibited the MIC values equal to 100 or more than 100 $\mu g\ ml^{-1}$ against the bacteria Escherichia coli and 50 $\mu g\ ml^{-1}$ against Bacillus subtilis. Coordination with the metal ions had a pronounced effect on the activity of the ligands as was evident from figs. 13 and 14 in which the curve for copper(II) complexes either runs above the curve for ligands or is contiguous that for cobalt(II) and nickel(II) complexes. The Co(II) and Ni(II) complexes, in general, exhibited more activity than the ligands. The structure-activity relationship established for the complexes $[M(L_I)_2]$- $[M(L_{IX})_2]$ suggested the order of activity

$$Cu > Ni > Co > Mn \simeq Zn$$

for the test organisms under identical in vitro growth inhibitory studies.

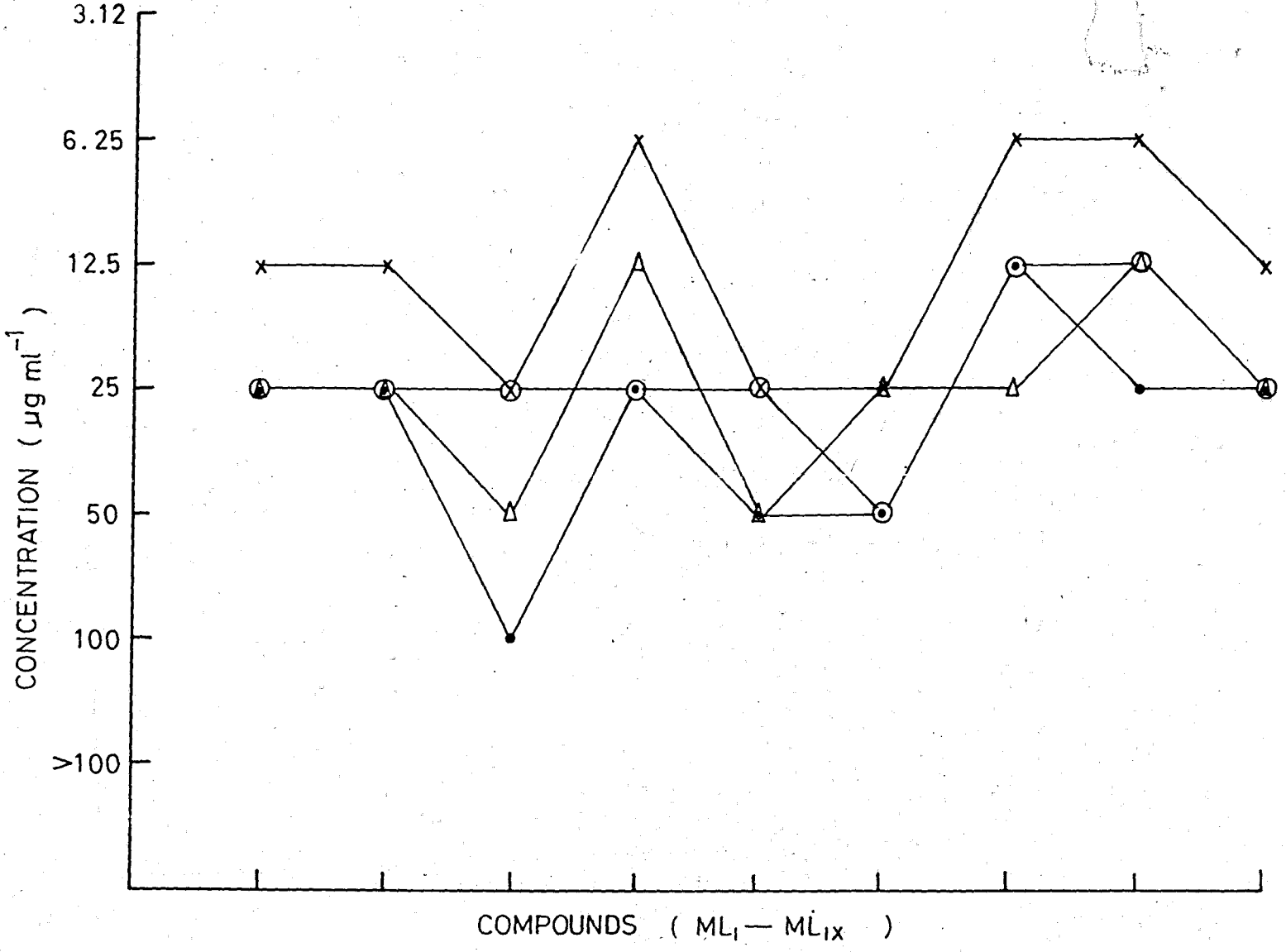


FIG.9 ANTIFUNGAL ACTIVITY OF COMPOUNDS $ML_I - ML_{IX}$ [M=H (•—•); Cu/2 (×—×); Ni/2 (△—△) OR Co/2 (○—○) AGAINST Alternaria alternata

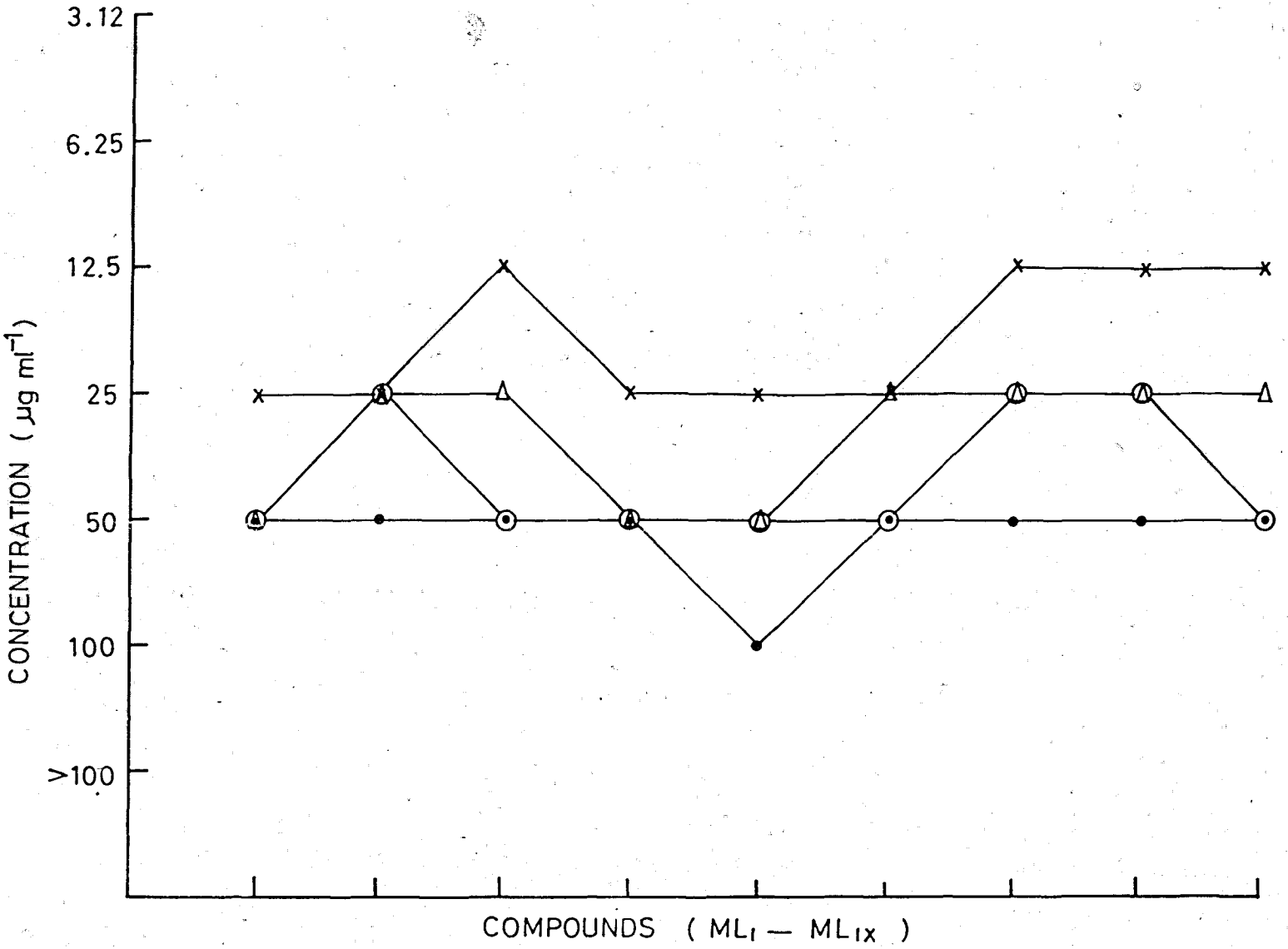


FIG.10 ANTIFUNGAL ACTIVITY OF COMPOUNDS ML_1– ML_{1X} [M=H (•—•); Cu/2 (×—×); Ni/2 (△—△) OR Co/2 (○—○) AGAINST Fusarium oxysporum

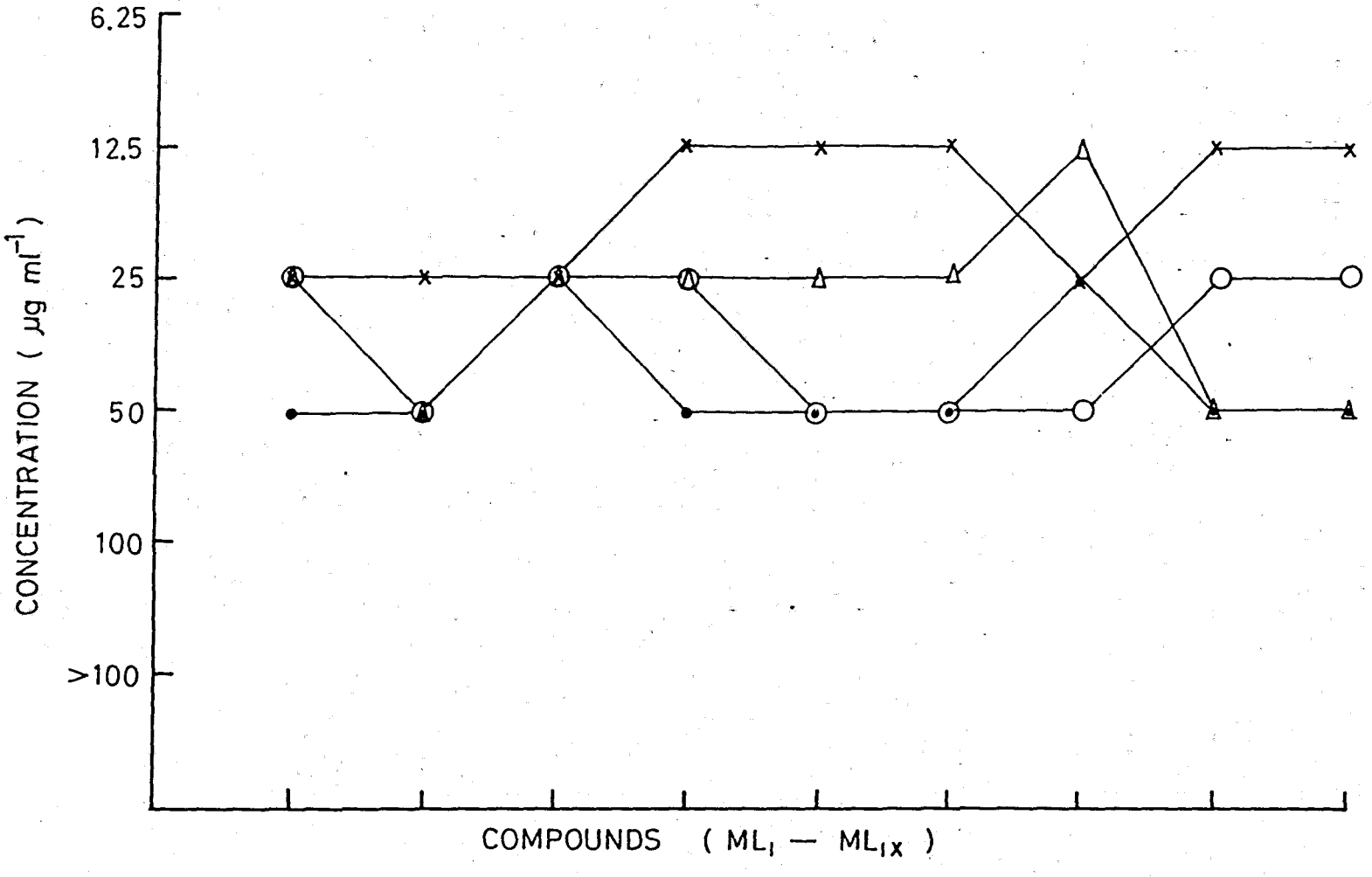


FIG.11 ANTIFUNGAL ACTIVITY OF COMPOUNDS ML_1–ML_{1X} [M=H (•—•); Cu/2 (×—×); Ni/2 (△—△) OR Co/2 (○—○) AGAINST Colletotrichum capsicum

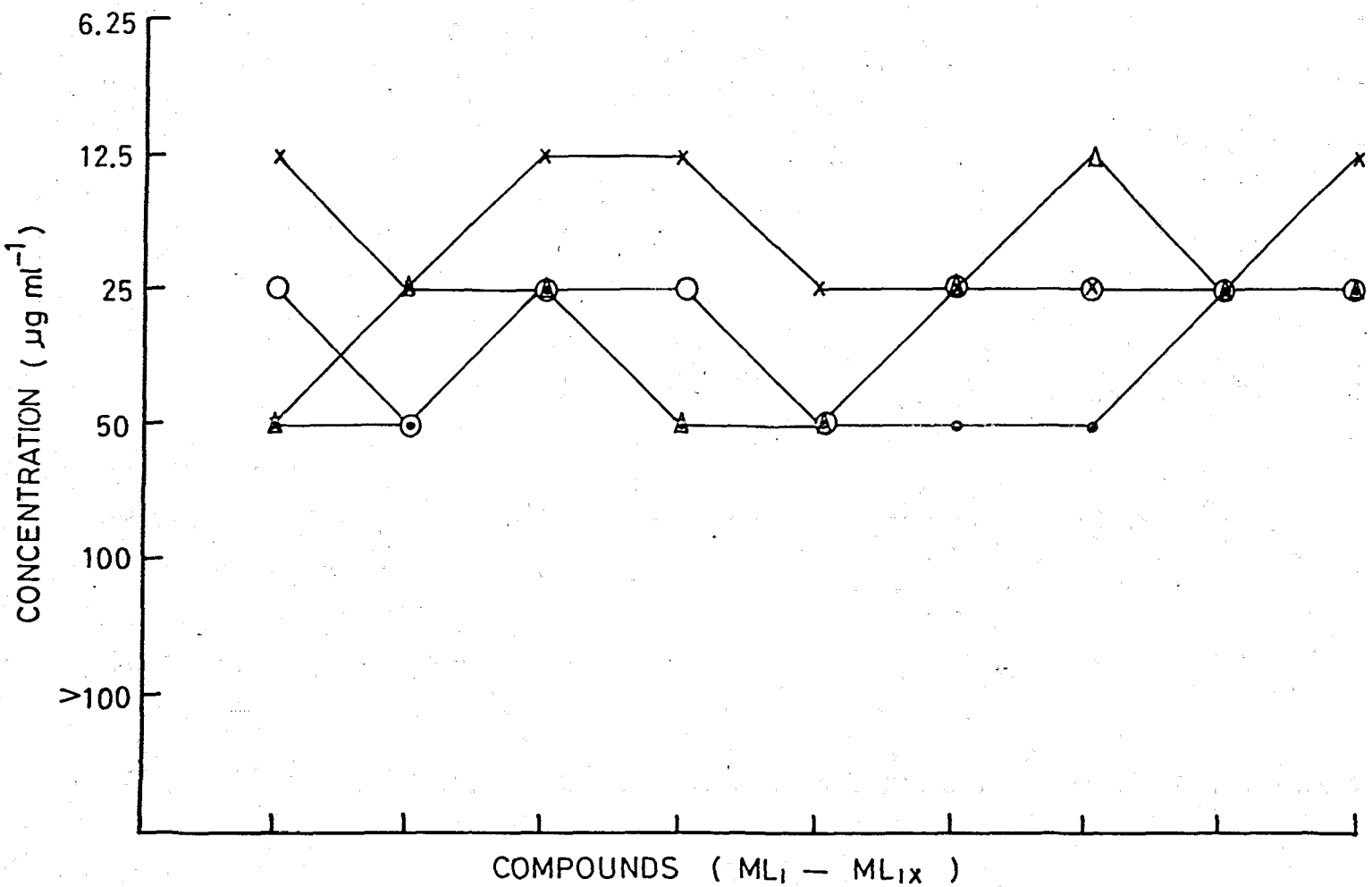


FIG.12 ANTIFUNGAL ACTIVITY OF COMPOUNDS ML_I — ML_{IX} [M=H (•—•); Cu/2 (×—×); Ni/2 (△—△) OR Co/2 (○—○) AGAINST Rhizoctonia solani

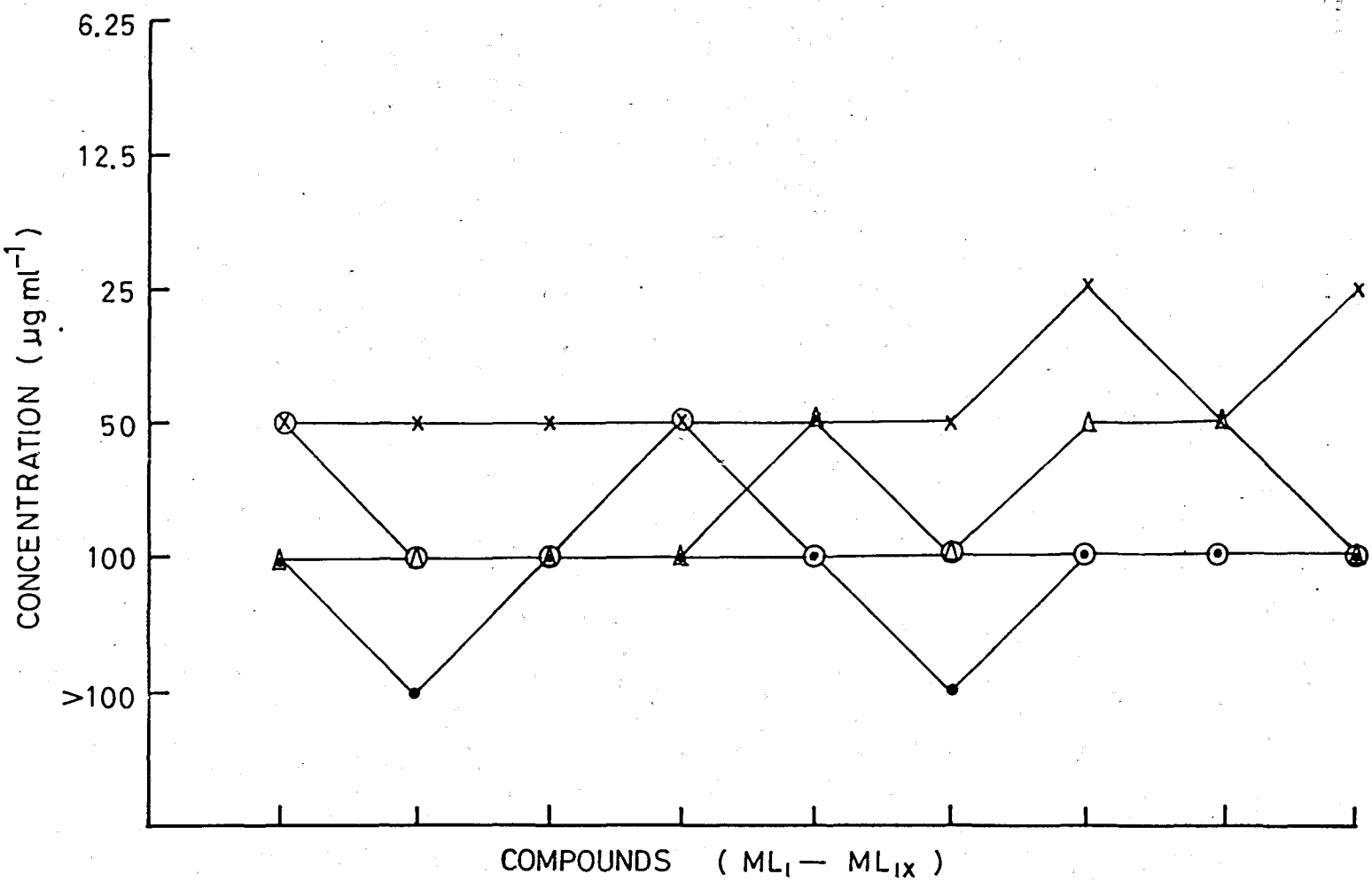


FIG.13 ANTIBACTERIAL ACTIVITY OF COMPOUNDS ML_1– ML_{1X} [M=H (•—•); Cu/2 (×—×); Ni/2 (△—△) OR Co/2 (○—○) AGAINST Escherichia coli

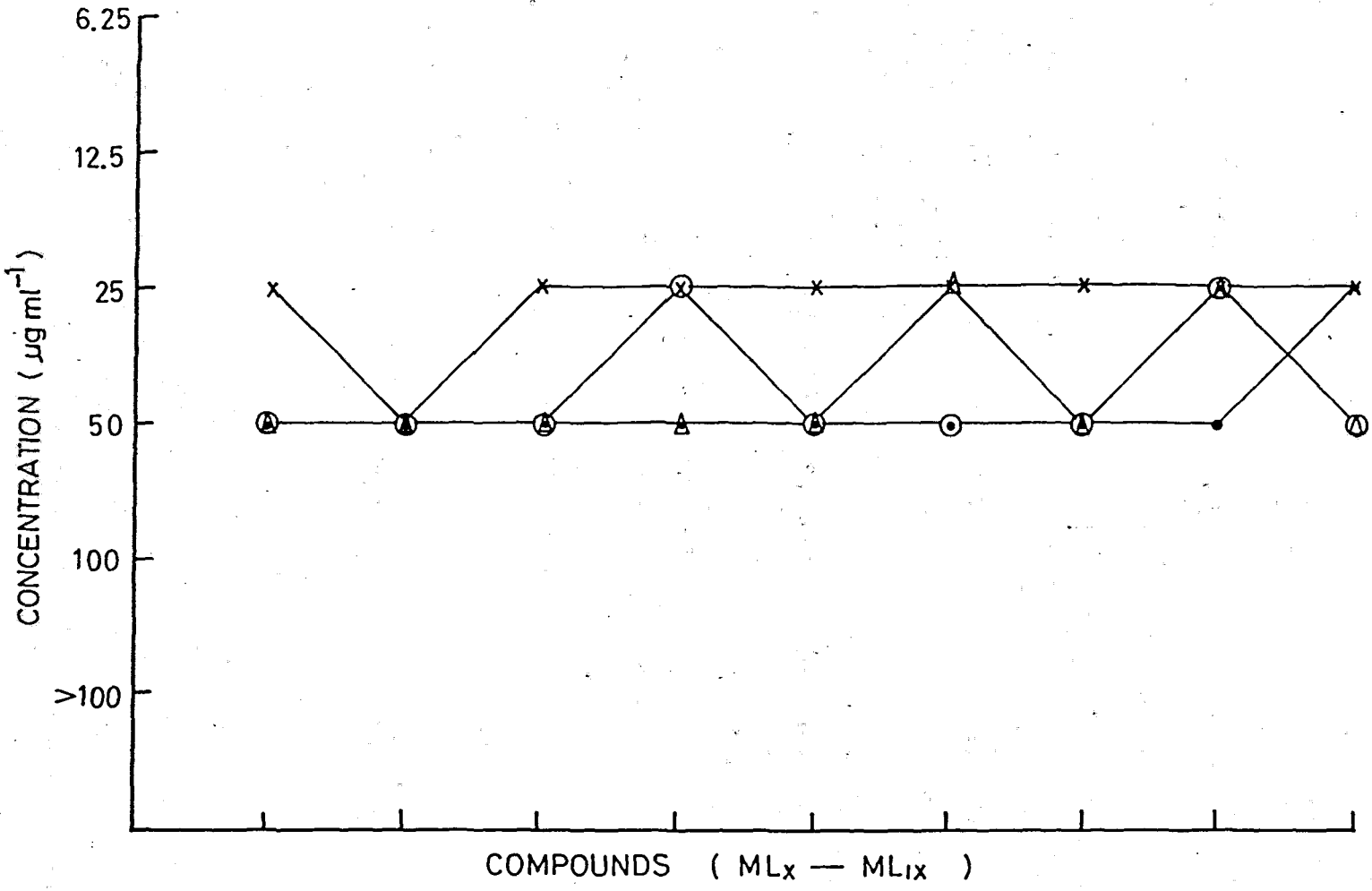


FIG. 14 ANTIBACTERIAL ACTIVITY OF COMPOUNDS ML_I– ML_{IX} [M = H (•—•); Cu/2 (×—×); Ni/2 (△—△) OR Co/2 (○—○) AGAINST Bacillus subtilis

The ligands, 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienyl-methylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides (HL_X-HL_{XVIII}) and their complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) also exhibited good antimicrobial activity against all the test organisms. No significant structure-activity relationship existed for this series of the ligands. Among the fungi, Colletotrichum capsicum was the least affected organism by the ligands but the activity increased on coordination with Cu(II), Ni(II) and Co(II). No significant alteration was observed on coordination of the ligands with Mn(II) and Zn(II). Among the complexes, Cu(II) compounds exhibited the highest activity in which MIC values were as low as 3.12 $\mu g\ ml^{-1}$ compared to 12.5 $\mu g\ ml^{-1}$ or more for the ligands. Fusarium oxysporum was moderately affected organism by the ligands but their complexes were quite active. Not much variation was observed in the activity of the ligands and their Ni(II) and Co(II) complexes against Alternaria alternata but the corresponding Cu(II) complexes were more toxic.

Most of the ligands showed complete growth inhibition at concentrations higher than 100 $\mu g\ ml^{-1}$ against E. coli and 25-50 $\mu g\ ml^{-1}$ for Bacillus subtilis but their corresponding metal complexes were more toxic. Among the complexes Cu(II) compounds were the more potential antibacterials than other metal complexes.

All the ligands and complexes were less effective fungicides than Bavistin, [2-(methoxycarbonyl) benzimidazole], (MIC value $< 1.5\ \mu g\ ml^{-1}$), used as a reference compound for comparing the in vitro growth inhibition of the test fungi. Streptopenicillin, (MIC value $< 1.5\ \mu g\ ml^{-1}$) used as a

standard antibacterial agent was also more effective than the ligands and the complexes studied in the present investigation.

It was clear from the fungicidal and bactericidal data that some of the complexes were more toxic in comparison to the parent ligands. The general trend of growth inhibition for the complexes against both fungi and bacteria was found to be in the order

$$Cu \gtrsim Ni > Co > Mn \simeq Zn.$$

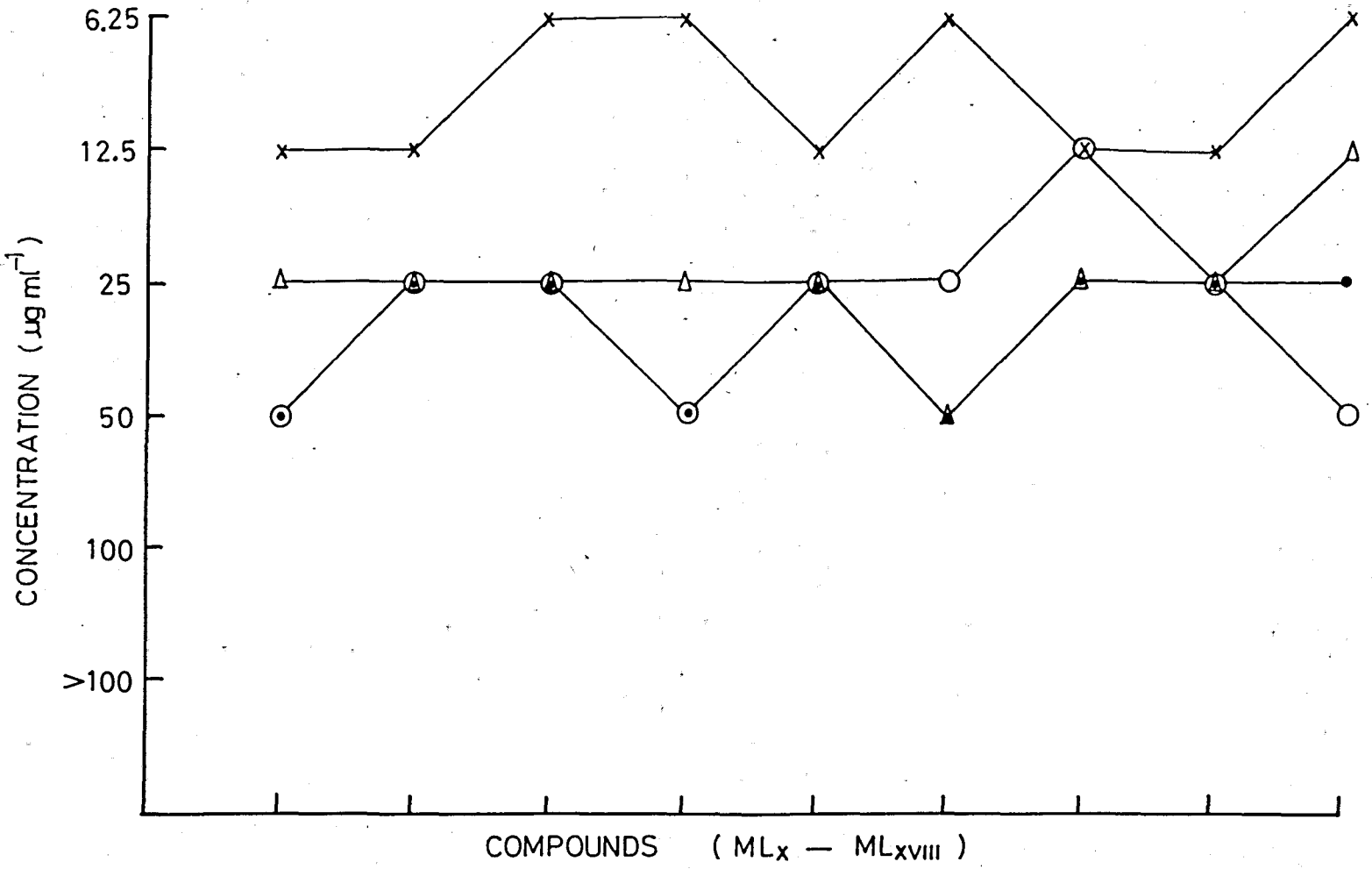


FIG. 15 ANTIFUNGAL ACTIVITY OF COMPOUNDS ML_x – ML_{xviii} [M = H (•—•) ; Cu/2 (×—×) ; Ni/2 (△—△) OR Co/2 (○—○) AGAINST Alternaria alternata

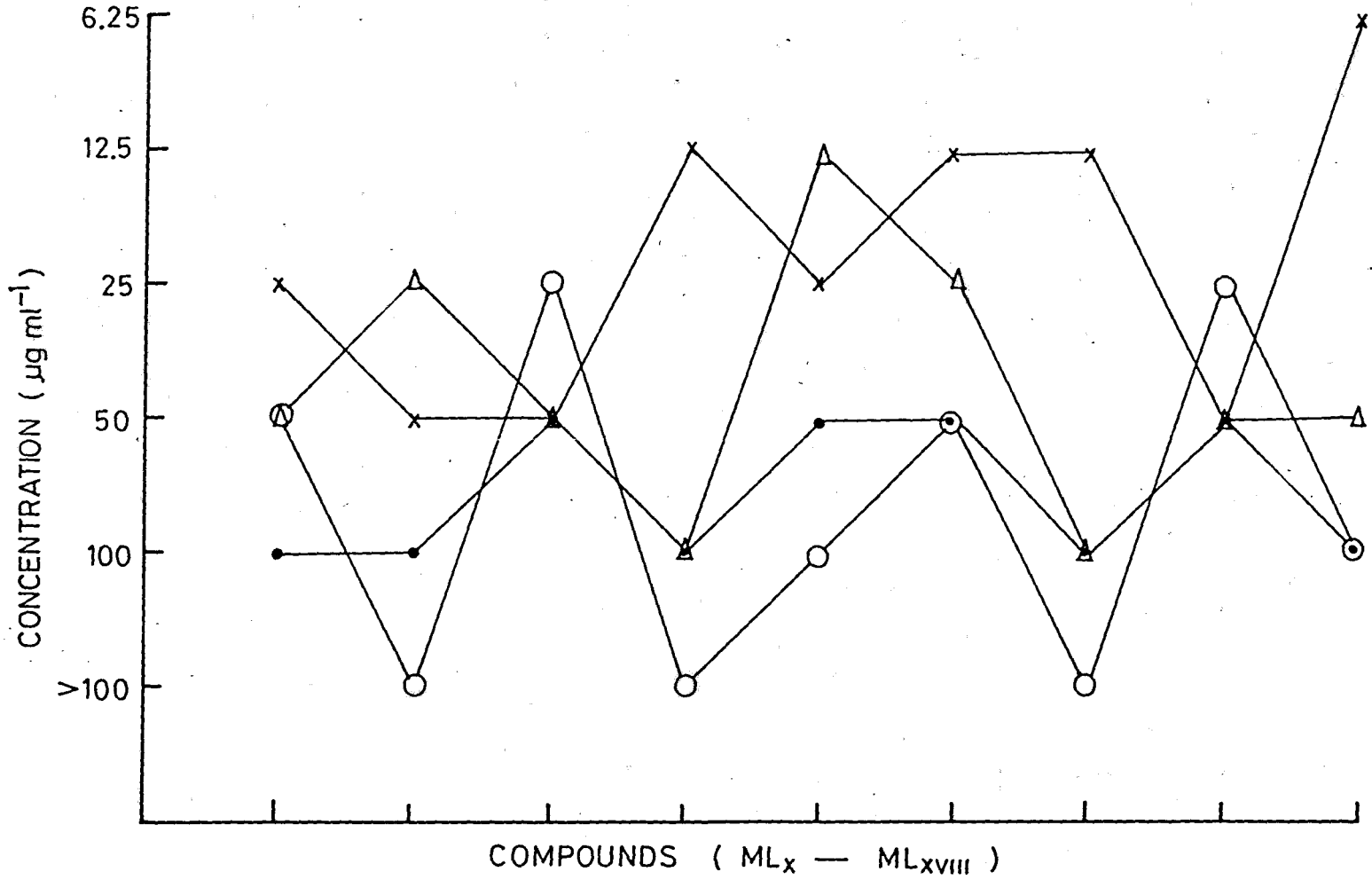


FIG.16 ANTIFUNGAL ACTIVITY OF COMPOUNDS $ML_X - ML_{XVIII}$ [M = H (•—•); Cu/2 (×—×); Ni/2 (△—△) OR Co/2 (○—○) AGAINST Fusarium oxysporum

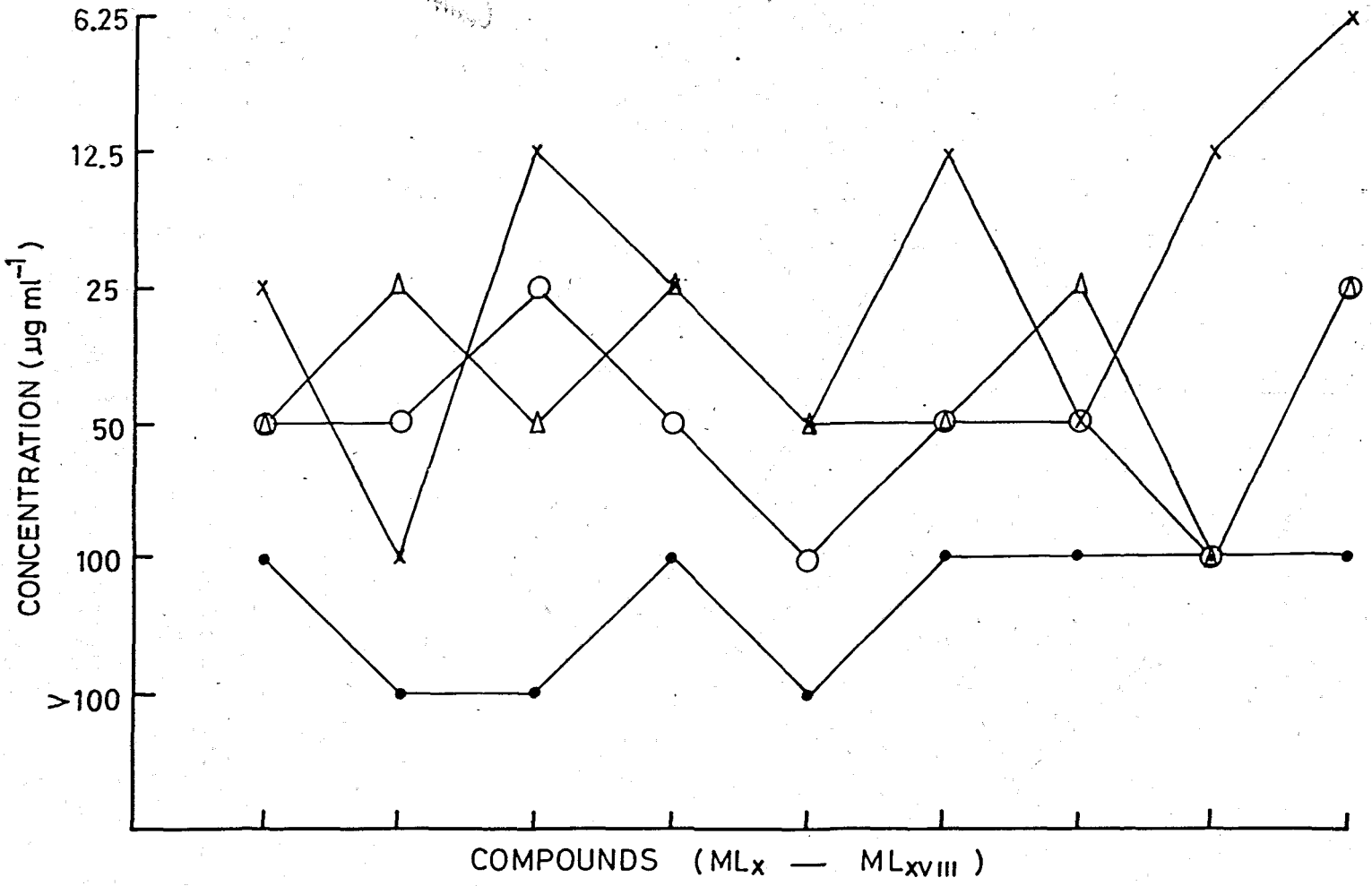


FIG.17 ANTIFUNGAL ACTIVITY OF COMPOUNDS ML_X-ML_{XVIII} [M=H (•—•); Cu/2 (×—×); Ni/2 (△—△) OR Co/2 (○—○) AGAINST Colletotrichum capsicum

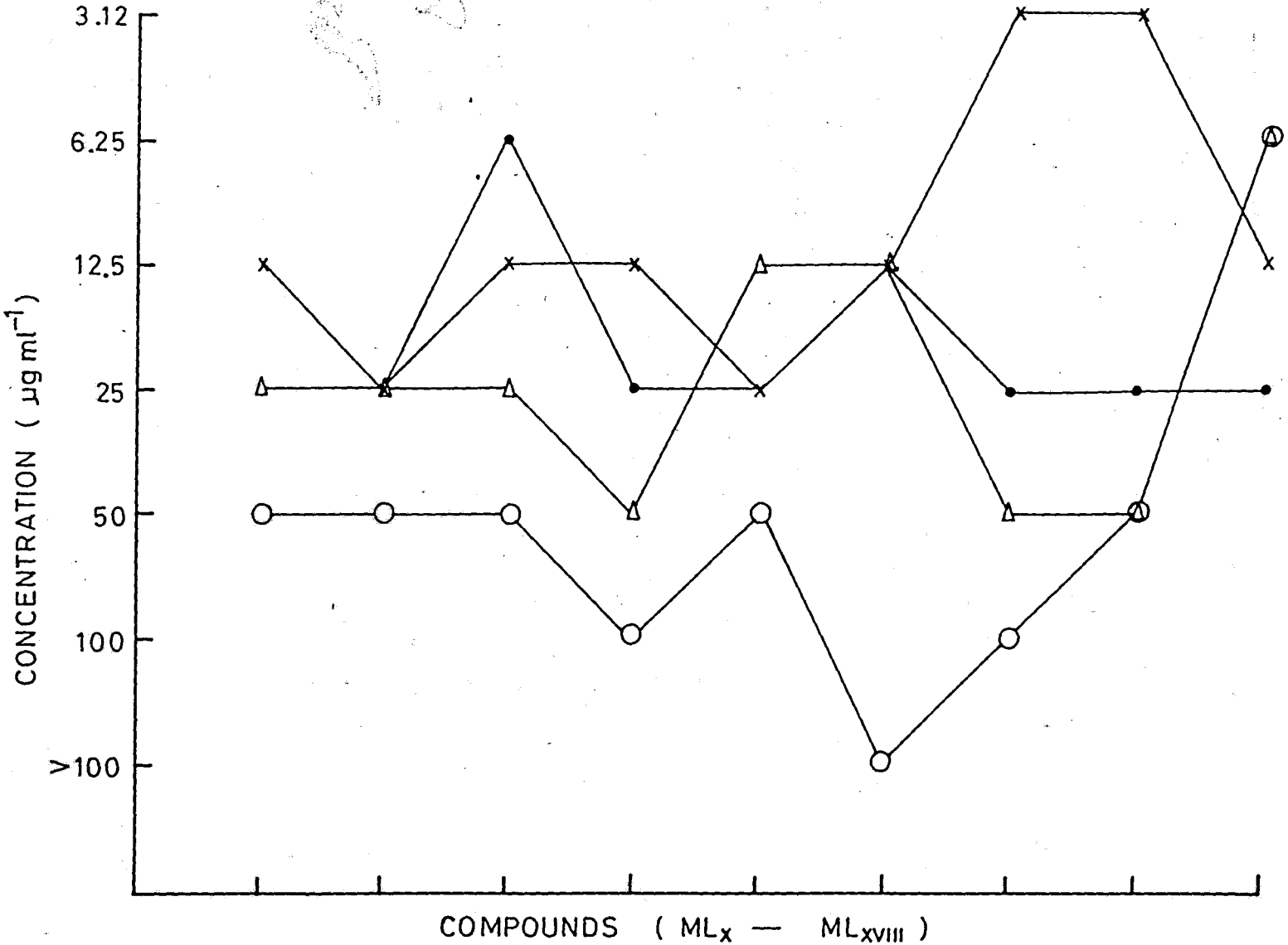


FIG.18 ANTIFUNGAL ACTIVITY OF COMPOUNDS ML_x — ML_{xviii} [M=H (•—•); Cu/2 (×—×); Ni/2 (△—△) OR Co/2 (○—○) AGAINST Rhizoctonia solani

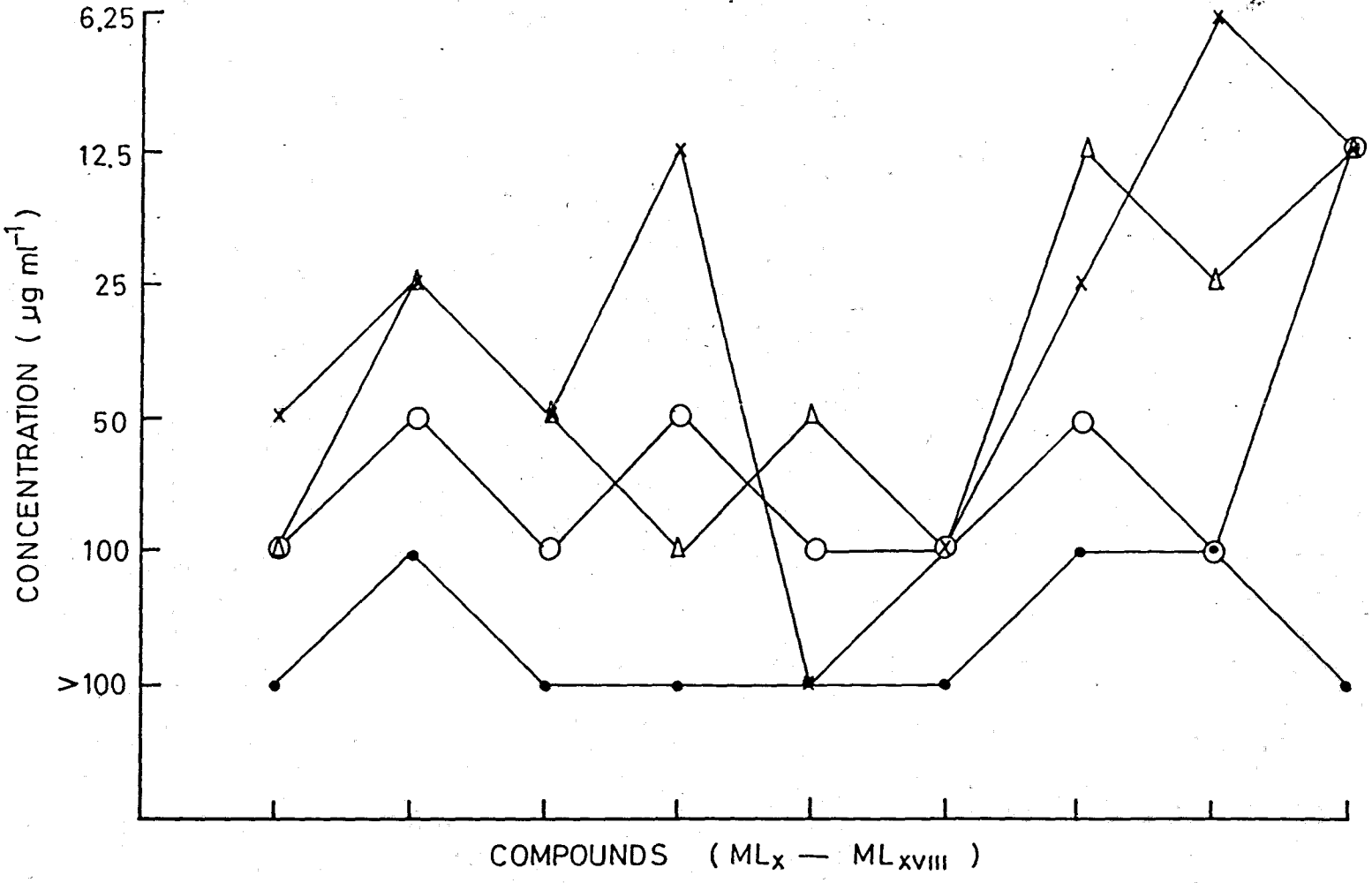


FIG.19 ANTIBACTERIAL ACTIVITY OF COMPOUNDS $ML_x - ML_{xviii}$ [M=H (•—•); Cu/2 (×—×); Ni/2 (△—△) OR Co/2 (○—○) AGAINST Escherichia coli

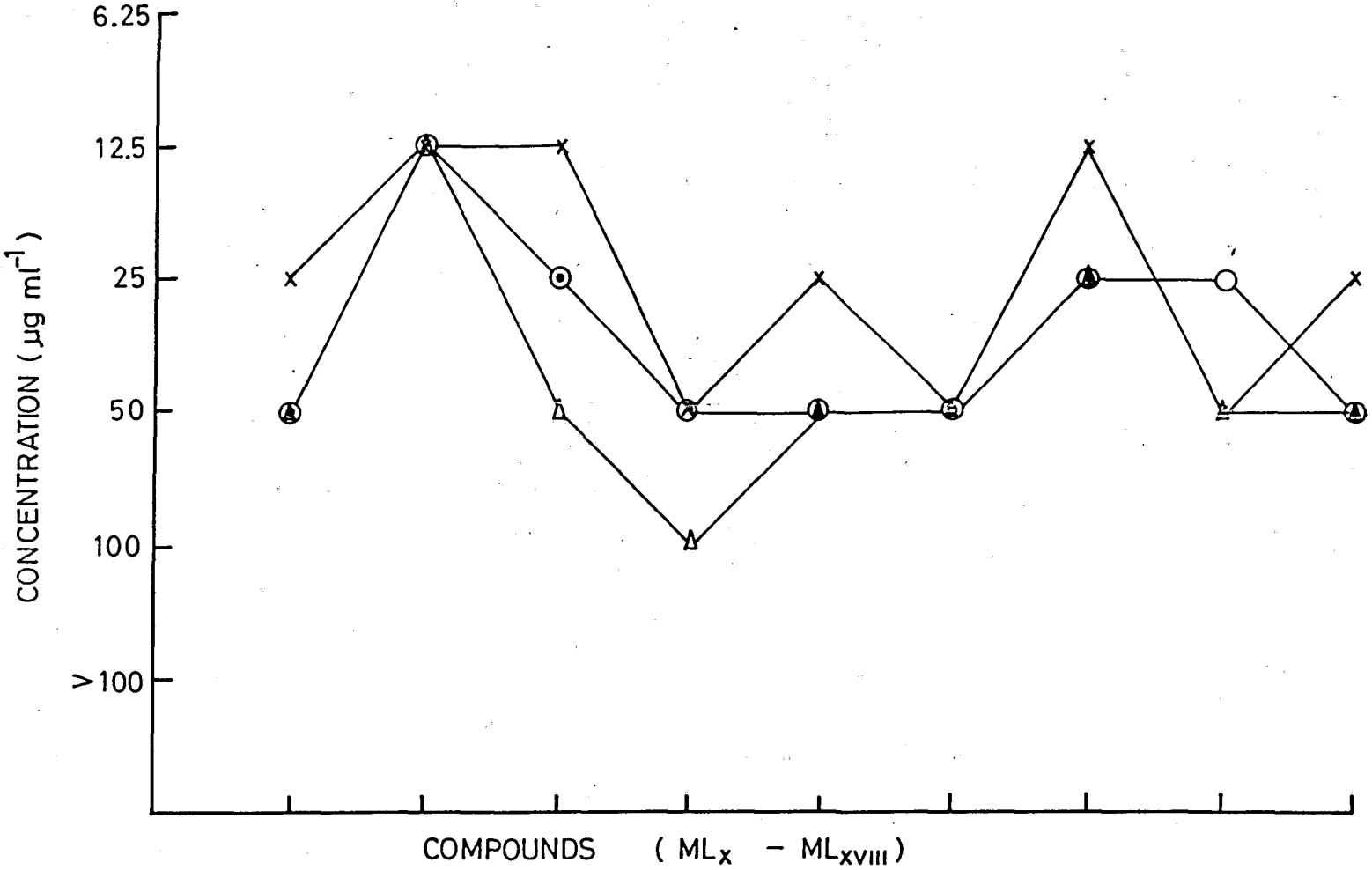


FIG. 20 ANTIBACTERIAL ACTIVITY OF COMPOUNDS MLx – MLxviii [M=H (•—•); Cu/2 (×—×); Ni/2 (△—△) OR Co/2 (○—○) AGAINST Bacillus subtilis

CHAPTER V

Summary

CHAPTER V

SUMMARY

Substituted acid hydrazides are known to exhibit a wide spectrum of biological activity in addition to their applications in industry and analytical chemistry. Tailoring these organic molecules in terms of substituents and side chains has a great relevance due to the altered biological activity of the resulting compounds. Further, the coordination of such substituted acid hydrazide with metal ion changes its activity pattern as a consequence of the physico-chemical manifestations acquired thereby. In view of the above facts, the present study was undertaken with the following objectives:-

- to synthesize some novel substituted acid hydrazides
- to prepare and characterize the coordination compounds of these ligands with some first series transition metal ions.
- to evaluate the comparative antimicrobial activity of the ligands and their complexes.

To achieve these objectives, two series of acid hydrazides namely, 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides and 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop2-en-1-oic acid hydrazides were synthesized followed by the preparation of their complexes with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II). Substituted benzene on condensation with succinic/maleic anhydride under Friedel-Crafts reaction conditions resulted in the formation of 4-substituted phenyl-4-oxo-1-propan/en oic acids. These acids on reaction with thionyl chloride yielded the corresponding acid chlorides which on condensation

with substituted-2-acetyl/carboxaldehyde thiophene resulted in the formation of required Schiff's bases. The complexes of the Schiff's bases with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) were prepared by reacting ethanolic solutions of metal salts and ligands in 1:2 molar ratios at pH 8-10. The synthesized ligands were characterized by elemental analysis, IR and ^1H NMR spectra and the complexes were characterized on the basis of elemental analysis, conductance measurements, magnetic susceptibility studies and IR and electronic spectral data.

The microanalytical data of the complexes of Schiff's bases prepared by reacting 4-susbtituted phenyl-4-oxo-1-propanoic acid hydrazides with substituted 2-acetyl/carboxaldehyde thiophene (HL_I-HL_{IX}) with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) suggested the formation of complexes of the general formula ML_2. These complexes were non-conducting and soluble in dimethylsulphoxide, nitrobenzene and dimethylformamide. A comparative study of the infra-red spectra of the free ligands with those of their complexes suggested a uninegative tridentate behaviour of the ligands wherein each ligand molecule coordinated through the deprotonated enolic oxygen, proximal azomethine nitrogen (N_2) and the sulphur of the thiophene moiety. The magnetic moment values and electronic spectra of the manganese(II), cobalt(II) and nickel(II) complexes suggested an octahedral geometry for these compounds, whereas for copper(II) complexes these structural studies suggested a distorted octahedral geometry. The diamagnetic zinc(II) complexes were assigned an octahedral geometry based on the tridentate ligand behaviour and the elemental analysis. Various ligand field parameters like ligand field splitting energy (10 Dq), Racah interelectronic repulsion parameter (B), nephelauxetic ratio (β) and ligand field stabilization energies (LFSE) and energy

ratios (ν_2/ν_1) calculated for various complexes were consistent with the assigned stereochemistry. The 10 Dq and LFSE values for copper(II) complexes also agreed well with those for distorted octahedral geometry. The f values calculated by using Jorgensen's equation for nickel(II) complexes placed the ligands near ethylenediamine (en) in the spectrochemical series.

The complexes of 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienyl-methylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides (HL_X-HL_{XVIII}) with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) were assigned 1:2 stoichiometry based on elemental analysis. The molar conductance values (0.5-20 ohm^{-1} cm^2 mol^{-1}) suggested a non-conducting behaviour of the complexes. The infra-red spectra of the ligands and their respective complexes revealed that each ligand coordinated through three donor atoms viz., carbonyl oxygen (enolic form) after deprotonation, azomethine nitrogen atom and sulphur of the thiophene ring. The magnetic moment values ($\mu_{eff.}$) and the electronic spectral characteristics of the complexes suggested an octahedral stereochemistry for manganese((II), cobalt (II) and nickel(II) complexes. Various ligand field parameters (Dq, B, β and LFSE) were also calculated and these values provided supporting evidence for the proposed octahedral geometry. The energy ratios (ν_2/ν_1) for these complexes were also calculated and the values were consistent with octahedral environment around the central metal ion. The electronic spectral absorptions and the various ligand field parameters for copper(II) complexes were characteristic of a distorted octahedral geometry. An octahedral configuration was proposed for the zinc(II) complexes on the basis of tridentate ligand behaviour established from infra-red spectra, elemental analysis and conductance measurements. The f values as

calculated by using Jorgensen's equation placed the ligands near ethylene-diamine(en) in the spectrochemical series.

The ligands and the complexes were screened for their in vitro growth inhibitory studies against four phytopathogenic fungi of economic significance viz., Alternaria alternata, Fusarium oxysporum, Colletotrichum capsicum and Rhizoctonia solani and two bacteria namely, gram positive Bacillus subtilis and gram negative Escherichia coli. The ligands and the complexes exhibited promising activity against all the test organisms. The ligands, 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazide (HL_I-HL_{IX}) were most active against Alternaria alternata, moderately active against Fusarium oxysporum and Collectotrichum capsicum and least active against Rhizoctonia solani. The ligands were more active against fungi than the bacteria. Bacillus subtilis was more affected than Escherichia coli on treatment with these compounds. However, no definite structure-activity relationship existed for the compounds (HL_I-HL_{IX}) under study. The activity of ligands was found to be enhanced on coordination with copper(II), nickel(II) and cobalt(II) but no significant alteration was observed on complexation with manganese(II) and zinc(II). The copper(II) complexes proved to be most effective antimicrobials. The activity of cobalt(II) and nickel(II) complexes was also more than that of the ligands but the manganese(II) and zinc(II) complexes possessed the antimicrobial activity almost equal to that for the ligands. The structure-activity relationship established from the antimicrobial data suggested the order

$$Cu > Ni > Co > Mn \simeq Zn \simeq \text{Ligand}$$

The Schiff's bases derived from 4-substituted phenyl-4-oxo-2-propenoic acid hydrazide and substituted-2-acetyl/carboxaldehyde thiophene and their complexes also exhibited good antimicrobial activity against all the test organisms. Among the fungi, Colletotrichum capsicum was the least affected organism by the ligands but their complexes with Cu(II), Co(II) and Ni(II) were quite active. No definite structure-activity relationship existed for the series of ligands evaluated. The ligands and the complexes exhibited more activity against Bacillus subtilis as compared to Escherichia coli. Among the complexes Cu(II) compounds were more potential antibacterials than other metal complexes. The general trend of growth inhibition for the complexes against both fungi and bacteria was found to be in the order.

$$Cu > Ni > Co > Mn \simeq Zn$$

It is concluded from the investigation that the Schiff's bases synthesized in the present study were moderately active against the test organisms and acted as uninegative tridentate ligands, coordinating with the metal ions through the deprotonated enolic oxygen, azomethine nitrogen and thiophene sulphur atoms. The synthesized complexes were octahedral and potentially active against the test organisms. The antimicrobial activity of the ligands was found to be enhanced significantly on coordination with copper(II), nickel(II) and cobalt(II) and the copper(II) complexes were the most effective antimicrobials.

BIBLIOGRAPHY

CHAPTER VI

BIBLIOGRAPHY

Abdullah, K.A.; Al-Daher, A.G.M. and Bashir, W.A. (1985). Thiophene-2-hydrazide as a reagent for the spectrophotometric determination of vanadium in aqueous solutions. Analyst (London), **110**, 409.

Aggarwal, R.C.; Narayan, D. and Surya, S. (1984). Pyridine carboxylic acid hydrazide complexes of cobalt(II), nickel(II) and zinc(II) acetylacetonates. Indian J. Chem., **23A**, 962.

Aggarwal, R.C. and Rao, T.R. (1973). J. Inorg. Nucl. Chem., **40**, 171.

Aggarwal, S.K.; Chandra, R.; Gupta, R. and Tutlani, D.R. (1987). Some hydrazides and Mannich bases as antibacterial agents. J. Inst. Chem. (India), **59**, 225.

Aleksieva, V. and Karanov, E. (1987). Growth retardant activity of mono and dihydrazides of dialiphatic dicarboxylic acids. Dokl. Prolg. Akad. Mauk., **40**, 87.

Ali, B.; Mirza, A. and Hussain, S.A. (1989). First transition series metal complexes of phthalic hydrazide or its anion. Pak. J. Sci. Ind. Res., **39**, 439.

Aminabhavi, T.M.; Biradar, N.S.; Patil, S.B. and Hoffman, E. (1987). Synthesis and characterization of biologically active organosilicon and organotin complexes of phenylglycyl hydrazones. Inorg. Chim. Acta., **135**, 139.

Arora, D.L.; Lal, K.; Gupta, S.P. and Katyal, M. (1985). Homobinuclear complexes of chromium(III), iron(III) and cobalt(III) with heptadentate (N_5O_2) donor schiff base derived from 2,6-dipicolinoyldihydrazine. Himalayan Chem. Pharm. Bull., **2**, 21.

Arutyunyan, V.S.; Kochikyan, T.V.; Kovalev, G.V. and Bugaeva, Z.I. (1985). Synthesis and pharmacological studies of γ-hydroxycarboxylic acid hydrazides. Arm. Khim. Zh., **38**, 523.

Azizov, T.A.; Zuparov, M.Z. and Abidova, L.A. (1986). Coordination compounds of Mn, Co and Ni formates and acetates with isonicotinic acid hydrazides and some of its derivatives. Novosibissk, 253.

Bahadur, S.; Goel, A.K. and Verma, R.S. (1975). Potential antimycobacterial agents: Part III. Condensation products of diphenylamine-2-carboxylic acid hydrazides with aldehydes and ketones and their evaluation as antibacterials. J. Indian Chem. Soc. **52**, 843.

Biradar, N.S. and Kulkarni, V.H. (1971). Spectroscopic study of tin(IV) complexes with bidentate schiff bases. J. Inorg. Nucl. Chem. **33**, 2451.

Biradar, N.S.; Patil, C.S. and Rudzinski, W.E. (1983). Inorg. Chim. Acta., **78**, 107.

Bontchev, P.; Boneva, M.; Mitewa, M.; Mehandjiev, D. and Golovinsky, E. (1981). J. Inorg. Nucl. Chem., **43**, 3163.

Bontchev, P. .; Boneva, M.; Arnaudov, M. and Golovinsky, E. (1985). Palladium(II) complexes of dihydrazide of aspartic acid. Dokl. Prolg. Akad. Nauk., **38**, 707.

Bontchev, P.; Boneva, M.; Nefedov, V.I. and Salin, Y.V. (1985). Platinum(II) complexes of hydrazides of aspartic and glutamic acids. Polyhedron, **4**, 1315.

Bychkova, T.I.; Boos, G.A. and Gilemkhanova, A.S. (1986). Coordination of copper(II) with hydrazides of benzoic acid and isonicotinic acid in aqueous DMF. Zh. Neorg. Khim., **31**, 712.

Carlin, R.L. (1965). Electronic structure and stereochemistry of cobalt(II). Transition Metal Chem., **1**, 1.

Chatt, J.; Dilworth, J.R.; Leigh, G.J. and Gupta, V.D. (1971). Some benzoylazo complexes of rhenium halides with tertiary phosphines and related compounds. J. Chem. Soc. (A), 2631.

Chaturvedi, K.K. and Kansal, R. (1975). Indian J. Pharm., **37**, 85.

Chauhan, A.K.S. and Mishra, B. (1985). Triorganotin (IV) complexes of isonicotinoyl hydrazones. Indian J. Chem., **24A**, 234.

Chundak, S.Y.; Leovac, V.M.; Obadovic, D.Z. and Petrovic, D.M. (1986). Nickel(II) and cobalt(II) complexes of the hydrazides of 1-naphthylacetic acid. Transition Met. Chem., **11**, 308.

Chundak, S.Y.; Leovae, V.M. and Bjelica, L.J. (1987). Coordination complexes of Co(II), Ni(II) and Cu(II) with capric acid hydrazides. Monatsh. Chem., **118**, 923.

Cotton, F.A. and Wilkinson, G. (1988). Advanced Inorganic Chemistry 5th ed. (John Wiley and Sons Inc., New York).

Crafts, A.S. (1964). The Chemistry and Mode of Action of Herbicides (Interscience, New York).

Cruichank, R. (1975). Medical Microbiology. The Practice of Microbiology, 12th Ed. (Churchill Livingstone, Edinburgh).

Cruickshank, P.A.; Disanzo, C.P.; Kondo, K. and Kono, H. (1982). Nematicidal use of hydrazine carboxamides and carbothioamides. US 4514419 (Cl 514-521; A 01 N33126), 30 Apr. 1985, US Appl. 375424, 06 May, 1982, spp. Chem. Abstracts **103**(17), 141645 (1985).

Cseh, G.; Lienhard, P. and Wiedemann, W. (1990). Heterocyclic 1:1 hydrazone-metal complex pigments for organic polymers and coating materials. Eur. Pat. Appl. EP 349189, 3 Jan. 1990. Chemical Abstracts, **113**(4), 25554 (1990).

Day, M.C. and Selbin, J. (1962). Coord. Chem.-II in: Theoretical Inorganic Chemistry, 2nd ed. (Van Nostrand Reinhold, New York), pp. 494.

Diana, M.R. and Thoman, V.O.H. (1990). Metal ion induced regulation of gene expression. In: Advances in Inorganic Biochemistry, Vol. 8 (Elsevier, New York), Eds. Eichhorn, G.L. and Marzilli, L.G., pp.2.

Dey, K. (1974). Schiff bases and their uses. J. Sci. Ind. Res., **33**, 76.

Donald, C.G. and Williams, A.R. (1955). Assay Methods of Antibiotics. A Laboratory Manual, Medical Encyclopedia.

D'Muhala, T.F. and Ward, R. (1985). Hydrazides of aminopolyacetic acids as chelate forming agents. Ger. Offen. DE 3429148 (Cl CO7C109/087), 25 Feb. 1985. Chemical Abstracts **102**(26), 225805 (1985).

Drago, R.S. (1971). Physical Methods in Inorganic Chemistry (East-West Press, New Delhi), pp 168, 410.

Dutta, A.A.; Mandal, P.K. and Chaudhauri, N.R. (1964). J. Inorg. Nucl. Chem., **28**, 2951.

Eilbeck, W.J.; Holmes, F. and Underhill, A.E. (1967). Cobalt(II), nickel(II) and copper(II) complexes of imidazole and thiazole. J. Chem. Soc. A, 757.

Ellis, V.M.; Vagg, R.S. and Walton, E.C. (1975). J. Inorg. Nucl. Chem., **36**, 1031.

Ferguson, J.; Wood, D.L. and Knox, K. (1963). Magnetic dipole character of the $^3A_{2g} \longrightarrow {}^3T_{2g}$ transition in octahedral nickel(II) compounds. J. Chem. Phys., **39**, 881.

Ferraro, J.R. (1971). Low Frequency Vibrations of Inorganic and Coordination Compounds (Plenum, New York).

Figgis, B.N. and Lewis, J. (1964). Prog. Inorg. Chem., **6**, 37.

Figgis, B.N. (1976). Introduction to Ligand Fields (Interscience, New York).

Fritz, H.R.; Lippest, B.P. and Kurt, H.S.R. (1977). Metal complexes of maleic acid hydrazide. Anorg. Chem., **32B**, 393.

Ghosh, S.; Bandyopadhayay, P.K.R. and Mitra, M.S. (1984). J. Inorg. Biochem., **20**, 79.

Goodgame, M. and Cotton, F.A. (1961). Magnetic investigations of spin-free cobaltous complexes. IV. Magnetic properties and spectrum of cobalt(II) orthosilicate. J. Phys. Chem., **65**, 791.

Goodgame, D.M.L.; Goodgame, M. and Cotton, F.A. (1961). Electronic spectra of some tetrahedral nickel(II) complexes. J. Am. Chem. Soc., **83**, 4161.

Gould, J.C. (1960). Brit. Med. Bull., **16**, 29.

Greenwood, N.N. and Earnshaw, A. (1990). Chemistry of the Elements. Pergamon Press, New York.

Gupta, A.A.; Rastogi, A.; Gupta, M.M.; Srivastava, N.; Sengupta, A.K. and Athar, M. (1983). Studies on potential juvenile harmone analogs: Part II-Synthesis of some new ethers, Schiff's bases, hydrazides and hydrazones derived from 7-hydroxy citronellal. Indian J. Chem. **22B**, 948.

Haskar, C.N.; Sethi, R.K. and Labdev, J. (1971). J. Sci. Tech. **9A**, 40.

Hathaway, B.J. (1971). Stereochemistry and electronic properties of the copper(II) ion. Essays in Chemistry (Academic Press; London), pp 61.

Heidt, L.J.; Koster, G.F. and Johnson, A.M. (1958). Experimental and crystal field study of the absorption spectrum at 2000 to 8000 A° of manganous perchlorate in aqueous perchloric acid. J. Am. Chem. Soc., **80**, 6471.

Huheey, J.E. (1983). Inorganic Chemistry: Principles of Structure and Reactivity. 3rd ed. (Harper and Row Publishers Inc., New York) pp. 385.

Ikekwere, P.O.; Patel, K.S. and Nwabueze, J.N. (1989). Complexes of Cu(II) sulphate with some cyclocarboxylic acid hydrazides. Synth. React. Inorg. Met.-Org. Chem., **19**, 599.

Jabulpurwala, K.E.; Venkatachallam, K.A. and Kabadi, M.B. (1964). J. Inorg. Nucl. Chem., **26**, 1027.

Jesson, J.P.; Trofimenko, S. and Eaton, D.R. (1967). Transition metal poly (1-pyrazolyl) borates. J. Am. Chem. Soc. **89**, 3148.

Johri, R.B. and Sharma, R.C. (1988). Synthetic and biocidal studies of some bivalent metal complexes of benzaldehyde-salicyloylhydrazones. J. Indian Chem. Soc., **65**, 793.

Jorgensen, C.K. (1958). Oxidation Numbers and Oxidation States (Springer Verlag, New York), pp 84.

Jorgensen, C.K. (1958). Discussions Faraday Soc., **26**, 110.

Juneja, H.D.; Chakravarty, B.B. and Munshi, K.N. (1987). Synthetic and structural studies on coordination polymers of manganese (II), cobalt(II), nickel(II), copper(II) and zinc(II) with azelaic acid bis-(phenyl hydrazide) and azelaic acid bis(2,4-dinitrophenylhydrazide). Indian J. Chem., **26A**, 257.

Kapadia, H.K. and Mehta, A.G. (1986). Complexes of some metal halides with β-aryl aminocinnamophenyl hydrazides. J. Inst. Chem. (India), **58**, 65.

Kogan, V.A.; Lukov, V.V.; Starikova, O.G. and Sadimenko, A.P. (1987). Preparation and physicochemical studies of new trinuclear copper(II) complexes with aroyl hydrazones based on acid dihydrazides and nitromalonaldehyde. Zh. Neorg. Khim., **32**, 113.

Konev, V.E.; Samura, B.A.; Eremina, Z.G.; Makurina, V.I. and Rogozhin, B.A. (1986). Synthesis, physicochemical properties and biological activity of amides and hydrazides of (arylsulfonyl) succinamic acids. Zh. (Kiev.), **5**, 37.

Kremer, S.; Heuke, W. and Reinen, D. (1982). High-spin-low-spin equilibria of cobalt(II) in the terpyridine complexes, Co $(terpy)_2$ $X_2.nH_2O$. Inorg. Chem., **21**, 3013.

Kulik, G.V.; Skrynik, E.M. and Bredikhina, A.N. (1974). Mikrobial Zh., **36**, 244.

Kumbhar, C.G. (1986). Polynuclear complexes of fumaric acid dihydrazide with copper(II), nickel(II) and cobalt(II). Def. Sci. J., **36**, 57.

Lachkova, V.; Ptrov, G. and Vasilev, G. (1985). O-ethyl-phenylmethanophosphonic hydrazide derivatives-synthesis and physiological activity. Izu Khim. **18**, 363.

Lakshmi Chandra, G. and Rai, R.A. (1984). Herbicidal and fungicidal activities of some transition metal complexes with benzoyl hydrazide and salicylhydrazide. Pesticides, **18**, 22.

Lever, A.B.P.; Nelson, S.M. and Shepherd, T.M. (1965). An analysis of the electronic spectra of some nickel(II) halide amine complexes. Inorg. Chem., **4**, 810.

Lever, A.B.P. (1966). Analysis of electronic spectra of bis-amine cobalt(II) halides-effect of steric hinderance. Adv. Chem. **62**, 435.

Lever, A.B.P. (1968). Electronic spectra of tetragonal metal complexes. Analysis and significance. J. Chem. Education., **45**, 711.

*Lever, A.B.P. (1984). Inorganic Electronic Spectroscopy (Elsevier Publishing Co., New York) pp.320.

Luo, M.; Ren, W.; Fan, H.; Zhang, J. and Gao, D. (1985). Antifungal agents: Synthesis and antifungal activity of some hydrazides and Meldrum's acid derivatives. Shanghai Key Daxue Xuebao, **4**, 103.

Machkhoshvili, R.I.; Gogitidze, D.A.; Shihelokov, R.N. and Shamilishvili, O.K. (1987a). Cerium sulfate and nitrate complexes with hydrazides. Zh. Neorg. Khim., **32**, 2120.

Machkhoshvili, R.I.; Gogitidze, D.A.; Shchelokov, R.N. and Shamilishvili, O.K. (1987b). Cerium bromide and isothiocyanate complexes with hydrazides. Zh. Neorg. Khim., **32**, 2409.

Maki, G. (1958). Ligand field theory of Ni(II) complexes. III. Electronic spectra and solution paramagnetism of some diamagnetic Ni(II) complexes. J. Chem. Phys., **29**, 1129.

Malhotra, R.; Malik, M.S.; Singh, J.P. and Dhindsa, K.S. (1992). Synthesis, characterization and microbicidal activity of α-methyl-(2-thiopheno-methylene) aryloxyacetic acid hydrazides and their metal complexes. J. Inorg. Biochem., **45**, 269.

Malhotra, R.; Kumar, S. and Dhindsa, K.S. (1992). Ligational behaviour of substituted acid hydrazides towards transition metals and potentiation of their microbiocidal activity. Proc. Natl. Acad. Sci. (In press).

Malhotra, R.; Kumar, S. and Dhindsa, K.S. (1992). Ligational behaviour of substitution acid hydrazides towards transition metals and potentiation of their activity. Indian J. Chem., Sect A, Accepted.

Malik, M.S.; Pal, V.; Sangwan, N.K.; Dhindsa, K.S.; Verma, K.K. and Bhatti, D.S. (1989). Nematicidal efficacy of substituted phenols, phenoxyacetic acid esters and hydrazides: A structure-activity relationship study. Nematologica., **35**, 366.

Mohan, M.; Gupta, N.S.; Chandra, L. and Jha, N.K. (1987). Synthesis, characterization and antitumour properties of some metal complexes of 3- and 5- substituted salicylaldehyde 2-pyridinylhydrazones. J. Inorg. Biochem., **31**, 7.

Mohan, M.; Gupta, M.P.; Chandra, L. and Jha, N.K. (1988). Synthesis, characterization and antitumour properties of some metal(II) complexes of 2-pyridinecarboxaldehyde 2'-pyridyl hydrazone and related compounds. Inorg. Chim. Acta, **151**, 61.

Mohan, M.; Sharma, P. and Jha, N.K. (1985). Metal (II) chelates of 4-methyl-5-amino-1-formylisoquinoline thiosemicarbazone: their preparation, characterization and antitumour activity. Inorg. Chim. Acta, **106**, 197.

Mostafa, M.M.; Maky, A.K.T. and Ibrahim, K.M. (1985). Metal complexes derived from isobutyric acid hydrazide with some bivalent metal ions. J. Indian Chem. Soc., **62**, 27.

Mueller, R.A. (1985). 8-chlorodibenz [b, f) [1,4]-oxazepine-10 (11H)-carboxylic acid 2-(alkoxycontaining acyl) hydrazides. US 4559337 (Cl 514-211 (o) D267/20) 17 Dec. 1985 April 705280, 25 Feb. 1985 5 pp. Chemical Abstracts, **104**(23), 207319 (1986).

Munshi, K.N. and Juneja, H.D. (1987). Coordination polymers of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with glutaric acid bis(2,4-dinitrophenyl-hydrazides). Indian J. Chem., **26A**, 708.

Nakamoto, K. (1970). Infrared Spectra of Inorganic and Coordination Compounds (Wiley Interscience, New York), pp 199, 228.

Narang, K.K. and Singh, M.K. (1987). Synthesis, IR spectra and other studies of some mercury(II) chloride, nitrate and thiocyanate complexes of organic acid hydrazides . Synth. React. Inorg. Met. Org. Chem., **17**, 57.

Nayler and Davis, E.A. (1950). Maleic hydrazide as plant growth inhibitor. Bot. Gaz., **112**, 112.

Nikonenko, E.A.; Morenkova, I.N.; Olikov, I.I. and Margolin, L.N. (1984). Spectroscopic studies of 3d metal hydrazine oxalate compounds of M C_2O_4 N_2H_4. x H_2O composition. Zh. Neorg. Khim., **29**, 1027.

Parashar, R.K. and Sharma, R.C. (1987). Synthesis and biocidal activity of zinc(II) complexes of some 2,2'-substituted diphenylamines. J. Inorg. Biochem., **29**, 225.

Parpiev, N.A.; Nasirdinov, S.D.; Yusupov, V.G.; Umarov, B.B. and Abdullaeva, K.S. (1985). Coordination compounds of some 3d metals from a product of condensation of malonic dihydrazide with acetone. Dokl. Akad. Nauk U_zSSR, **12**, 33.

Pin, Y. and Xiaoping, Z. (1989). Synthesis and characterization of new chromium (III), vanadium (IV) and titanium(III) complexes with biologically active isonicotinic acid hydrazide. J. Inorg. Biochem., **37**, 61.

Prabhakar, B.; Reddy, K.L. and Lingaiah, P. (1989). Synthesis, thermal, spectral and magnetic studies of complexes of cobalt(II), nickel(II), copper(II), ruthenium(II), palladium(II) and platinum(II) with 2,3-disubstituted quinazolin (3,4)4-ones. Proc. Indian Acad. Sci., **101**, 121.

Rainsford, K.D. and Whitehouse, M.W. (1976). Gastric irritancy of aspirin and its congeners: antiinflammatory potential antiulcer activity. J. Pharm. Pharmacol., **28**, 83.

Ramalingam, T. and Sattur, P.B. (1989). Synthesis and biological activity of α-(3-pentadecylaryloxy) isobutyric acids, their hydrazides and cyclic derivatives; oxadiazoles and pyrroles. Indian J. Chem., **28B**, 611.

Rana, A.K. and Shah, J.R. (1986). Copper(II), nickel(II), cobalt(II), manganese(II), iron(II), zinc(II), chromium(III), oxovanadium(IV) and dioxouranium(VI) complexes of 4-benzoylsemicarbazone 1-phenyl-3-methyl-2-pyrazoline-5-one. J. Indian Chem. Soc., **63**, 281.

Rao, T.R.; Sahay, M. and Aggarwal, R.C. (1984). Synthesis and structural studies on complexes of some first row transition metal ions with l-tyrosine hydrazide. Indian J. Chem., **23A**, 214.

Rao, T.R.; Sahay, M. and Aggarwal, R.C. (1985a). Studies on manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of the schiff base derived from l-tyrosine hydrazide and *o*-hydroxyacetophenone. Indian J. Chem., **24A**, 649.

Rao, T.R.; Khan, I.A. and Aggarwal, R.C. (1985). Synthesis and structural studies of some trivalent lanthanide complexes of isonicotinic acid hydrazide. Current Sci., **54**, 218.

Rao, T.R.; Sahay, M. and Aggarwal, R.C. (1985b). Synthesis and structural studies of some bivalent 3d metal complexes of 0-hydroxyacetophenone (N-benzoyl) glycyl hydrazone. Synth. React. Inorg. Met. Org. Chem., **15**, 175.

Rao, T.R.; Khan, I.A. and Aggarwal, R.C. (1986). Synthesis and structural studies of some trivalent lanthanide complexes of 0-hydroxyacetophenone isonicotinoyl hydrazone. J. Less Common Met. **115**(2), 325-30.

Rao, T.R. and Khan, I.A. (1987). Some trivalent lanthanide complexes of l-tyrosine hydrazide. Indian Acad. Sci. (Chem. Sci.), **98**, 273.

Rastogi, D.K.; Sharma, K.C.; Dua, S.K. and Teotia, M.P. (1975). Electronic spectral data vis-a-vis nephelauxetic effect-calculation and accuracy of the interelectronic repulsion parameter in vanadium (II), chromium (III), cobalt(II) and nickel(II) complexes of amino ligands. J. Inorg. Nucl. Chem., **37**, 685.

Ravinder, V.; Swamy, S.J.; Srihari, S. and Lingaiah, P. (1984). Studies on cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) complexes with substituted benzoic acids. Indian J. Chem., **23A**, 219.

Romanenko, N.I.; Priimenko, B.A.; Fedulova, I.V.; Chervinskii, A.Y.; Orestenko, L.P.; Pekhtereva, T.M. and Kochergin, P.M. (1984). Synthesis and biological activity of derivatives of β-(3-methyl-7-xanthinyl) propionic acids. Khim-Farm. Zh., **18**, 1462.

Ryakhovskikh, L.A.; Ivanov, M.G. and Kalinichenko, I.I. (1986). Preparation and study of indium(III) chloride complexes with carboxylic acid hydrazides. Koord. Khim., **12**, 321,

Sacconi, L. (1952). Chemical reactions of complexes.I. Action of hydrazides on nickel disalicylaldehyde. J. Am. Chem. Soc., **74**, 4503.

Sacconi, L. (1968). Electronic structure and stereochemistry of nickel(II). Transition Metal Chem., Ser Advan., **4**, 199.

Sakamoto, M. (1987). Synthesis and characterization of lanthanoid (III) complexes with a pentadentate ligand derived from 2,6-diacetyl pyridine and benzoylhydrazide. Inorg. Chim. Acta., **131**, 139.

Sallomi, I.J. and Dawood, Z.F. (1984). Some new complexes of indium(III) salts with acid hydrazides. J. Indian Chem. Soc. **61**, 833.

Sangwan, N.K.; Verma, B.S. and Dhindsa, K.S. (1986). 2,4-Bis (substituted cinnamoyi/pyrazol-3-yl)phenoxyacetic acid esters and hydrazides as potential antimicrobial agents. Indian J. Chem., **25B**, 672.

Savel'eva, Z.A. and Larionov, S.V. (1985). Complexes of cobalt(III) with thioacetic acid hydrazide. Zh. Neorg. Khim., **30**, 1752.

Schulte, K.; Puetter, R. and Loew, D. (1985). Antiinflammatory pharmaceutical. Ger. Offen. DE 3409415 (Cl A 61K 31/415), 26 Sept. 1985. Appl. 14 Mar, 1984, 17 pp. Chemical Abstracts, **104(4)**, 33897 (1986).

Schwarz, K. (1977). Clinical Chemistry and Chemical Toxicology of Metals (Elsevier, North Holland), 3.

Sekkina, M.M.A. and El-Azm, M.G.A. (1984). Thermochemical analysis of solid isonicotinic hydrazide transition metal complexes. Thermochim. Acta. **79**, 47.

Sengupta, A.K.; Gupta, M.M. and Gupta, A.A. (1984). Synthesis and in vitro antibacterial activity of substituted phenoxyacetic acid hydrazides. J. Indian Chem. Soc., **61**, 643.

Sharma, M.P.; Varshney, V.K. and Sharma, R.C. (1991). Synthesis and antimicrobial study of some hydrazone metal complexes. Proc. Natl. Acad. Sci., India, **61** Section A, 447.

Sharma, R.C. and Parashar, R.K. (1988). Synthesis and microbicidal activity of N-(2-substituted) phenyl ureas and their metal complexes. J. Inorg. Biochem., **32**, 163.

Sharma, S. (1987). Chemical behaviour of some metal complexes of O and N donor ligands. J. Indian Chem. Soc., **64**, 434.

Shvelashvili, A.E.; Zedelashvili, E.N.; Zhorzholiani, N.B. and Kokhtashvili, M.V. (1986). Synthesis and IR spectra of coordinated compounds of manganese (II) and magnesium (II) with carboxylic acid dihydrazides. Soobshch Akad. Nauk Gr. U_zSSR, **123**, 81.

Singh, B.; Singh, R.N. and Aggarwal, R.C. (1984). Synthesis and structural studies of oxovanadium (IV), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and mercury(II) complexes with 2-thenoyl-acetone hydrazone. Indian J. Chem. **23A**, 480.

Singh, N.K.; Aggarwal, N. and Aggarwal, R.C.(1984). Synthesis, characterization and antibacterial studies of iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of pyridine-4-carboxaldehyde isonicotinoyl hydrazone. Indian J. Chem., **23A**, 1011.

Singh, N.K.; Aggarwal, N. and Aggarwal, R.C. (1986). Synthetic, structural and antibacterial studies of cobalt(II), nickel(II), copper(II) and zinc(II) complexes of pyridine-2-carboxaldehyde thioisonicotinoylhydrazone. Acta Chim. Hung., **121**, 313.

Socrates, G. (1980). Infrared Characteristic Group Frequencies (John Wiley, New York).

Soliman, M.S.; Shallaby, A.M.; El-Shazely, R.M. and Mostafa, M.M. (1987). Polyhedron **6**, 1319.

Sorensen, J.R.J. (1976). Some copper coordination compounds and their antiinflammatory and antiulcer activities.

Sonth, L.T. and Summers, M.F. (1990). Zinc binding fingers. In: Advances in Inorganic Biochemistry, Vol.8 (Elsevier, New York) eds. Eichhorn, G.L. and Marzilli, L.G. pp 199.

Spooner, D.F. and Sykes, G. (1972). Methods in Microbiology (Academic Press, London).

Srivastava, R.S. (1981). Pseudooctahedral Co(II), Ni(II) and Cu(II) complexes of N'-(0-chlorophenyl)-2-(2',4'-dihydroxyphenyl)-2-benzylazomethine. Their fungicidal and herbicidal activity. Inorg. Chim. Acta, **56**, L65.

Srivastava, V.; Pandey, O.P.; Sengupta, S.K. and Tripathi, S.C. (1987). Aliphatic acid dihydrazide derivatives of dicyclopentadienyl zirconium (IV) chloride and their reaction with β diketones, formation of cyclic compounds. J. Organomet. Chem., **321**, 27.

Starikova, O.G.; Kogan, V.A.; Lukov, V.V. and Sokolov, V.P(1987). Preparation and magnetic properties of mono- and dinuclear copper(II) and nickel(II) complexes with aroyl hydrazones based on acid dihydrazides and β carbonyl compounds. Koord. Khim., **13**, 33.

Syamal, A. and Maurya, M.R. (1986a). Synthesis and characterization of nickel(II), cobalt(II), copper(II), manganese(II), zinc(II), zirconium(IV), oxomolybdenum(V) and dioxouranium(VI) complexes of the schiff base derived from salicyldehyde and thiophene-2-carboxylic acid hydrazide. Synth. React. Inorg. Met.-Org. Chem., **16**, 39.

Syamal, A. and Maurya, M.R. (1986b). Dioxomolybdenum (VI) complexes with tridentate dibasic schiff bases derived from various hydrazides. Trans. Met. Chem., **11**, 235.

Takematru, T.; Takeuchi, Y.; Hirakshi, K.; Nishimura, S.; Fujii, T.; Suzuki, M. (1986). Hydrazide compounds as herbicides. Jpn. Kokai Tokyo Koho Jp. 61137, 863 [86, 137, 863]. Chem. Abstracts, **105** (25) 226087t (1986).

Tanabe, Y. and Sugano, S. (1954). J. Phys. Soc. Japan, **9**, 753,766.

Tembe, G.L.; Koktanur, S.B. and Murty, A.S.R. (1986). Mixed ligand complexes of bis(acetylacetonato) nickel(II) and cobalt(II) with N and N,N'-substituted thioureas. Proc. Indian Acad. Sci. (Chem. Sci.), **97**, 19.

Tsintsadze, G.V. and Bazgadze, I.G. (1986). Synthesis and IR spectra of coordination compounds of lanthanoids on the basis of thiocyanate and those of bromides with picolinic acid hydrazide. Izu. Akad. Nauk Graz. SSR Ser. Khim., **12**, 256.

Tsintsadze, G.V.; Kurtanidze, R.S.; Mdivani, M.A. and Narimanidze, A.P. (1986). Coordination compounds of Fe(II) and Fe(III) with pyridine carboxylic acid hydrazide and derivatives of isonicotinic acid hydrazide. Novosibissk, 211-16.

Tsintsadze, G.V.; Tsivadze, A.Y.; Bazgadze, I.G. and Kurtanidze, R.S. (1985). Preparation and IR absorption spectra of lanthanide coordination compounds based on thiocyanate and bromides with nicotinic acid hydrazide. Koord. Khim., **11**, 1068.

Tsvetanova, A.; Miteva, M. and Boneva, M. (1987). Stability constants of copper(II) complexes with hydrazides. J. Prakt. Chem., **329**, 534.

Tuite, J. (1969). Plant Pathological Methods: Fungi and Bacteria (Minneapolis, Burgers Publishing Company).

Vardosanidze, T.O.; Shvelashvili, A.E.; Sobolev , A.N. and Porai-Koshits, M.A. (1985). Crystal and molecular structure of a manganese(II) sulphate complex with dihydrazide of malonic acid. Zh. Neorg. Khim., **30**, 364.

Vardosanidze, T.O.; Sobolev, A.N.; Shvelashvili, A.E. and Charelirhuili, L.S. (1985). Synthesis and structure of M (DM)SO_4.3H_2O type complex compounds [M=Cobalt(II), manganese(II), iron(II), nickel(II)]. Soobrhch. Akad. Nauk-Gr U_zSSR, **119**, 305.

Vardosanidze, T.O.; Sokol, V.I.; Sobolev, A.N.; Shvelashvili, A.E. and Porai-Koshits, M.A. (1985). X-ray structural study of and β modifications of crystals of the manganese-malonic acid dihydrazide compound. Zh. Neorg. Khim., **30**, 1745.

Wilson, C.O.; Gisvold, O. and Doerge, R.E. (1977). Text book of Organic Medicinal and Pharmaceutical Chemistry, 7th Ed. (Lippincott, Philadelphia).

Zelentsov, V.V.; Martynova, I.G.; Razumov, A.I.; Moskva, V.V.; Tarasova, R.I.; Syrneva, L.P. and Olikova, V.A. (1986). Coordination compounds of cobalt(II), nickel(II) and copper(II) with diphenylphosphinyl acetic acid hydrazide. Zh. Neorg. Khim., **31**, 2177.

Zhang, M. and He, M. (1984). Synthesis of N-acyl-N'-(2-indolylcarbonyl) hydrazides and their physiological activity. Yaoxue Xuebao, **19**, 737.

Zhorzholiani, N.B.; Shvelashvili, A.E.; Sobolev, A.N.; Vardosanidze, T.O. and Sokol, V.I. (1987). Synthesis and X-ray analysis of the manganese coordination compounds $Mn(DS)_nX_2.mH_2O$ (DS=Succinic acid dihydrazide). Izv. Akad. Nauk. Gr. U_zSSR Ser. Khim., **13**, 102.

"Synthesis, Characterization and Biological Activity of Transition Metal Complexes of Substituted Acid Hydrazides"

By

Jai Pal Singh

Major Advisor: Dr. M.P. Gupta
Associate Professor of Chemistry
Department of Chemistry and Biochemistry
CCS Haryana Agricultural University
Hisar-125004.

(An abstract of the thesis submitted to the CCS Haryana Agricultural University, Hisar, in partial fulfilment of the requirements for the degree of Ph.D.).

In view of the wide spectrum of biological activity exhibited by acid hydrazides, variously substituted hydrazides viz., 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-propanoic acid hydrazides (HL_I-HL_{IX}) and 4-substituted phenyl-4-oxo-1-[2-N-(substituted-2-thienylmethylene/methylmethylene)]-prop-2-en-1-oic acid hydrazides (HL_X-HL_{XVIII}) and their complexes with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) were synthesized and evaluated for their in vitro antimicrobial activity. The complexes were characterized on the basis of elemental analysis, molar conductance, magnetic moment data and IR and electronic spectral studies. All the ligands behaved as uninegative tridentate and coordinated through the deprotonated enolised oxygen, proximal azomethine nitrogen and sulphur of the thiophene moiety. The 1:2 metal-ligand complexes were assigned octahedral stereochemistry based on the magnetic and spectral studies. The ligand field parameters for nickel(II) and cobalt(II) complexes were also calculated. The synthesized ligands and their metal complexes were screened for their antimicrobial activity against four phytopathogenic fungi viz., Alternaria alternata, Colletotrichum capsicum, Fusarium oxysporum and Rhizoctonia solani and two bacteria viz., Bacillus subtilis and Escherichia coli. Coordination of metal ions, in general, enhanced the activity of the ligands against all the test organisms.