“Synthesis and characterization of some transition metal complexes”

A Thesis Submitted to
The Saurashtra University

In the Faculty of Science
For The Degree of

Doctor of Philosophy

IN
CHEMISTRY

BY
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Under the Guidance of
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Dedicated to My Family

Statement under *O. Ph. D. 7* of Saurashtra University

The work included in the thesis is done by me under the supervision of Dr. Manish K. Shah and the contribution made thereof is my own work.

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Certificate

This is to certify that the present work submitted for the degree of Ph. D. in chemistry of Saurashtra University by Mr. Rakesh M. Tada has been the result of work carried out under my supervision and is a good contribution in the field of organic and inorganic chemistry.

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It is a moment of gratification and pride to look back with a sense of contentment at the long traveled path, to be able to recapture some of the fine moments, to be able to think of the infinite number of people, some who were with me from the beginning, some who joined me at some stage during the journey, whose kindness, love and blessings has brought me to this day. I wish to thank each one of them from the bottom of my heart.

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Rakesh M. Tada

Table of Contents

General remarks

1. NMR spectra were recorded on Bruker avance II 400 MHz NMR spectrometer using TMS as an internal reference.

2. Mass spectra of ligands were recorded on GC-MS QP-2010 spectrometer, The ESI mass spectra of metal complexes were carried out using a micromass Q-Tof Micro spectrometer.

3. IR spectra were recorded on Shimadzu FT-IR-8400 spectrometer.

4. Elemental analyses were carried out on EURO EA Elemental Analyzer, EA-3000, RS-232.

5. UV-Vis spectra were recorded on Shimadzu, Pharmaspec UV-1700, UV-Visible Spectrophotometer.

6. Molar conductivities were measured using a direct reading ELICO CM-180 conductivity meter.

7. Thin layer chromatography was performed on Silica Gel (Merck G60 F_{254}).

8. The chemicals used for the synthesis of compounds were purchased from Spectrochem, Merck, Thomas-baker and SD fine chemical.

9. Melting Points were taken in open capillary and are uncorrected.

10. All the structures are drawn according to ACS Document 1996 style.

List of Abbreviations

TSC	Thiosemicarbazone
HSV	Herpes simplex virus
HIV	Human Immunodeficiency Virus
SOD	Superoxide Dismutase
RDR	Ribonucleotide Diphosphate Reductase
RR*a*	Ribonucleotide Reductase
ROS	Reactive Oxygen Species
TR	Trypanothione Reductase
tbp	Trigonal Bipyramidal
sbp	Square-based Pyramidal
CP MAS	Cross-Polarization Magic Angle Spinning
MDR*a*	Multidrug Resistance
P-gp	P-glycoprotein
NCI-60	National Cancer Institute 60 cell line panel
PIH	Pyridoxal isonicotinoyl Hydrazone
DFO	Desferrioxamine
gl. HAC	Glacial Acetic Acid
MES	Maximal electroshock
scPTZ	subcutaneous pentylenetetrazole
SCE	Sister Chromatid Exchange
MDA	Malondialdehyde
PAL	Positron Annihilation Lifetime
FT-IR	Fourier Transform- Infrared spectroscopy
^{1}H-NMR	^{1}H- Nuclear Magnetic Resonance spectroscopy
^{13}C-NMR	^{13}C- Nuclear Magnetic Resonance spectroscopy
TLC	Thin Layer Chromatography
R_f	Retardation factor
Conc.	Concentrated
hrs / h.	Hours
MS	Mass Spectrometry
ESI	Electro spray Ionization

List of Abbreviations

DMSO	Dimethyl sulfoxide
mL	Milliliter
mp	Melting Point
Anal. Calcd.	Analytical Calculated
IR	Infrared
TMS	Trimethylsilane
MHz	Megahertz
MIC	Minimum Inhibitory Concentration
MTCC	Microbial Type Culture Collection
NCCLS	National Committee for Clinical Laboratory Standards
DNA	Deoxyribonucleic Acid
cfu	Colony Forming Unit
mg	Miligram
aq.	Aqueous
Wt.	Weight
L	Ligand
M	Metal
UV-Vis	Ultra Violet Visible
LMCT	Ligand-to-Metal Charge Transfer
MLCT	Metal-to-Ligand Charge Transfer
TGA	Thermo Gravimetric Analysis
DTA	Differential Thermal Analysis
DSC	Differential Scanning Calorimetry
TMA	Thermal Mechanical Analysis
DMF	Dimethylformamide
EtOH	Ethanol
MeOH	Methanol
NaOH	Sodium hydroxide
HCl	Hydrochloric acid
H_2SO_4	Sulphuric acid
KBr	Potassium bromide
$CDCl_3$	Deuteriated chloroform
KOH	Potassium hydroxide

Synthesis and characterization of ligands

Section - A

1.1 Literature survey of thiosemicarbazones

Chemical reactions were known to man long before chemistry had attained the status of science. It was found that substances changed their properties under certain external conditions, and this observation is a characteristic of chemical reactions. Thus the ancient Egyptians found that if malachite, a green ore, was fired with charcoal, a red metal was obtained, called copper. Medicinal application of metals can be traced back to almost 5000 years[1]. The development of modern medicinal inorganic chemistry, stimulated by the discovery of cis-dichlorodiammine platinum(II) [cisplatin] and its subsequent use as a drug in the treatment of several human tumors[2,3], has been facilitated by the inorganic chemist's extensive knowledge of the coordination and redox properties of metal ions. Metal centers, being positively charged, are favored to bind to negatively charged biomolecules and the constituents of proteins and nucleic acids offer excellent ligands for binding to metal ions. The pharmaceutical use of metal complexes therefore has excellent potential.

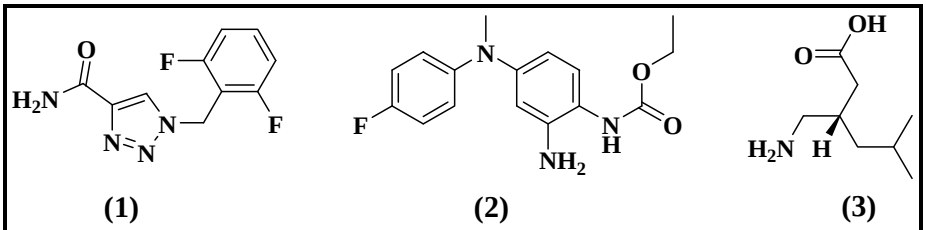
Thiosemicarbazones (hydrazine carbothioamides) are a family of compounds with beneficial biological activity. They are very good ligands, and it has been shown that their biological activity is related to their ability to coordinate to metal centres in enzymes. One interesting thing is that the more pharmaceutically promising thiosemicarbazone derivatives possess additional functional groups that are not coordinated to their "primary" metal ion, suggesting that the biological activity may also depend on the non-coordinating groups.

1.1.1 Thiosmicarbazones in the biological field - a survey

Thiosemicarbazones and their metal complexes have been widely explored for nearly 50 years[4,5] because of their versatile biological activity and prospective use as drugs[6]. Owing to the interest they generate through a variety of biological properties ranging from anticancer[7], antitumour[8], antifiungal[9] antibacterial[10] antimalarial[11], antitilarial[12] antiviral[13] and anti-HIV[14] activities, thiosemicarbazones and their metal complexes have been extensively studied. The hypoxic selectivity of certain copper bis(thiosemicarbazones) and their use as vehicles for the delivery of radioactive copper isotopes to tumors[15] or leucocytes[16] has attracted much recent attention[17]. The hypoxic selectivity is strongly dependent on the substituents on the carbon backbone. Earlier studies on the biological properties of thiosemicarbazones

and their metal complexes revealed that the biologically active thiosemicarbazone molecules were planar and a pyridine ring or a NNS tridentate system were present[18]. It is now well understood that the biological activity depends on the parent aldehyde or ketone[19,20] and the presence of a bulky group at the terminal nitrogen considerably increases the activity[21]. Reports on N(4)-substituted thiosemicarbazones have concluded that, an additional potential bonding site together with the presence of bulky groups at the N(4) position of the thiosemicarbazone moiety greatly enhances biological activity[22-24].

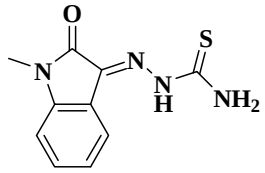
Epilepsy, one of the most frequent neurological disorders, is a major public health issue, affecting about 4% of individuals over their lifetime[25]. Recent studies revealed that a number of aryl semicarbazones possessed anticonvulsant activity in the maximal electroshock (MES) and subcutaneous pentylenetetrazole (scPTZ) screens when administered by the intraperitoneal route to mice[25-31]. In recent years, aryl and heteroaryl semicarbazones and thiosemicarbazones have emerged as structurally novel anticonvulsants[32]. Aryl semicarbazides have also been reported to display excellent anticonvulsant activity in mice and rats[33]. During the past decade, several new drugs have been approved (Rufinamide(1), Retigabine(2), Pregabaline(3), etc.). Despite advances in the drug treatment of epilepsy, a number of limitations of antiepileptic drug therapy continue to exist. Thus the search for new anticonvulsant drugs continues to be an active area of investigation in medicinal chemistry[27].



Strutures of Rufinamide, Retigabine, Pregabaline.

Thiosemicarbazones can be used for making electrodes due to formation of easy complexes with some metals. In the previous study, benzyl bis-thiosemicarbazones have been used for the construction of electrodes[34]. In another study, the bis(thiosemicarbazone) complexes of copper have shown special promise as radiopharmaceuticals, as illustrated by a per fusion imaging agent[35-39]. In the recent studies, appear to be a structural class with anti-pox virus activity[40]. Isatin

derivatives such as methisazone (marboran(4)), the β-thiosemicarbazone of N-methyl isatin, have been described as smallpox chemoprophylactic agents[41]. Methisazone decreases morbidity and mortality when given to susceptible contacts, but has no direct therapeutic efficacy vs variola and is no longer manufactured as a drug substance[42].



(4)

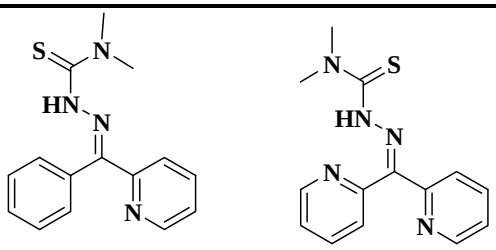
Strutures of methisazone (marboran).

The ability of thiosemicarbazone molecules to chelate with traces of metals in the biological system is believed to be a reason for their activity. By coordination, the lipophilicity, which controls the rate of entry into the cell, is modified, and some side effects may be decreased[43,44]. It has been proved that thiosemicarbazones block DNA synthesis in mammalian cells by inhibiting the enzyme, ribonucleosidediphosphate reductase, presumably either via chelation with an iron ion required by the enzyme or because a preformed metal chelate of the inhibitor interacts with the target enzyme[45,46]. Reports also point out the capacity of thiosemicarbazones to sever the DNA strands[47]. A major clinical challenge in successful treatment of cancer with anticancer drugs is that certain tumour cells develop a particular phenotype, called multi drug resistance (MDR), which makes these cells resistant to other classes of anticancer agents to which the tumor cells have not been treated previously[48]. Synthesis and characterization of a palladium complex of phenathrenequinone thiosemicarbazone and evaluation of its antiproliferative properties in breast cancer cells and normal cells have been described[49]. The study suggests that the complex is a potent antineoplastic agent that has selective activity against tumour cells and is effective against drug resistant breast cancer cells.

A number of authors have been interested in investigating the biological and medicinal properties of transition metal complexes of thiosemicarbazones in recent years. New square planar complexes of general formula, [M(NNS)CI] (M = Pd(II), Pt(II); NNS = anionic forms of the 6-methyl-2-formylpyridine Schiff bases of S-methyl and S-benzyldithiocarbazates) have been prepared. Both the Schiff bases

exhibit strong cytotoxicity against the human ovarian cancer (Caov-3) cell lines, the S-methyl derivative being two times more active than the S-benzyl derivative[50]. Palladium (II) and platinum(II) complexes of 5-chloro-1,3-dihydro-3-[2-(phenyl)-ethylidene]-2*H*-indoi-2-one-hydrazine carbothioamide have been prepared and screened for their antimicrobial activity against the fungi *Macrophomina phaseolina* and *Fusarium oxysporum* by agar plate technique. The results prove that the compounds exhibit antimicrobial properties and it is important to note that the metal chelates show more inhibitory effects than the parent ligands. The increased lipophilic character of these complexes seems to be responsible for their enhanced biological potency[51].

The iron(II) complexes of 2-benzoylpyridine thiosemicarbazone(5) as well as its N(4)-methyl and N(4)-phenyl analogues have been found to undergo oxidation giving the iron(III) analogues, which could be reduced back by cellular thiols such as thioredoxine, suggesting that this process could occur in biological media. The thoisemicarbazones have antifungal activity against *Candida albicans* that significantly decreases on coordination[52]. Cancer cells need more iron than normal body cells to sustain their abnormally rapid growth. Very recently, Prem Ponka from McGill University, Canada, and Des Richardson's group at the University of Sydney, Australia, have identified Dp44mT(6) (di-2-pyridylketone-4,4,-dimethyl-3-thiosemicarbazone) as a particularly potent substance that can bind iron in a tight chelate complex and thus deplete tumors. Chelating behavior of di-2-pyridylketone thiosemicarbazones is an ongoing study in our laboratory also[7].

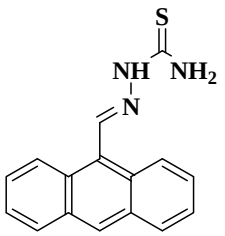


(5) **(6)**

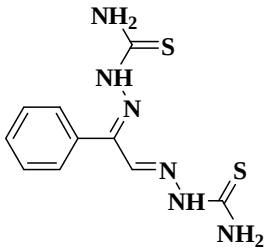
Antifungal activity of iron(II) complexes of (5) and anti cancer activity of iron(II) complexes of (6)

The antitumor activities of Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} chelates of anthracene-9-carboxaldehyde thiosemicarbazone(7)[53] and the cytotoxic activity of

phenylglyoxal bis(thiosemicarbazone)(8) against *Ehrlich ascites* carcinoma cells have been reported. These compounds were also screened for antimicrobial activity on *B.subtilis* and *E.coli* and it was found that they inhibited the bacterial growth considerably[54].



(7)



(8)

Antitumor activities of Mn(II), Co(II), Ni(II) and Cu(II) complexes of (7) and cytotoxic activity of Mn(II), Co(II), Ni(II) and Cu(II) complexes of (8)

Platinum complexes of 2-acetylpyridine thiosemicarbazone have been synthesized in which intermolecular hydrogen bonds, π-π and weak Pt-Pt and Pt- π contacts lead to aggregation and to a two-dimensional supramolecular assembly. The complexes were found to have a completely lethal effect on Gram+ bacteria. Additionally, some of them showed effective antifungal activity towards yeast[55]. The effect of Pt(II) and Pd(II) complexes of 2-acetylpyridine thiosemicarbazone (HAcTsc) on sister chromatid exchange (SCE) rates, human lymphocyte proliferation kinetics, and leukemia P388 have been investigated. Among these compounds, $[Pt(AcTsc)_2]•H_2O$ and $[Pd(AcTsc)_2]$were found to be the most effective in inducing antitumor and cytogenetic effects[56]. Antifungicidal, antibacterial and antifertility activities of biologically active heterocyclic thoisemicarbazones and their coordination complexes with the dimethylsilicon moiety have been described. Some ligands and their corresponding dimethylsilicon(IV) complexes have been tested for their effects on several pathogenic fungi and bacteria. Two representative complexes have also been found to act as sterilizing agents by reducing the production of sperm in male mice[57].

Adverse biological activities of thoisemicarbazones have been widely studied in rats and in other animal species using different doses, times and routes of administration. In this study, the rats were injected subcutaneously with a new thiosemicarbazone (HL) and its Cu(II) and Zn(II) complexes. The aim of this study

was to determine the effect of the new compounds on the serum antioxidant vitamins (A, E, C), selenium (Se), malondialdehyde (MDA) levels, erythrocyte GSH-Px enzyme activity and morphological changes in the liver, kidney and adrenal gland tissues. It was observed that erythrocyte GSH-Px activity, serum MDA and vitamins A, E concentrations were statistically changed, but serum levels of selenium, and vitamin C were not changed. In conclusion, the parameters measured show that Cu(II) caused considerable oxidative stress and Zn(II) behaved as an antioxidant[58].

1.1.2 Thiosemicarbazones in the analytical field

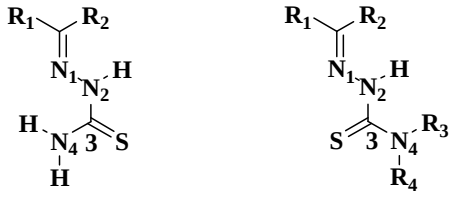
Thiosemicarbazones have applications in analytical field also. Some of the thiosemicarbazones produce highly colored complexes with metal ions. These complexes have been proposed as analytical reagents that can be used in selective and sensitive determinations of metal ions[59,60]. Ferrocene derivatives containing thiosemicarbazone side chain have been investigated by cyclic voltammetry and positron annihilation lifetime (PAL) measurements. Positrons can form the positronelectron pair in molecular solids. Interest in the behaviour of the positron-electron pair is great because the probability of its formation and its lifetime depend upon the physical and chemical properties of the solid. It has been shown that the redox and the electron capture processes took place on the Fe atom[61]. Cu(II), Co(II) and Fe(II) in pharmaceutical preparations could be determined using pre-column derivatization and solvent extraction with 2-acetylpyridine-4-phenyl-3-thiosemicarbazone as complexing reagent[62].

The inhibition of corrosion of aluminium in HCI solution by some derivatives of thiosemicarbazones has been studied using weight loss and hydrogen evolution techniques. The thosemicarbazone dreivatives used are 2-acetylpyridine-4-phenyl thiosemicarbazone, 2-acetylpyridine-4-phenylisomethyl thiosemicarbazone and 2-acetylpyridine-4-phenylisoethyl thiosemicarbazone. The inhibition efficiency depended on the compound concentation[63].

1.1.3 Thiosemicarbazones - the coordinating agents

Thiosemicarbazones are thiourea derivatives obtained by condensation of thiosemicarbazide or N(4)-substituted thiosemicarbazide with a suitable aldehyde or ketone. Thiosemicarbazones are represented by the general formula **(9)**, and when

N(4) is substituted they can be represented by the general formula **(10)**. The numbering scheme shown in the figure is in accordance with the IUPAC system of numbering for thiosemicarbazones. However, it should be noted that the numbering schemes in the crystal structures are based on the types of different atoms present. In the formula **(10)**, R^3 and R^4 can be alkyl or aryl groups or a part of a cyclic system. According to the IUPAC recommendations for the nomenclature of organic compounds, derivatives of thiourea represented by the general formula R^1R^2C=N-NH-CS-N R^3R^4, may be named by adding the class name thiosemicarbazone after the name of condensed aldehyde or ketone[64].

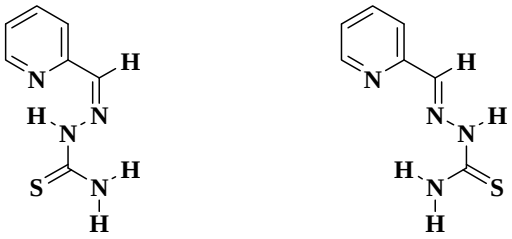


(9) **(10)**

General structures of thiosemicarbazones

Presence of C=N, make thiosemicarbazones exist as *E* and *Z* stereoisomers. Considering the thermodynamic stability, *E* isomer will predominate in the mixture[65]. The structure of the C=N-NH-CS-N backbone is usually almost planar with the S atom trans to azomethine N. Zhi Min Jin *et al.* have reported the crystal structure of pyridine-2-carbaldehyde thiosemicarbazone showing the *E* configuration[66].

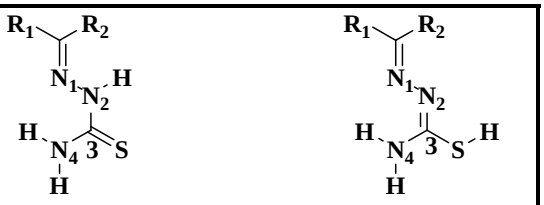
Recently, Kurup and co-workers have reported the crystal structure of pyridine-2-carbaldehyde N(4)-phenethylthiosemicarbazone in which the thiosemicarbazone group adopts an *EE* configuration, i.e., *trans* configurations are observed about both the azomethine and hydrazinic bonds[67]. Although there are several electronic and steric factors that may contribute to the adoption of this arrangement, the most important is probably that the trans arrangement places the amine and azomethine nitrogen atoms in relative positions more suitable for intramolecular hydrogen bonding[68]. In fact, the complete substitution of amine hydrogens results in crystallization with S atom *cis* with azomethine nitrogen giving *Z* configuration.



Z isomer(11) **E isomer(12)**

Z and E isomers of pyridine-2-carbaldehyde thiosemicarbazone

Presence of NH-C=S group in thiosemicarbazones can bring about thione-thiol tautomerism. In solution thiosemicarbazones exist as an equilibrium mixture of thione **(13)** and thiol **(14)** forms.



(13) **(14)**

Thione and thiol forms of thiosemicarbazones

Enolization into the thiol form results in an effective conjugation along the thiosemicarbazone skeleton thus enhancing electron delocalization along the moiety. In the case of hetero aromatic thiosemicarbazones, delocalization of electron cloud is extended along with the generation of new potential sites for coordination. Upon coordination to a metal centre, the delocalization is further increased through the metal chelate rings. This is one of the reasons for choosing pyridine-2-carbaldehyde as the carbonyl base of our ligands. Though thiosemicarbazones can coordinate to metals in the neutral thione form, usually chelation takes place through the anion formed by deprotonation of the hydrazinic NH group, *via* enolization to the thiol form. The stereochemistry adopted by the thiosemicarbazone ligand with transition metal ion depends essentially on the presence of additional coordination sites in the ligand moiety and the charge on the ligand which in turn is influenced by the thione-thiol equilibrium, and pH of the medium used for reaction. Studies have revealed that the steric effects of the various substituents in the thiosemicarbazone moiety considerably affect the stereochemistry.

Thiosemicarbazones can adopt a variety of different coordination modes. In most of the cases, thiosemicarbazones coordinate as bidentate ligands via azomethine nitrogen and thione/thiolato sulfur. When additional coordination functionality is present in the proximity of the donating centers, the ligands will coordinate in a tridentate manner. This can be accomplished either by the neutral molecule or by the monobasic anion upon loss of hydrogen. Although the thione form predominates in the solid state, solutions of thiosemicarbazone molecules show a mixture of both tautomers. As a result, depending upon the preparative conditions, the metal complex can be cationic neutral or anionic. There are cases where both the neutral and anionic forms of the ligand are involved in coordination[21].

1.1.4 Scope and significance of the present work

The significance of present work, apart from their diverse chemical and structural characteristics, stems from not only their potential but also their proved application as biologically active molecules. The relationship between structure and biological activity has been covered in several papers[65,69]. Pyridine-2-carbaldehyde thiosemicarbazone was the first α-(N)-heterocyclic carboxyaldehyde thiosemicarbazone, reported to have carcinostatic effects[46,70]. Reports show that greatest activity occurs for 2-substituted pyridine thiosemicarbazones with differences observed for 2-formylpyridine, 2-acetylpyridine and 2-benzoylpyridine derivatives and their metal complexes[71]. The highest biological activity for pyridine related thiosemicarbazones is achieved when N(4) position bears bulky groups[72-74]. Recently, the partial transformation of thioamide group into nitrile in pyridine-2-carbaldehyde thiosemicarbazonato copper(II) entities in aqueous basic medium was report ed[75].

Thus, it is worthwhile to carry out following syntheses of substituted thiosemicarbazones with different structural features as well as their metal complexes.

l Synthesis and physico-chemical characterization of following new thiosemicarbazones:

1. 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide
2. 1-(4,5-dimethoxy-2-nitrobenzylidene)thiosemicarbazide
3. 1-((2-chloroquinolin-3-yl)methylene)thiosemicarbazide
4. 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide

5. 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide
6. 1-((1,3-diphenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide
7. 1-((3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide
8. 1-((3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide
9. 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide
10. 1-(2,4-dichlorobenzylidene)-4-(pyridin-2-yl)thiosemicarbazide
11. 1-(4-methoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide
12. 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide
13. 1-(3-hydroxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide
14. 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide
15. 1-(3,4-dimethoxybenzylidene)-4-(4-bromophenyl)thio-semicarbazide

2. Synthesis of copper(II), cobalt(II) and nickel(II) complexes of these ligands.
3. Probable structures of the complexes and their spectral properties.
4. The stability constant of metal complexes.
5. Biological activities of newly synthesized ligands and their metal complexes.

1.2 CHAPTER-I

Synthesis and characterization of 1-substituted aryl/pyrazolyl/quinolinyl thiosemicarbazide

1.3 CHAPTER-II

Synthesis and characterization of 1-substituted arylidene-4-(pyridin-2-yl) thiosemicarbazide

1.4 CHAPTER-III

Synthesis and characterization of 1-substituted arylidene-4-(4-bromophenyl)thiosemicarbazide

CHAPTER-I

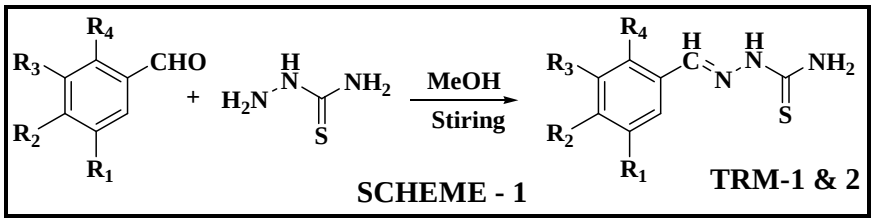
SYNTHESIS AND CHARACTERIZATION OF 1-SUBSTITUTED ARYL/PYRAZOLYL/ QUINOLINYL THIOSEMICARBAZIDE

1.2.1 EXPERIMENTAL SECTION

Synthesis of Ligands

General procedure for the synthesis of 1-substituted aryl thiosemicarbazide.

The thiosemicarbazide (0.01M) was dissolved in 10 ml of methanol in a 100 ml round bottom flask, a solution of 0.01M substituted aromatic aldehyde in methanol was added drop wise over a 10 min. period with continues stirring, after addition the reaction mixture was stirred for 3 hours at room temperature, reaction was monitored by TLC. After completion solvent was evaporated and residue was washed with cold methanol and dried at room temperature.



SCHEME - 1 **TRM-1 & 2**

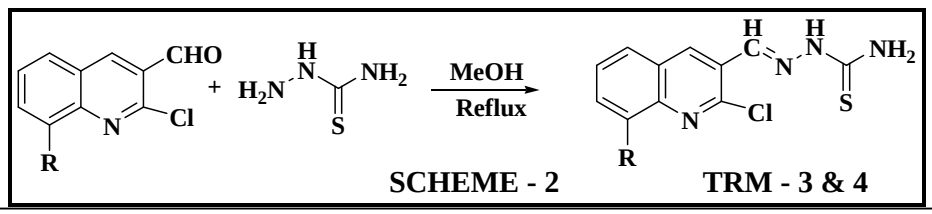
TABLE - I

Comp. Code	R_1	R_2	R_3	R_4	Yield %	M. P. °C	R_f
TRM-1	$-OCH_3$	-OH	-Br	-H	86	200	0.31
TRM-2	$-OCH_3$	$-OCH_3$	-H	$-NO_2$	82	288	0.34

TLC Solvent system – benzene:acetone **(**8:2)

General procedure for the synthesis of 1-substituted quinolinyl thiosemicarbazide.

A mixture of a thiosemicarbazide (0.01M) and substituted quinoline aldehyde (0.01 M) was dissolved in 70-80 ml of methanol, add 1 ml of 20% NaOH solution, the resulting reaction mixture was reflux for 10 hours on boiling water bath, reaction was monitored by TLC. After completion of reaction, the reaction mixture was poured in ice-cold water, was filtered and washed repeatedly with cold methanol and dried at room temperature.



SCHEME - 2 **TRM - 3 & 4**

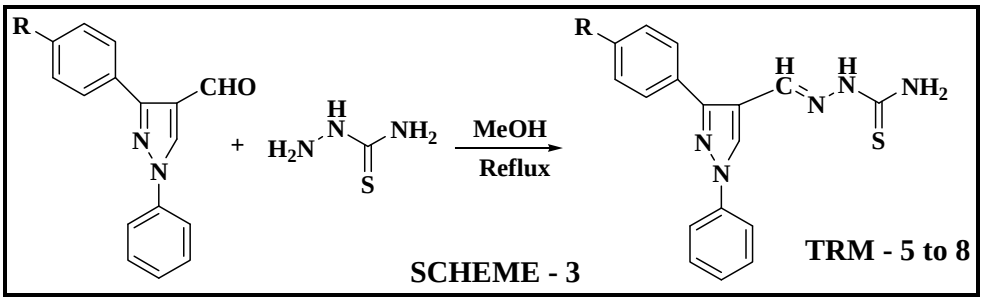
TABLE - II

Comp. Code	R	Yield %	M. P. ºC	R_f
TRM-3	-H	79	232	0.50
TRM-4	$-CH_3$	81	244	0.53

TLC Solvent system - benzene:acetone **(**8:2)

General procedure for the synthesis of 1-substituted pyrazolyl thiosemicarbazide.

An equimolar amount of a thiosemicarbazide (0.01M) and substituted pyrazole aldehyde (0.01 M) were dissolved in 80 ml methanol. The resulting mixture was reflux for 10 hours in the presence of catalytic amount of gl. acetic acid, reaction was monitored by TLC. After completion of the reaction, reaction mixture was poured into crushed ice. The separated product was filtered wash with cold methanol and dried at room temperature.



SCHEME - 3

TABLE - III

Comp. Code	R	Yield %	M. P. ºC	R_f
TRM-5	$-OCH_3$	85	140	0.39
TRM-6	-H	82	212	0.45
TRM-7	-Cl	88	192	0.47
TRM-8	$-NO_2$	78	200	0.43

TLC Solvent system - benzene:acetone **(**8:2)

1.2.2 SPECTRAL DATA OF THE SYNTHESIZED LIGANDS

[1] 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide(TRM-1).

Colour: White; **Anal. Calcd**. For $C_9H_{10}BrN_3O_2S$ (304.16 g/mol): C, 35.54%; H, 3.31%; N, 13.81%; S, 10.54%. **Found:** C, 35.41%; H, 3.26%; N, 13.68%; S, 10.37%; **MS** (m/z): 305 (M+1); **IR (KBr, cm^{-1}):** *ν*(OH) 3470; *ν*(NH) 3354; *ν*(NH_2) 3254; *ν*(C=N) 1678; *ν*(N-N) 1047; *ν*(C=S) 1280; δ(C=S) 837; *ν*(Ar–C-H) 3136-3010; *ν*(Ar–C=C) 1498; *ν*(C-Br) 607; **^{1}H-NMR (DMSO-d_6):** δppm 3.87 (s, 3H, OMe); 7.41, (d, 1H, *J* = 1.6 Hz, Ar-H); 7.47, (d, 1H, *J* = 1.6 Hz, Ar-H); 8.05, 8.12 (d, 2H, NH_2); 8.43 (s, 1H, HC=N); 9.98 (s, br, 1H, OH); 11.32 (s, 1H, NH); **^{13}C-NMR (DMSO-d_6):** δppm 56.40 (O-CH_3); 109.0, 109.29, 124.26, 126.49, 145.44, 148.52 (Ph); 141.25 (HC=N); 177.64 (C=S); **UV-Vis:(DMF)** (λ_{max}/ nm): 268, 338.

[2] 1-(4,5-dimethoxy-2-nitrobenzylidene)thiosemicarbazide(TRM-2).

Colour: Yellow; **Anal. Calcd**. For $C_{10}H_{12}N_4O_4S$ (284.29 g/mol): C, 42.25%; H, 4.25%; N, 19.71%; S, 11.28%. **Found:** C, 42.14%; H, 4.20%; N, 19.62%; S, 11.19%; **MS** (m/z): 284 (M); **IR (KBr, cm^{-1}):** *ν*(NH) 3375; *ν*(NH_2) 3292; *ν*(C=N) 1628; *ν*(N-N) 1060; *ν*(C=S) 1286; δ(C=S) 833; *ν*(Ar–C-H) 3171-3005; *ν*(Ar–C=C) 1527; *ν*(C-NO_2) 1323; **^{1}H-NMR (DMSO-d_6):** δppm 3.87, (s, 3H, OMe); 3.95, (s, 3H, OMe); 7.56, (s, 1H, Ar-H); 7.69, (s, 1H, Ar-H); 8.14, 8.34 (d, 2H, NH_2); 8.55 (s, 1H, HC=N); 11.33 (s, 1H, NH); **^{13}C-NMR (DMSO-d_6):** δppm 56.14, 56.54 (O-CH_3); 107.52, 108.68, 123.06, 138.04, 149.46, 152.77 (Ph); 141.37 (HC=N); 178.19 (C=S); **UV-Vis:(DMF)** (λ_{max}/ nm): 270, 294.

[3] 1-((2-chloroquinolin-3-yl)methylene)thiosemicarbazide (TRM-3).

Colour: Greenish; **Anal. Calcd**. For $C_{11}H_9ClN_4S$ (264.73 g/mol): C, 49.91%; H, 3.43%; N, 21.16%; S, 12.11%. **Found:** C, 49.86%; H, 3.35%; N, 21.03%; S, 12.08%; **MS** (m/z): 264 (M); **IR (KBr, cm^{-1}):** *ν*(NH) 3310; *ν*(NH_2) 3234; *ν*(C=N) 1591; *ν*(N-N) 1082; *ν*(C=S) 1292; δ(C=S) 862; *ν*(Ar–C-H) 3144-2966; *ν*(Ar–C=C) 1475; *ν*(C-Cl) 765; **^{1}H-NMR (DMSO-d_6):** δppm 7.67, (tri, 1H, Ar-H); 7.80, (tri, 1H, Ar-H); 7.93, (d, 1H, *J* = 8.4 Hz, Ar-H); 7.97, (d, 1H, *J* = 8.0 Hz, Ar-H); 8.25, (s, 1H, Ar-H); 8.45, 8.49 (d, 2H, NH_2); 9.28 (s, 1H, HC=N);

11.79 (s, 1H, NH); **^{13}C-NMR (DMSO-d$_6$):** δppm 126.15, 126.96, 127.70, 127.82, 128.42, 131.49, 135.98, 146.90, 148.40 (Ph); 136.74 (HC=N); 178.40 (C=S).

[4] 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide(TRM-4).

Colour: Yellowish; **Anal. Calcd**. For $C_{12}H_{11}ClN_4S$ (278.76 g/mol): C, 51.70%; H, 3.98%; N, 20.10%; S, 11.50%. **Found:** C, 51.63%; H, 3.88%; N, 20.04%; S, 11.42%; **MS** (m/z): 278 (M); **IR (KBr, cm^{-1}):** *ν*(NH) 3352; *ν*(NH_2) 3271; *ν*(C=N) 1599; *ν*(N-N) 1107; *ν*(C=S) 1280; δ(C=S) 850; *ν*(Ar–C-H) 3140-3001; *ν*(Ar–C=C) 1491; *ν*(C-Cl) 759; **^{1}H-NMR (DMSO-d$_6$):** δppm 2.66, (s, 3H, CH_3); 7.58, (tri, 1H, Ar-H); 7.69, (d, 1H, *J* = 7.2 Hz, Ar-H); 7.832, (d, 1H, *J* = 8.0 Hz, Ar-H); 8.27, (s, 1H, Ar-H); 8.46, 8.51 (d, 2H, NH_2); 9.28 (s, 1H, HC=N); 11.80 (s, 1H, NH); **^{13}C-NMR (DMSO-d$_6$):** δppm 17.25 (Ar-CH_3); 125.91, 126.33, 127.04, 127.57, 131.43, 135.55, 136.32, 146.03, 147.52 (Ph); 136.84 (HC=N); 178.40 (C=S); **UV-Vis:(DMF)** (λ_{max}/ nm): 286, 360.

[5] 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide(TRM-5).

Colour: Cream; **Anal. Calcd**. For $C_{18}H_{17}N_5OS$ (351.43 g/mol): C, 61.52%; H, 4.88%; N, 19.93%; S, 9.12%. **Found:** C, 61.48%; H, 4.83%; N, 19.84%; S, 9.08%; **MS** (m/z): 351 (M); **IR (KBr, cm^{-1}):** *ν*(NH) 3367; *ν*(NH_2) 3221; *ν*(C=N) 1597; *ν*(N-N) 1043; *ν*(C=S) 1290; δ(C=S) 839; *ν*(Ar–C-H) 3159-3005; *ν*(Ar–C=C) 1502; **^{1}H-NMR (DMSO-d$_6$):** δppm 3.84, (s, 3H, OMe); 7.08, (d, 2H, Ar-H); 7.38, (tri, 1H, Ar-H); 7.57, (tri, 2H, Ar-H); 7.64, (d, 2H, Ar-H); 7.79, (s, 1H, Ar-H); 7.90, (d, 2H, Ar-H); 8.24, (s, 2H, NH_2); 9.16 (s, 1H, HC=N); 11.33 (s, 1H, NH); **^{13}C-NMR (DMSO-d$_6$):** δppm 55.21 (O-CH_3); 114.11, 116.90, 118.36, 123.82, 124.48, 126.77, 127.50, 129.40, 129.58, 135.16, 136.04, 149.55, 151.20, 159.54 (Ph); 139.03 (HC=N); 177.53 (C=S); **UV-Vis:(DMF)** (λ_{max}/ nm): 290, 334.

[6] 1-((1,3-diphenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide(TRM-6).

Colour: White; **Anal. Calcd**. For $C_{17}H_{15}N_5S$ (321.40 g/mol): C, 63.53%; H, 4.70%; N, 21.79%; S, 9.98%. **Found:** C, 63.45%; H, 4.68%; N, 21.70%; S,

9.94%; **MS** (m/z): 321 (M); **IR (KBr, cm^{-1}):** *v*(NH) 3348; *v*(NH_2) 3254; *v*(C=N) 1597; *v*(N-N) 1060; *v*(C=S) 1284; δ(C=S) 871; *v*(Ar–C-H) 3140-2976; *v*(Ar–C=C) 1502; **^{1}H-NMR (DMSO-d$_6$):** δppm 7.37, (tri, 1H, Ar-H); 7.51, (m, 5H, Ar-H); 7.67, (d, 2H, *J* = 6.8 Hz, Ar-H); 7.76, (s, 1H, Ar-H); 7.89, (d, 2H, *J* = 7.6 Hz, Ar-H); 8.22, (s, 2H, NH_2); 9.17 (s, 1H, HC=N); 11.31 (s, 1H, NH); **^{13}C-NMR (DMSO-d$_6$):** δppm 117.20, 118.45, 126.92, 127.64, 128.08, 128.52, 128.67, 129.62, 132.07, 134.90, 151.31 (Ph); 138.99 (HC=N); 177.55 (C=S).

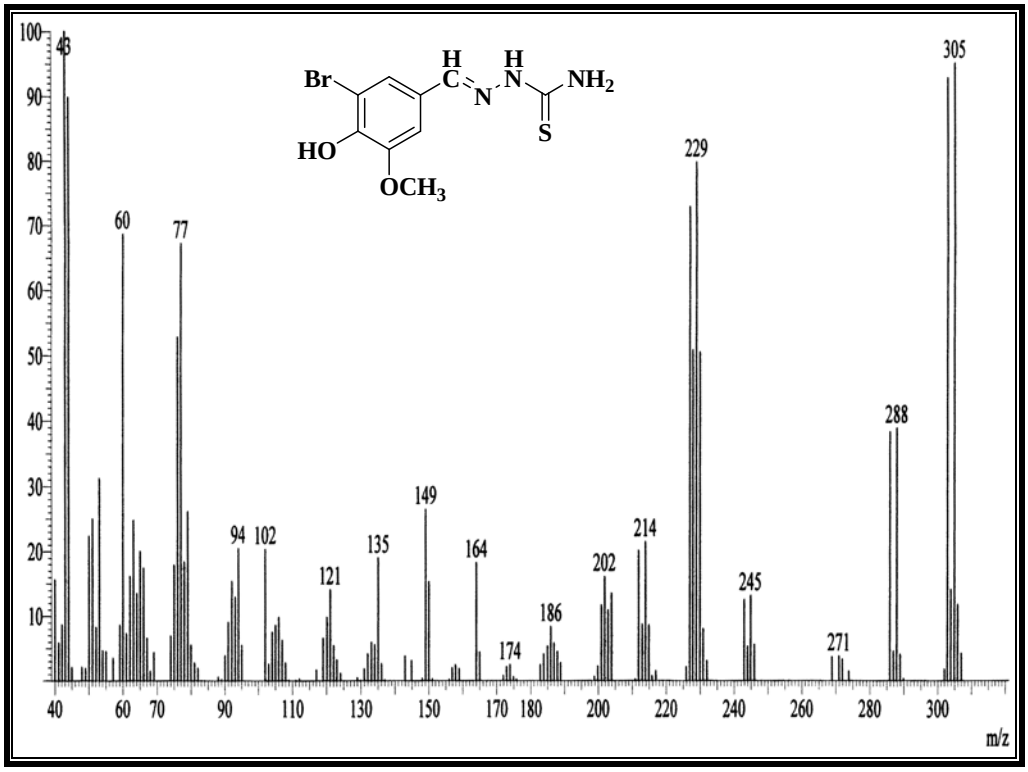
[7] 1-((3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide(TRM-7).

Colour: Yellow; **Anal. Calcd**. For $C_{17}H_{14}ClN_5S$ (355.84 g/mol): C, 57.38%; H, 3.97%; N, 19.68%; S, 9.01%. **Found:** C, 57.30%; H, 3.93%; N, 19.61%; S, 8.94%; **MS** (m/z): 355 (M); **IR (KBr, cm^{-1}):** *v*(NH) 3380; *v*(NH_2) 3198; *v*(C=N) 1599; *v*(N-N) 1093; *v*(C=S) 1288; δ(C=S) 842; *v*(Ar–C-H) 3146-3018; *v*(Ar–C=C) 1504; *v*(C-Cl) 752; **^{1}H-NMR (DMSO-d$_6$):** δppm 7.37, (tri, 1H, Ar-H); 7.56, (m, 4H, Ar-H); 7.70, (d, 2H, *J* = 8.4 Hz, Ar-H); 7.76, (s, 1H, Ar-H); 7.88, (d, 2H, *J* = 7.6 Hz, Ar-H); 8.24, (d, 2H, NH_2); 9.16 (s, 1H, HC=N); 11.31 (s, 1H, NH); **^{13}C-NMR (DMSO-d$_6$):** δppm 117.28, 118.51, 127.04, 127.88, 128.72, 129.62 , 129.76, 130.94, 133.32, 134.66, 150.03 (Ph); 138.91 (HC=N); 177.59 (C=S).

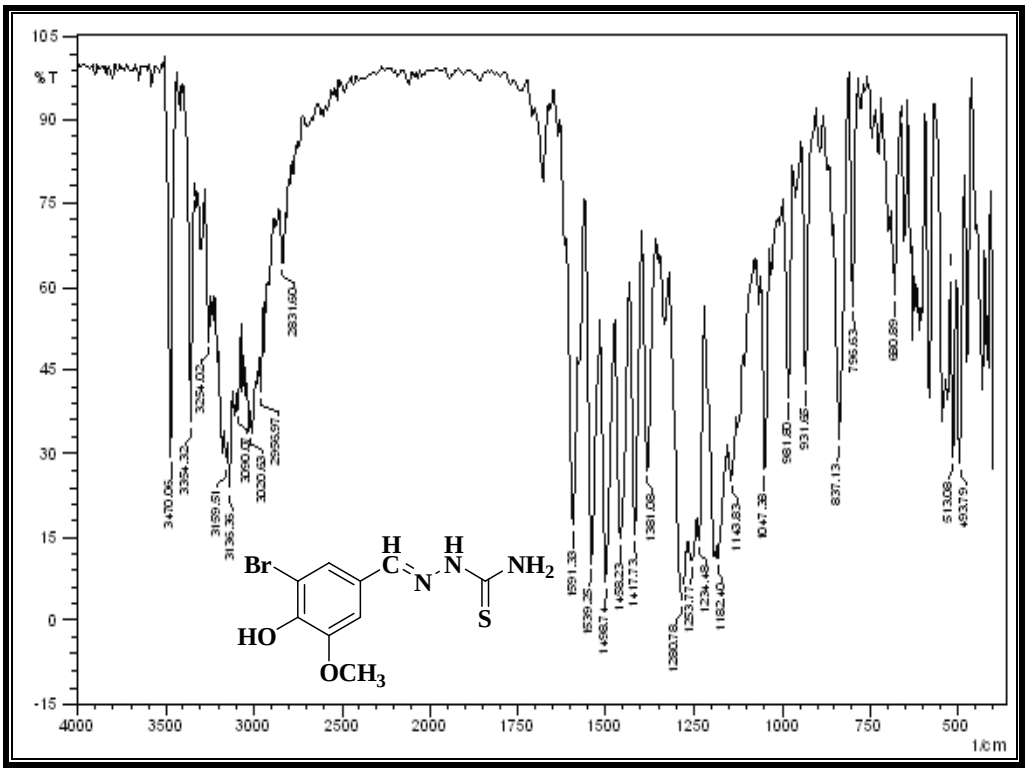
[8] 1-((3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide (TRM-8).

Colour: Orange; **Anal. Calcd**. For $C_{17}H_{14}N_6O_2S$ (366.4 g/mol): C, 55.73%; H, 3.85%; N, 22.94%; S, 8.75%. **Found:** C, 55.69%; H, 3.80%; N, 22.83%; S, 8.66%; **MS** (m/z): 366M); **IR (KBr, cm^{-1}):** *v*(NH) 3371; *v*(NH_2) 3182; *v*(C=N) 1597; *v*(N-N) 1062; *v*(C=S) 1292; δ(C=S) 862; *v*(Ar–C-H) 3140-3014; *v*(Ar–C=C) 1508; *v*(C-NO_2) 1342; **^{1}H-NMR (DMSO-d$_6$):** δppm 7.40, (tri, 1H, Ar-H); 7.57, (tri, 2H, Ar-H); 7.76, (s, 1H, Ar-H); 7.91, (d, 2H, *J* = 7.6 Hz, Ar-H); 7.97, (d, 2H, *J* = 8.8 Hz, Ar-H); 8.25, (s, 2H, NH_2); 8.34, (d, 2H, *J* = 8.4 Hz, Ar-H); 9.22 (s, 1H, HC=N); 11.34 (s, 1H, NH); **^{13}C-NMR (DMSO-d$_6$):** δppm 117.96, 118.69, 123.87, 127.36, 128.43, 129.03, 129.69, 134.25, 138.54, 147.16, 148.89 (Ph); 138.78 (HC=N); 177.67 (C=S).

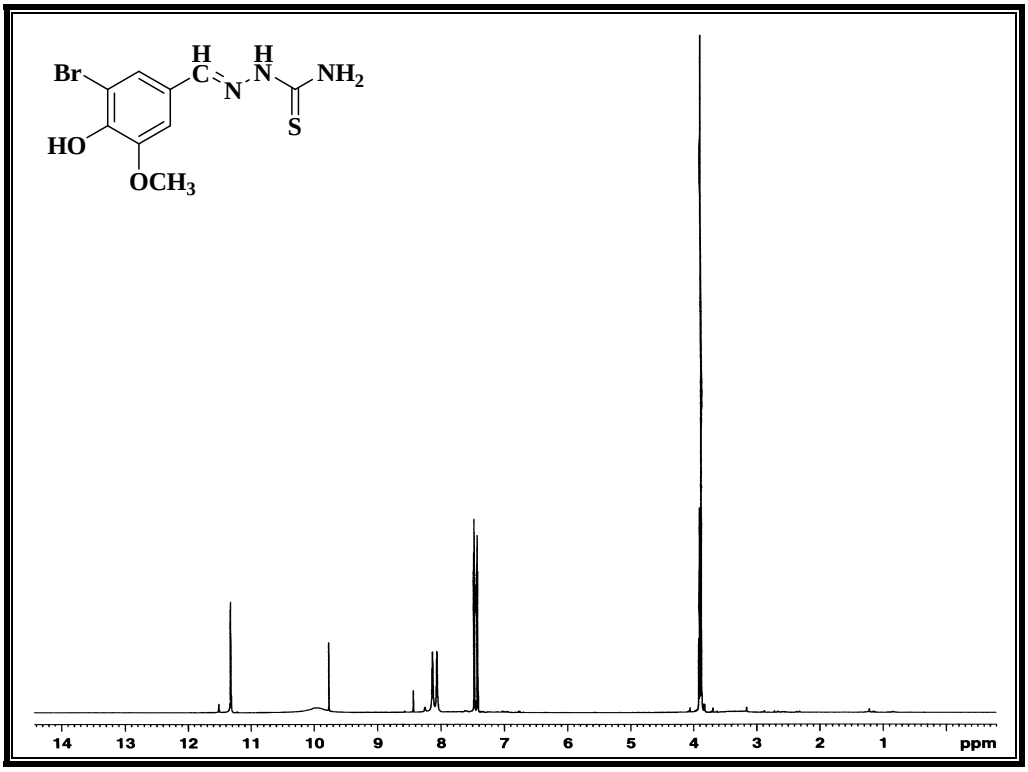
Mass spectrum of TRM-1



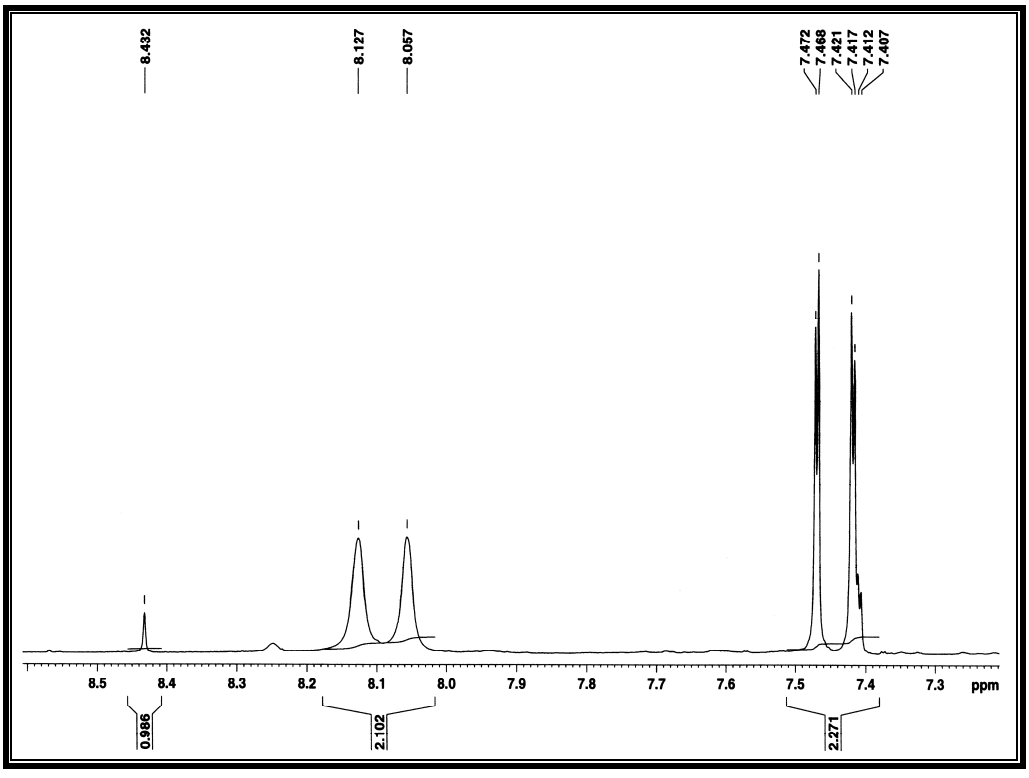
IR spectrum of TRM-1



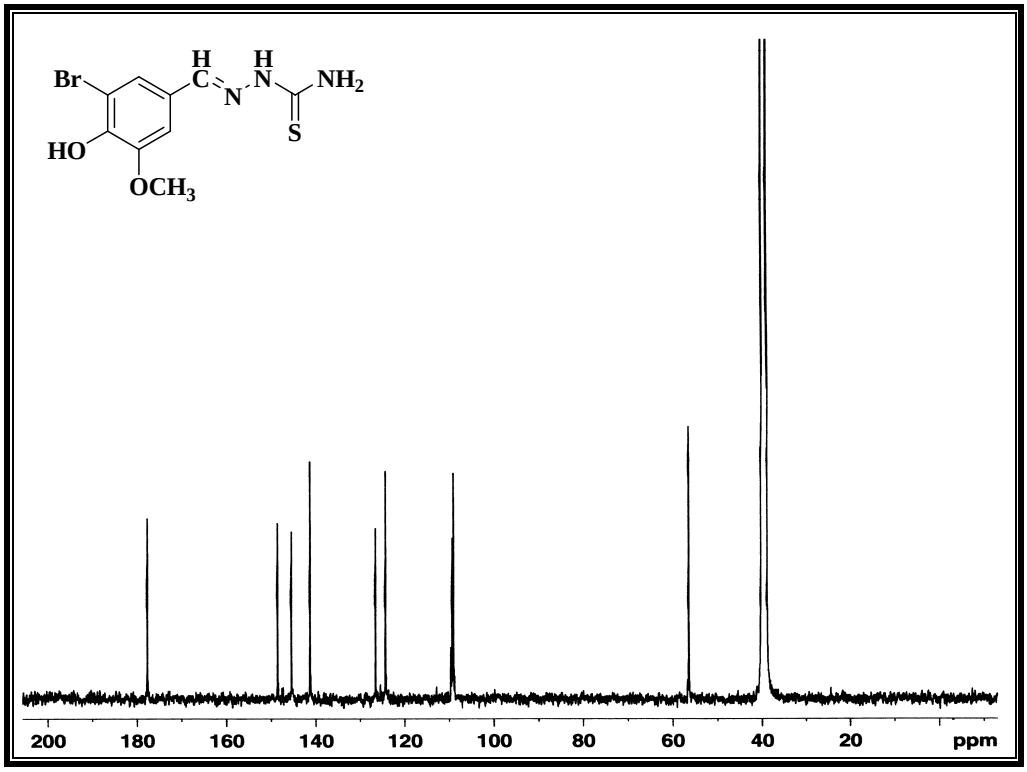
^{1}H NMR spectrum of TRM-1



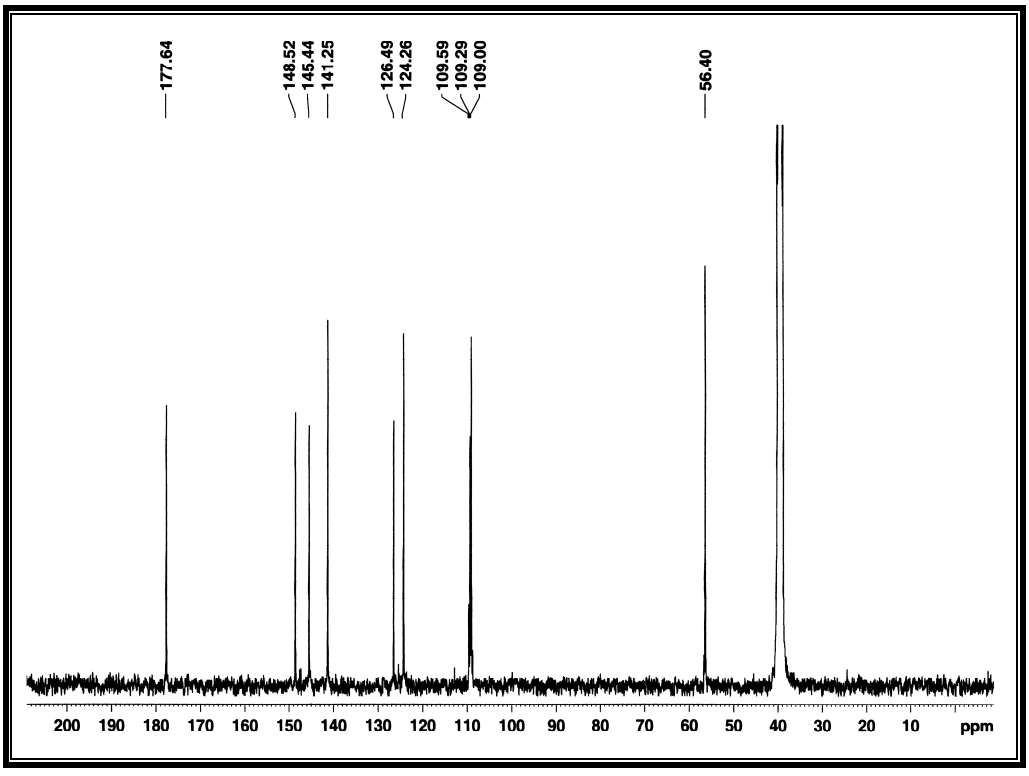
Expanded ^{1}H NMR spectrum of TRM-1



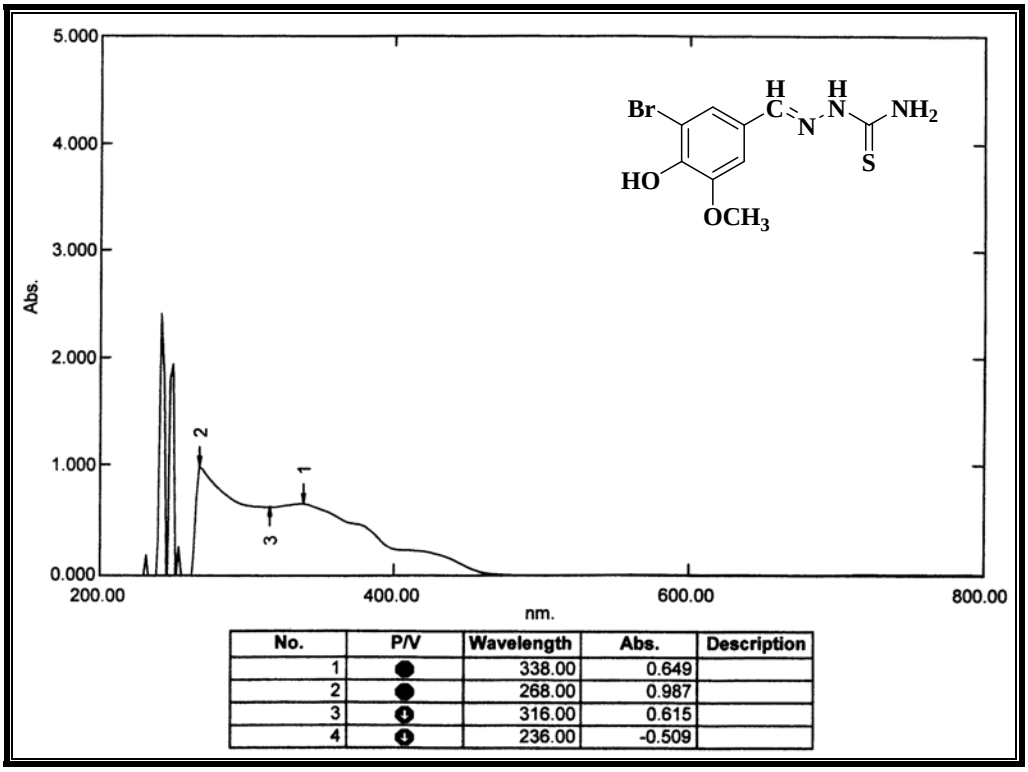
^{13}C NMR spectrum of TRM-1



Expanded ^{13}C NMR spectrum of TRM-1



UV-Visible spectrum of TRM-1



No.	P/V	Wavelength	Abs.	Description
1	●	338.00	0.649	
2	●	268.00	0.987	
3	◆	316.00	0.615	
4	◆	236.00	-0.509	

Results & Discussion

In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M+1) corresponding to their molecular weight.

Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3354 cm^{-1}, 1047 cm^{-1} and 1280 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1678 cm^{-1}. The other bands of -OH due to at 3470 cm^{-1} and -NH_2 due to at 3254 cm^{-1} and aromatic -C-H and -C=C bands due to at 3136-3010 cm^{-1} and 1498 cm^{-1} respectively.

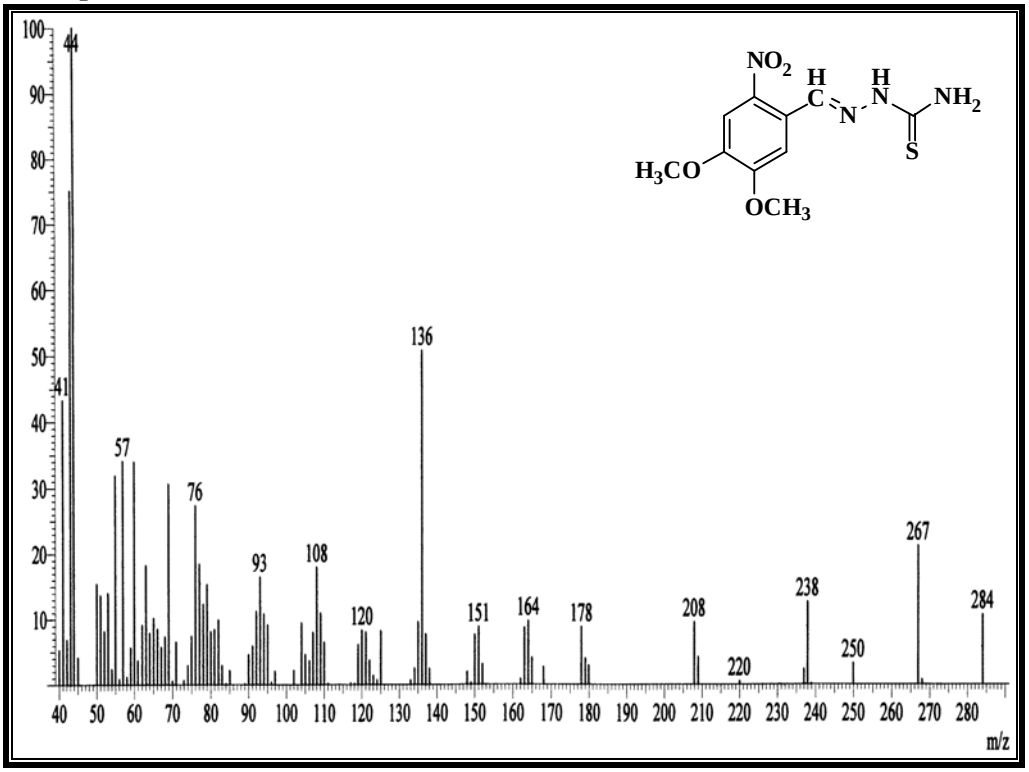
In the ^1H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 8.43 ppm as a singlet. The, -N-NH and NH_2 protons were observed at 11.32 ppm and 8.12 ppm as a singlet, respectively. The -O-CH_3 and -OH

protons were observed at 3.87 ppm and 9.98 ppm as a singlet, respectively. All the aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 141.25 ppm and -C=S carbon, appeared at 177.64 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

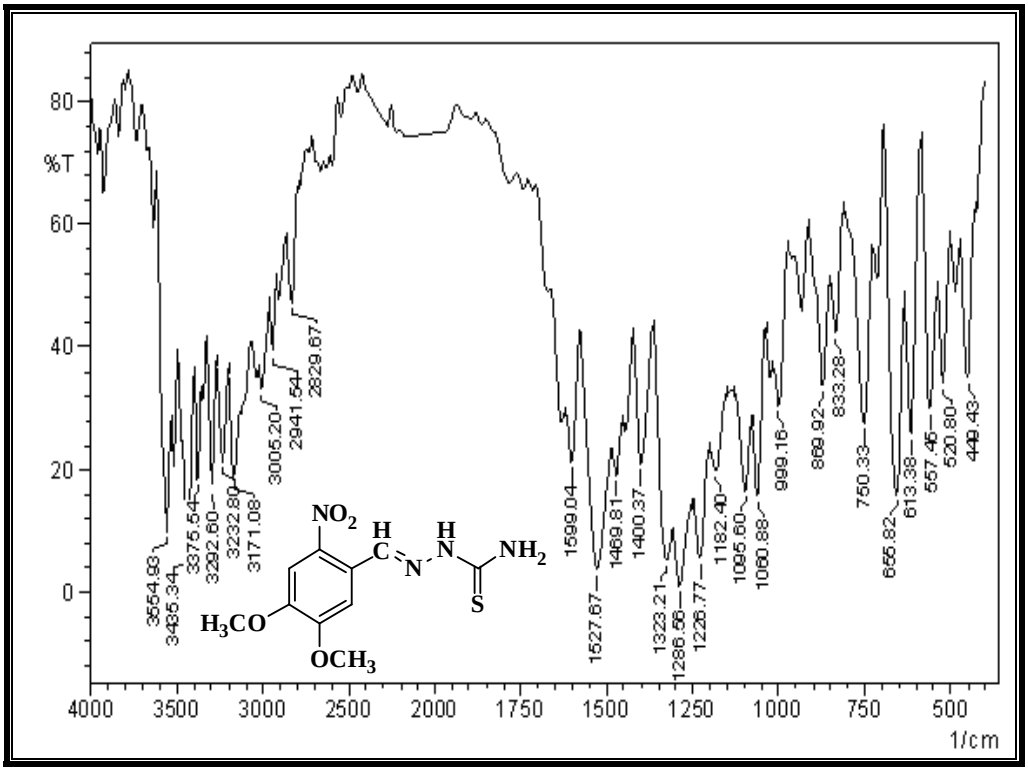
Electronic spectroscopy is a very important tool for the structural identification of synthesized thiosemicarbazone. It is usually measured in the range 200-800 nm. This compound absorb in the region 250-350 nm and the bands are mainly due to at 268 nm $\pi \rightarrow \pi^*$ and 338 nm $n \rightarrow \pi^*$ transitions.

All spectral characterization and elemental analysis confirm the structure of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide(TRM-1).

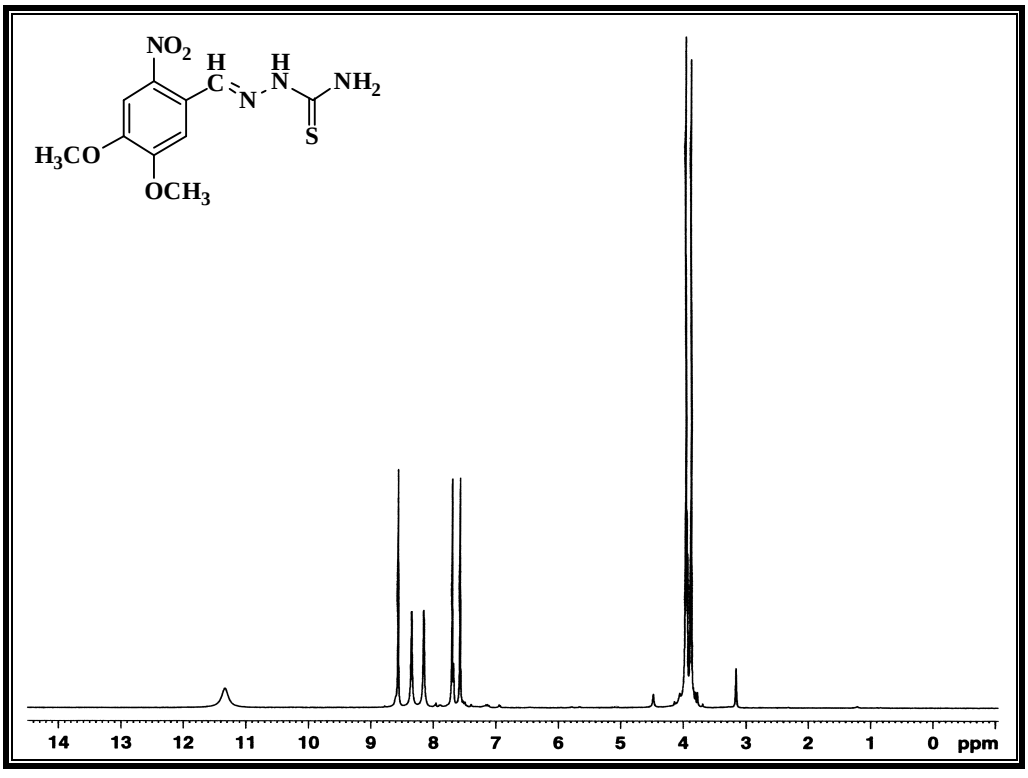
Mass spectrum of TRM-2



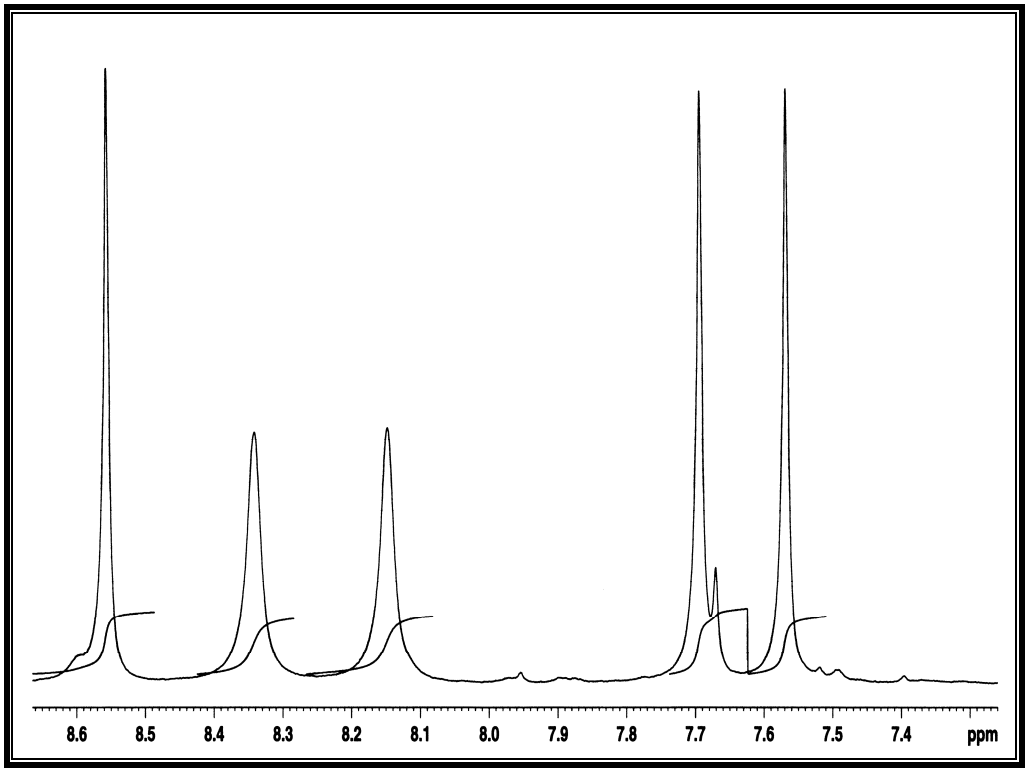
IR spectrum of TRM-2



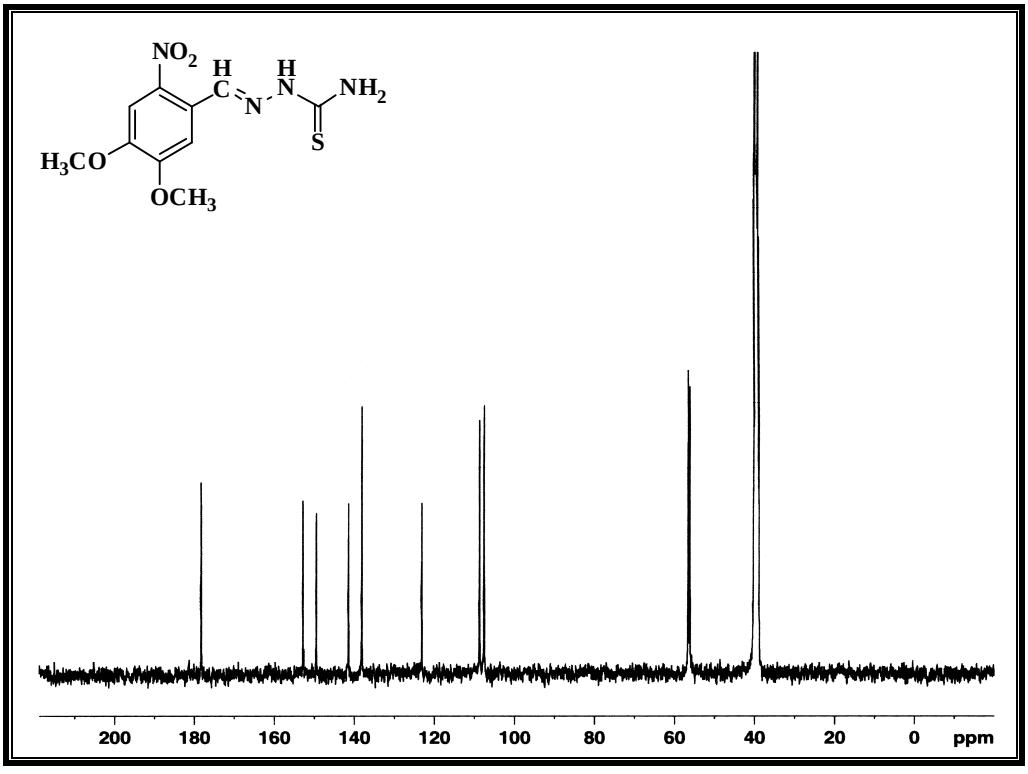
^{1}H NMR spectrum of TRM-2



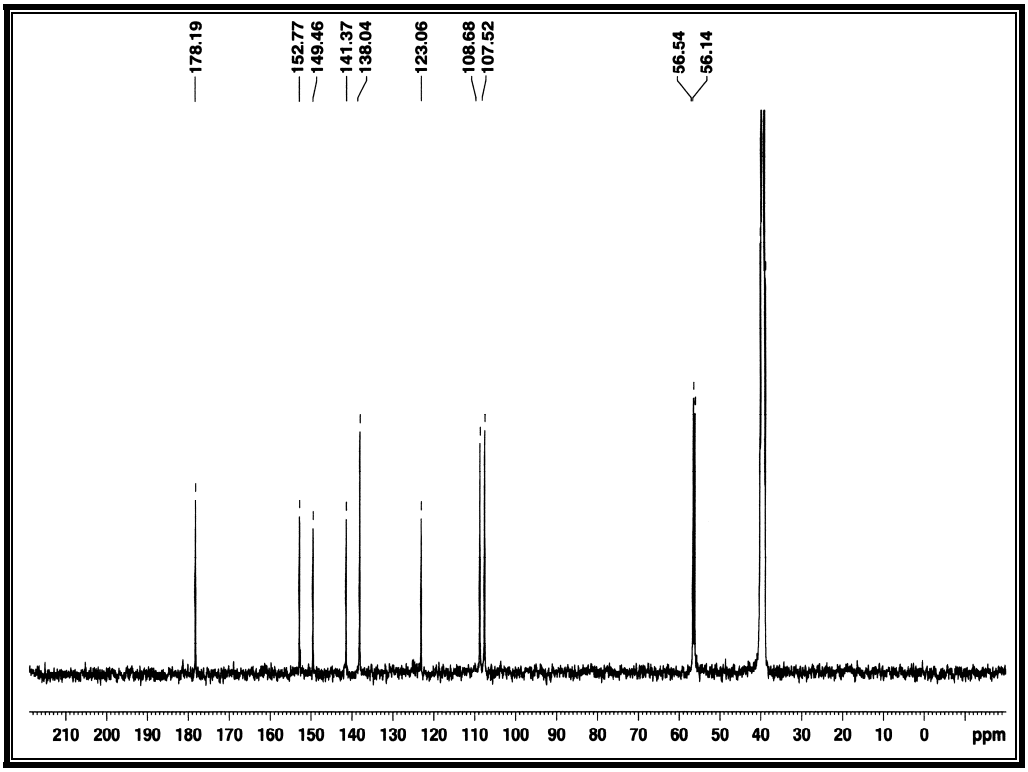
Expanded ^{1}H NMR spectrum of TRM-2



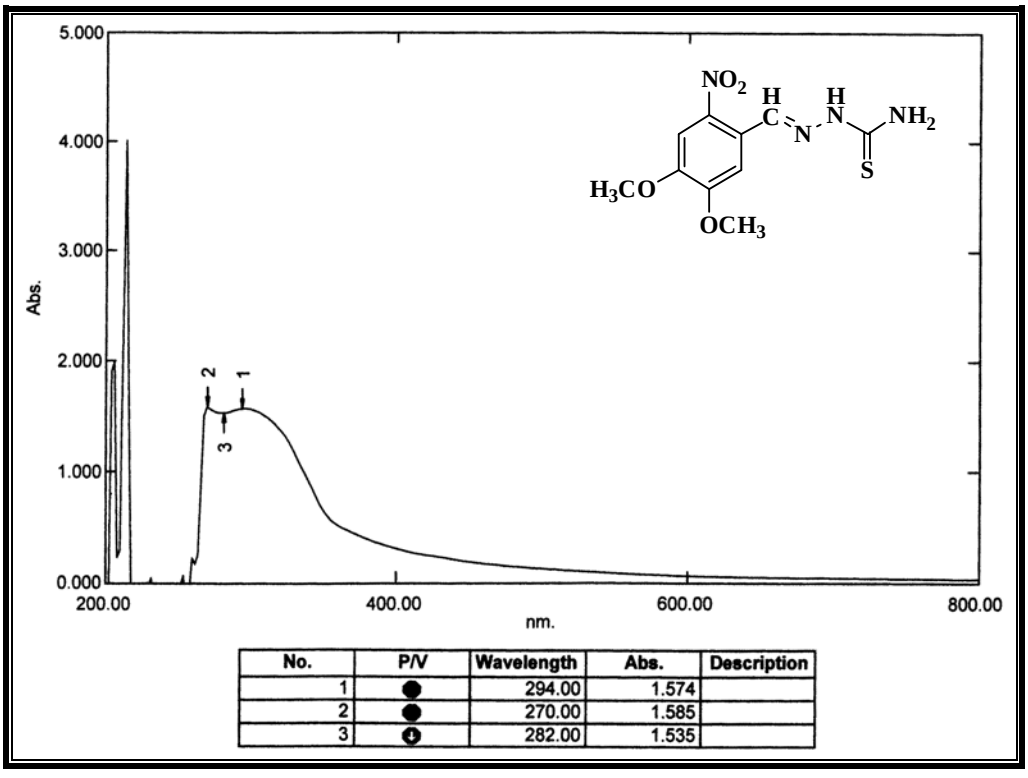
^{13}C NMR spectrum of TRM-2



Expanded ^{13}C NMR spectrum of TRM-2



UV-Visible spectrum of TRM-2



No.	P/V	Wavelength	Abs.	Description
1	●	294.00	1.574	
2	●	270.00	1.585	
3	●	282.00	1.535	

Results & Discussion

In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M+) corresponding to their molecular weight.

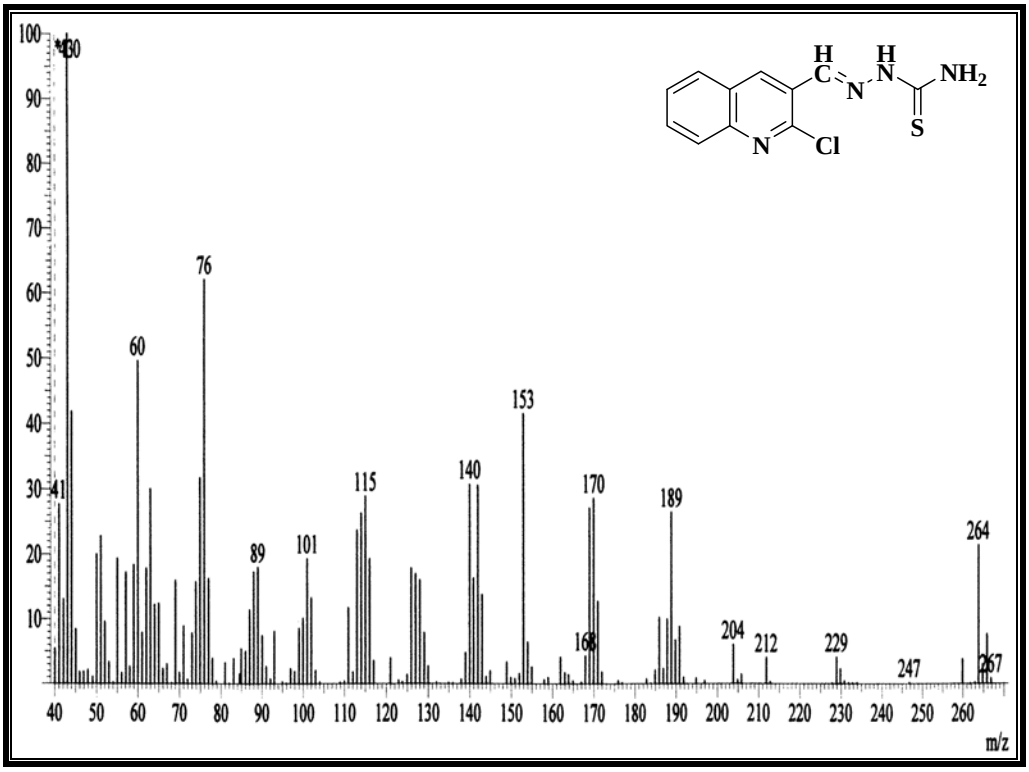
Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3375 cm^{-1}, 1060 cm^{-1} and 1286 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1628 cm^{-1}. The other bands of $-NH_2$ due to at 3292 cm^{-1} and aromatic -C-H and -C=C bands due to at 3171-3005 cm^{-1} and 1527 cm^{-1} respectively.

In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 8.55 ppm as a singlet. The, -N-NH and NH_2 protons were observed at 11.33 ppm and 8.34 ppm as a singlet, respectively. The $-O-CH_3$ protons were observed at 3.87 ppm as a singlet. All the aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 141.37 ppm and -C=S carbon, appeared at 178.19 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

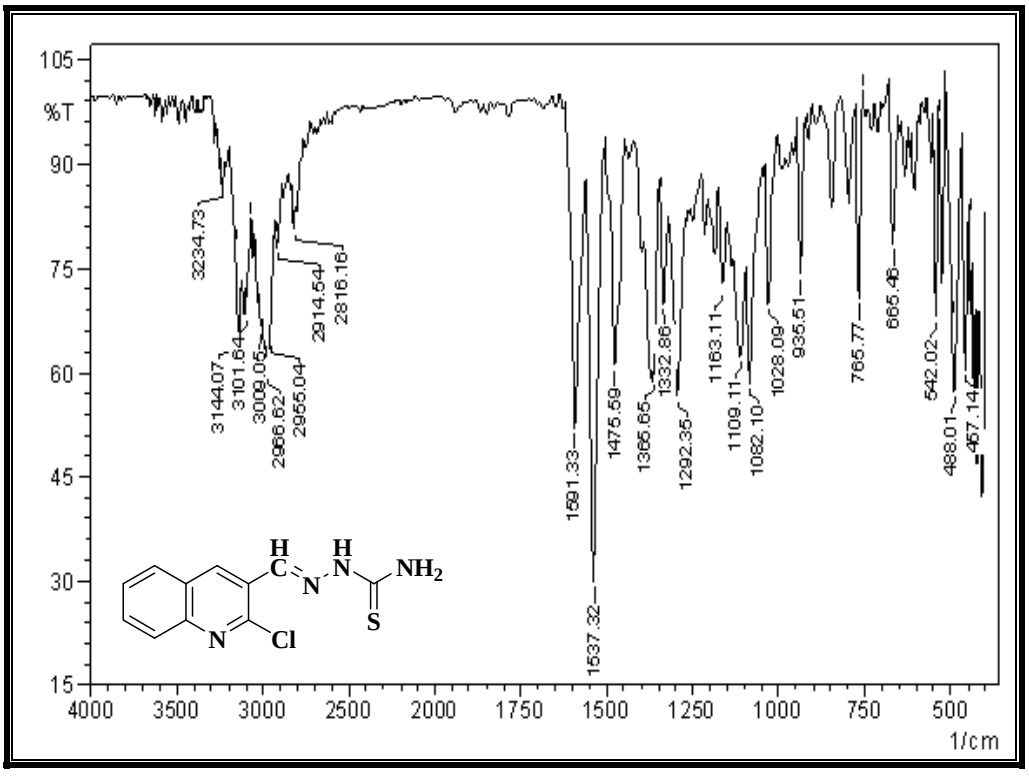
Electronic spectroscopy is a very important tool for the structural identification of synthesized thiosemicarbazone. It is usually measured in the range 200-800 nm. This compound absorb in the region 250-350 nm and the bands are mainly due to at 270 nm $\pi \rightarrow \pi^*$ and 294 nm $n \rightarrow \pi^*$ transitions.

All spectral characterization and elemental analysis confirm the structure of 1-(4,5-dimethoxy-2-nitrobenzylidene)thiosemicarbazide(TRM-2).

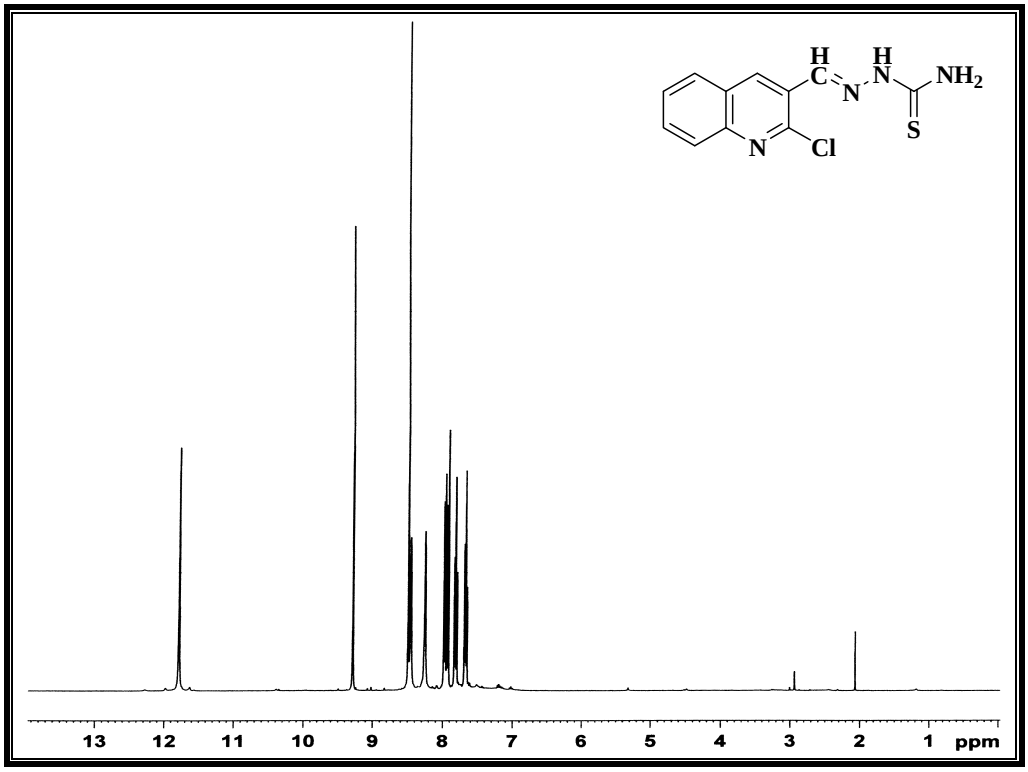
Mass spectrum of TRM-3



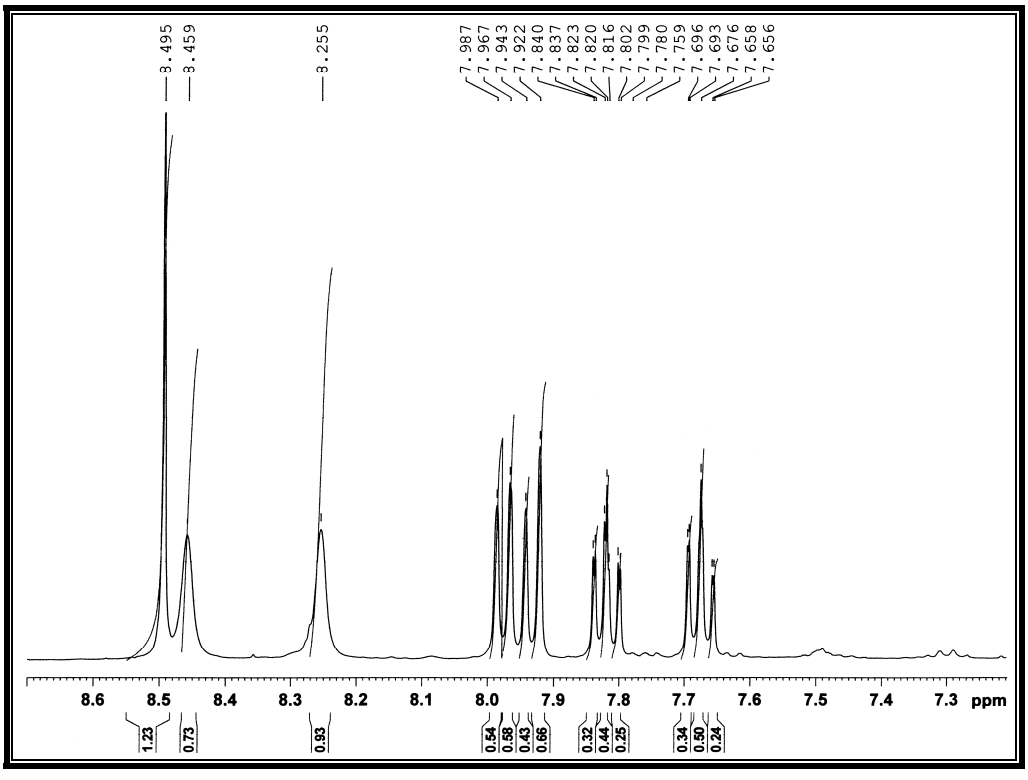
IR spectrum of TRM-3



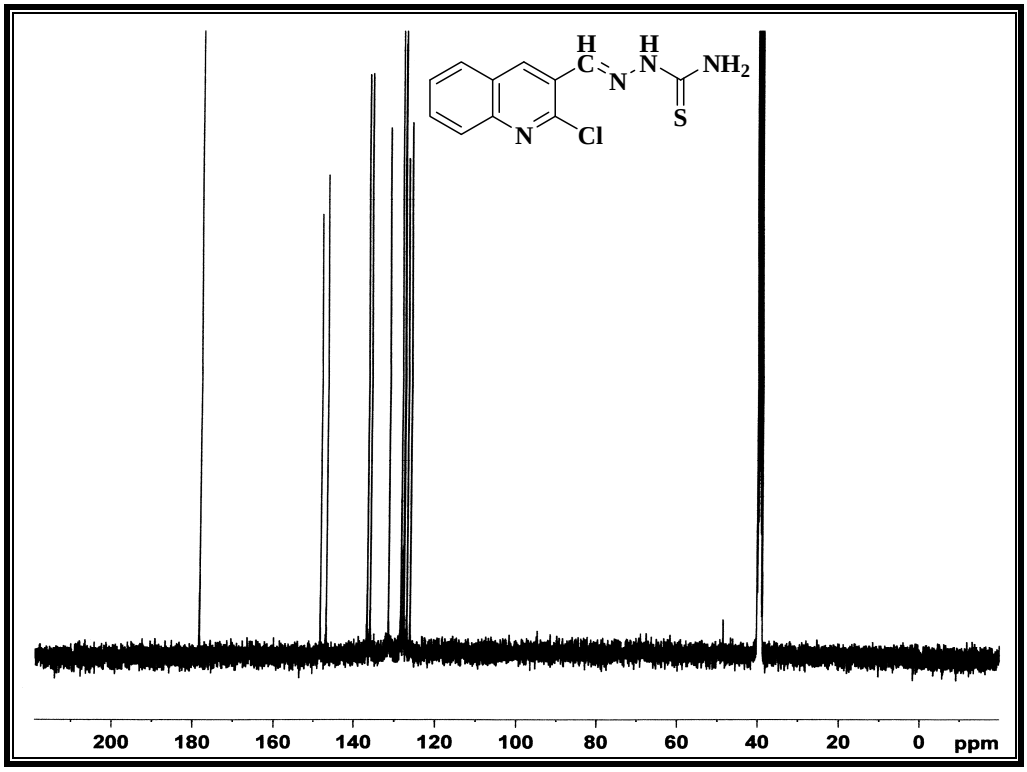
^{1}H NMR spectrum of TRM-3



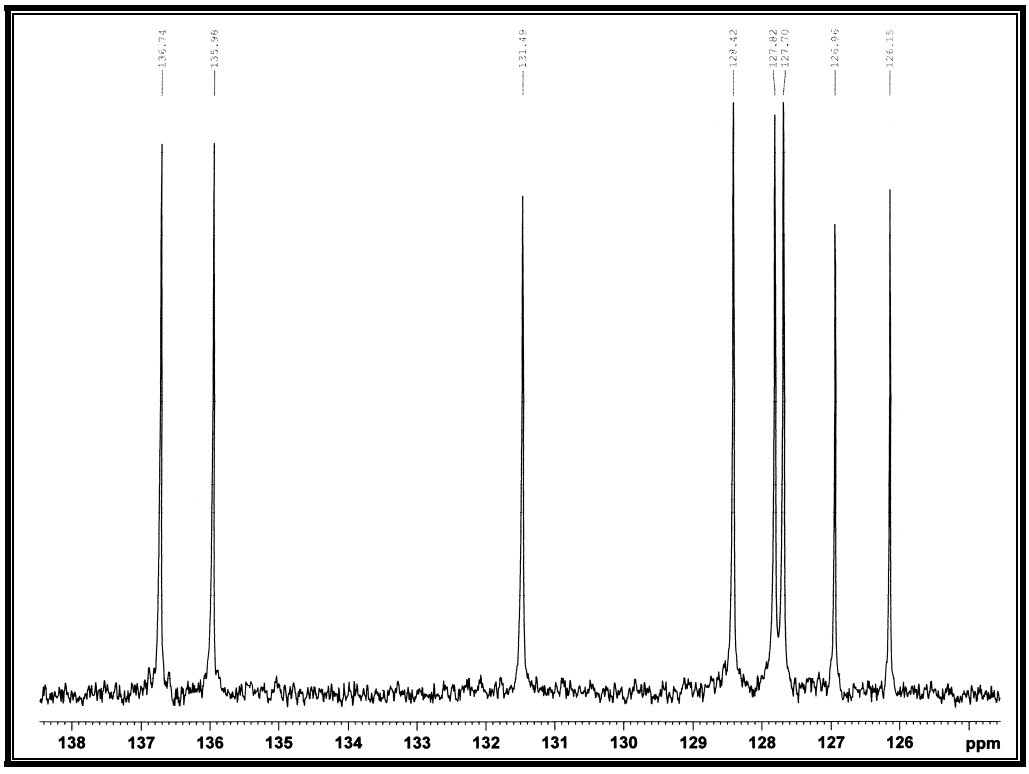
Expanded ^{1}H NMR spectrum of TRM-3



^{13}C NMR spectrum of TRM-3



Expanded ^{13}C NMR spectrum of TRM-3



Results & Discussion

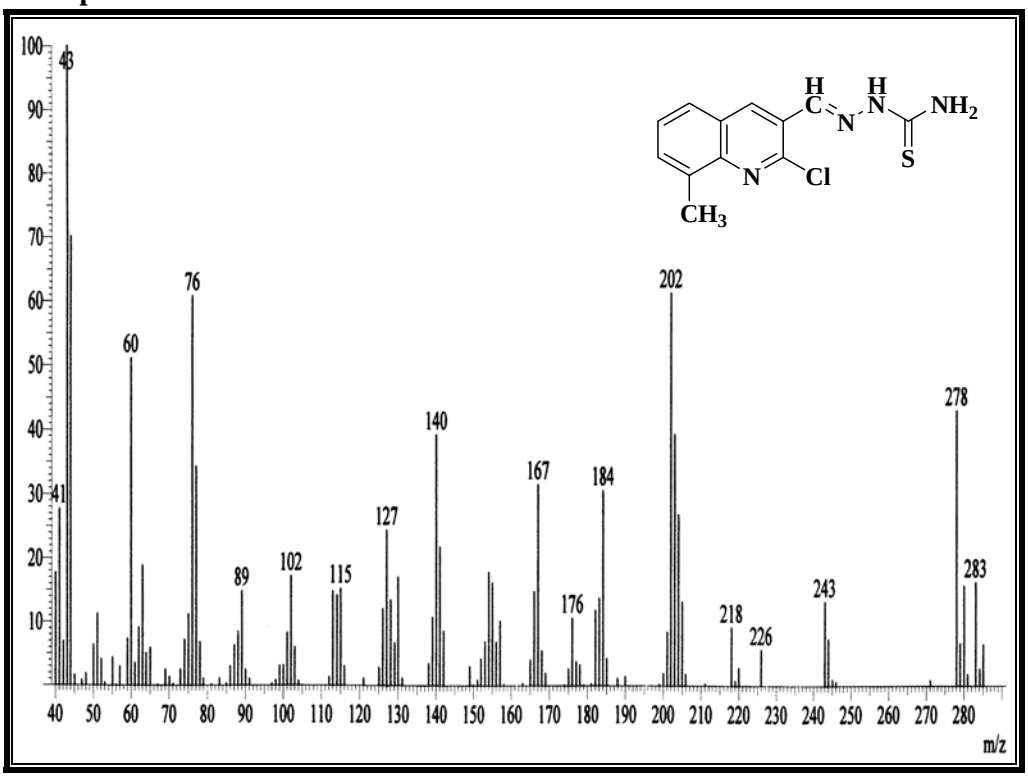
In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M+) corresponding to their molecular weight.

Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3310 cm^{-1}, 1082 cm^{-1} and 1292 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1591 cm^{-1}. The other bands of $-NH_2$ due to at 3234 cm^{-1} and aromatic -C-H and -C=C bands due to at 3144-2966 cm^{-1} and 1475 cm^{-1} respectively.

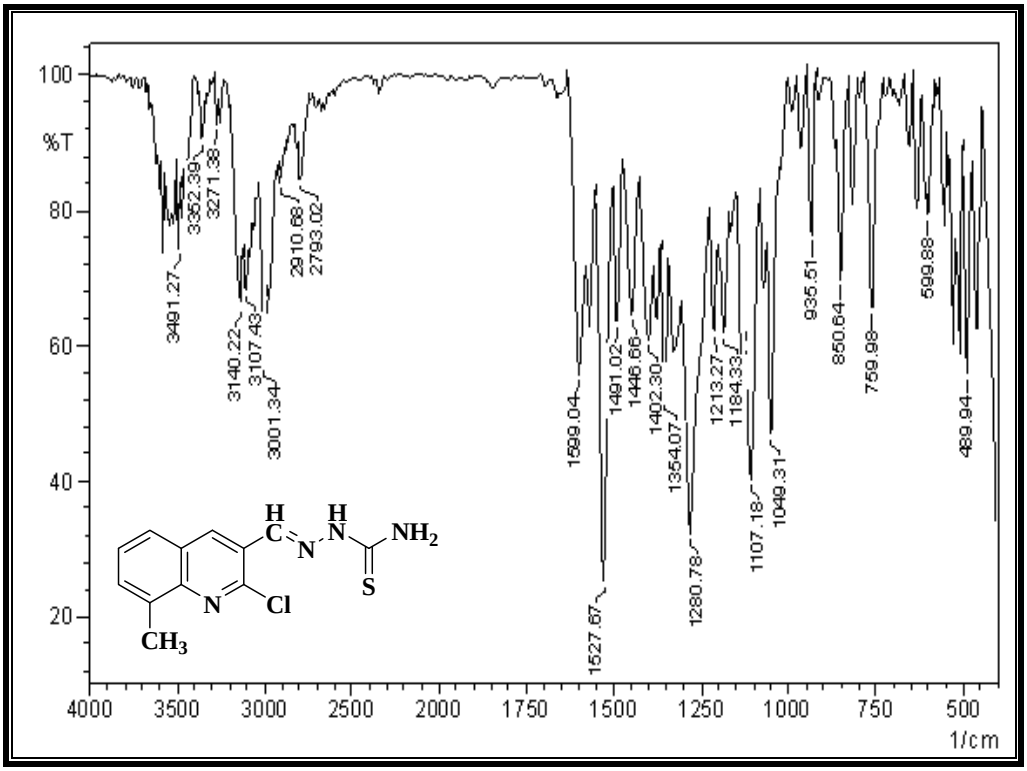
In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 9.28 ppm as a singlet. The, -N-NH and NH_2 protons were observed at 11.79 ppm and 8.49 ppm as a singlet, respectively. All the aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 136.74 ppm and -C=S carbon, appeared at 178.40 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

All spectral characterization and elemental analysis confirm the structure of 1-((2-chloroquinolin-3-yl)methylene)thiosemicarbazide(TRM-3).

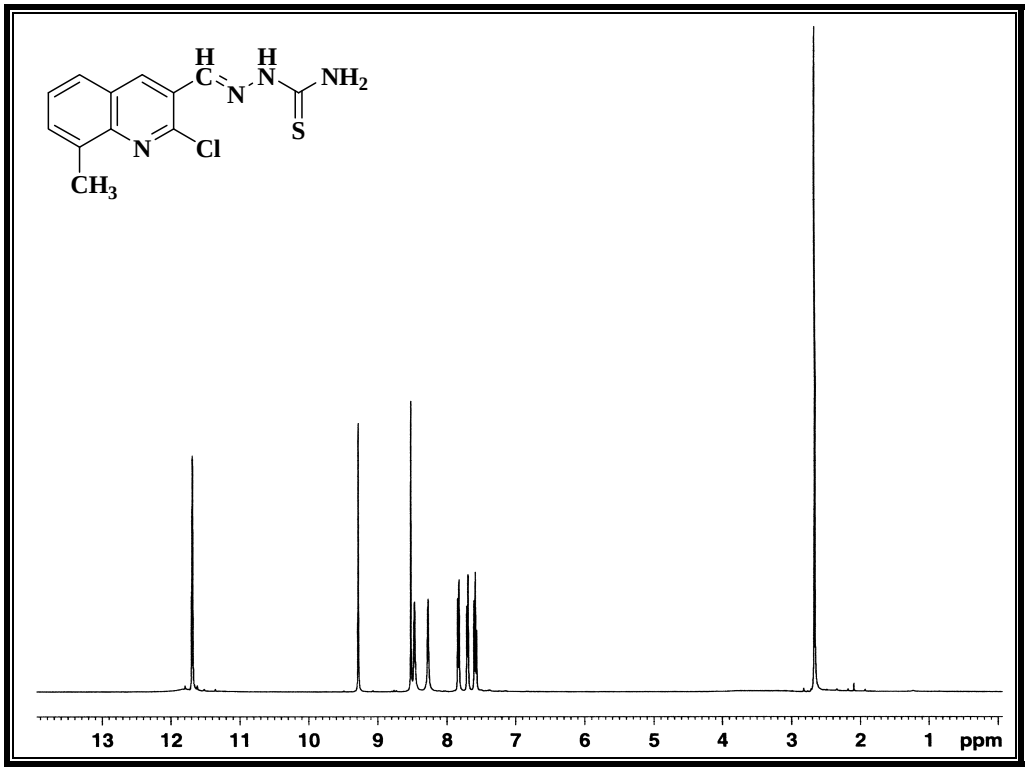
Mass spectrum of TRM-4



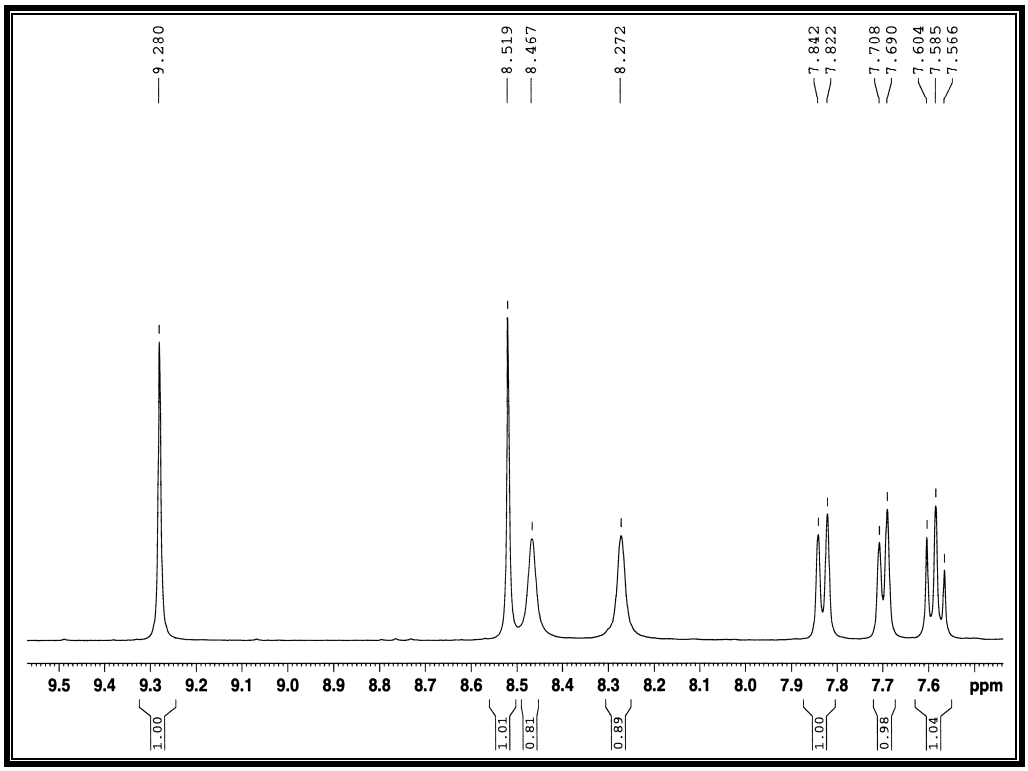
IR spectrum of TRM-4



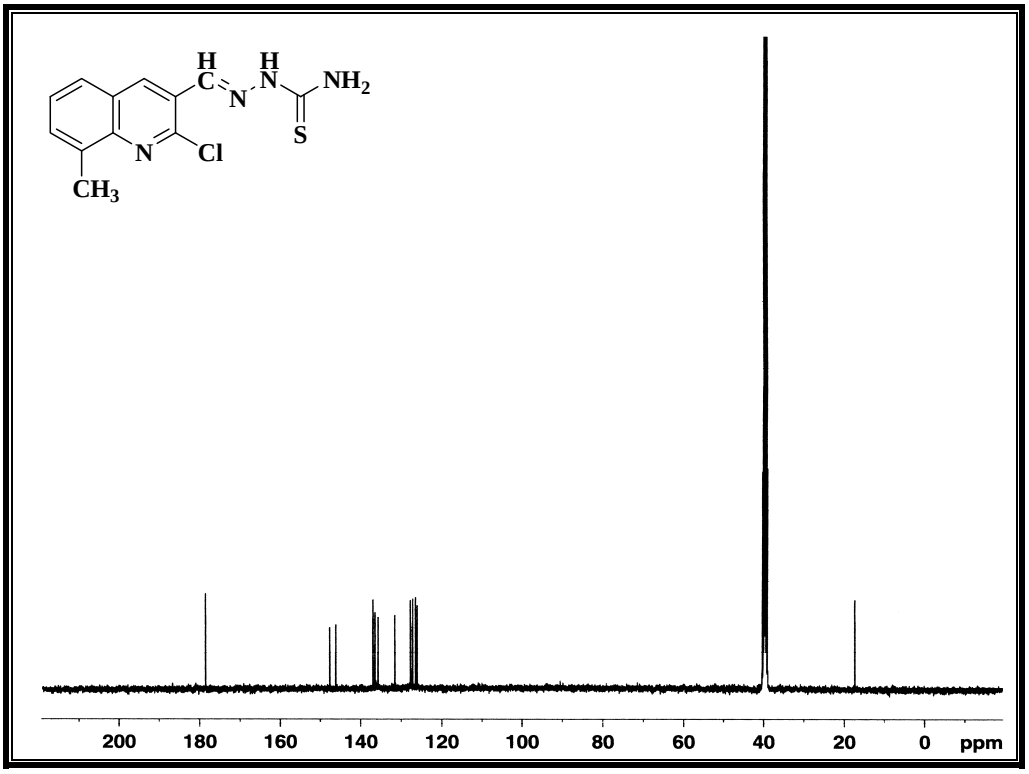
^{1}H NMR spectrum of TRM-4



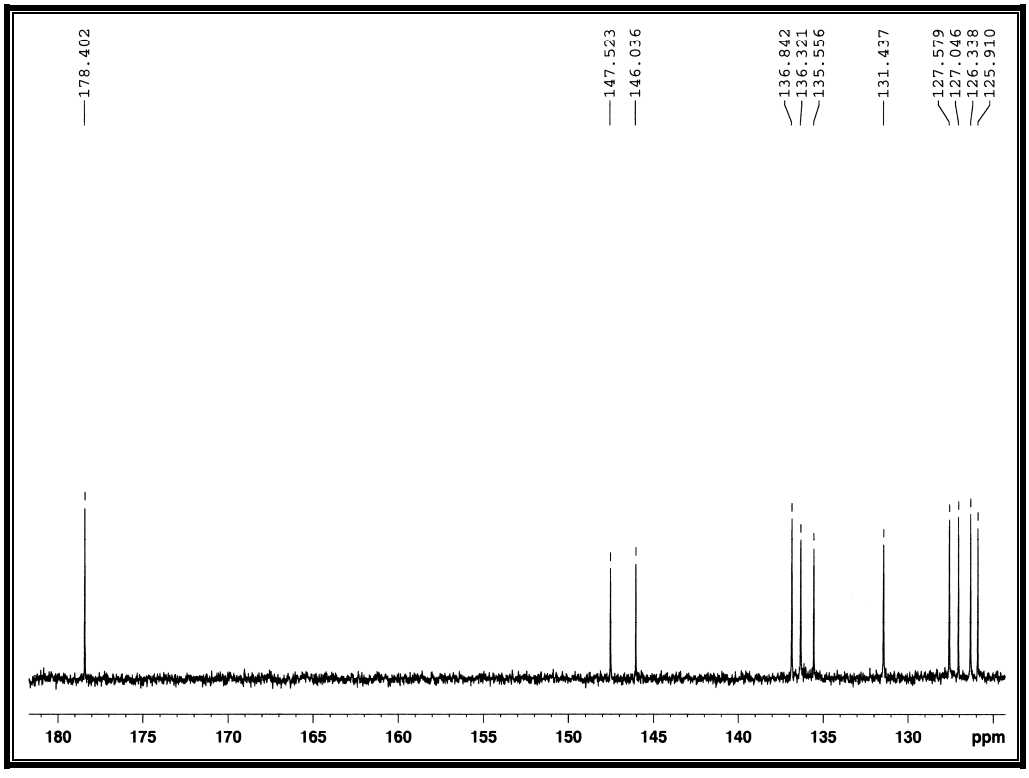
Expanded ^{1}H NMR spectrum of TRM-4



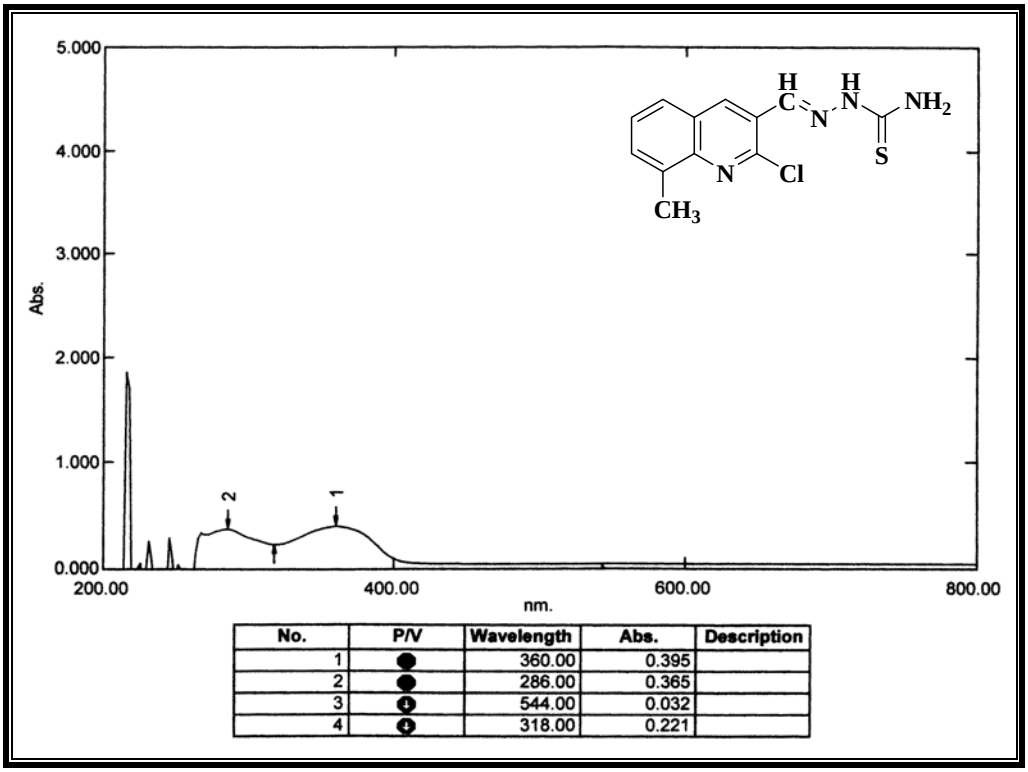
^{13}C NMR spectrum of TRM-4



Expanded ^{13}C NMR spectrum of TRM-4



UV-Visible spectrum of TRM-4



No.	P/V	Wavelength	Abs.	Description
1	●	360.00	0.395	
2	●	286.00	0.365	
3	◆	544.00	0.032	
4	◆	318.00	0.221	

Results & Discussion

In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M+) corresponding to their molecular weight.

Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3352 cm^{-1}, 1107 cm^{-1} and 1280 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1599 cm^{-1}. The other bands of $-NH_2$ due to at 3271 cm^{-1} and aromatic -C-H and -C=C bands due to at 3140-3001 cm^{-1} and 1491 cm^{-1} respectively.

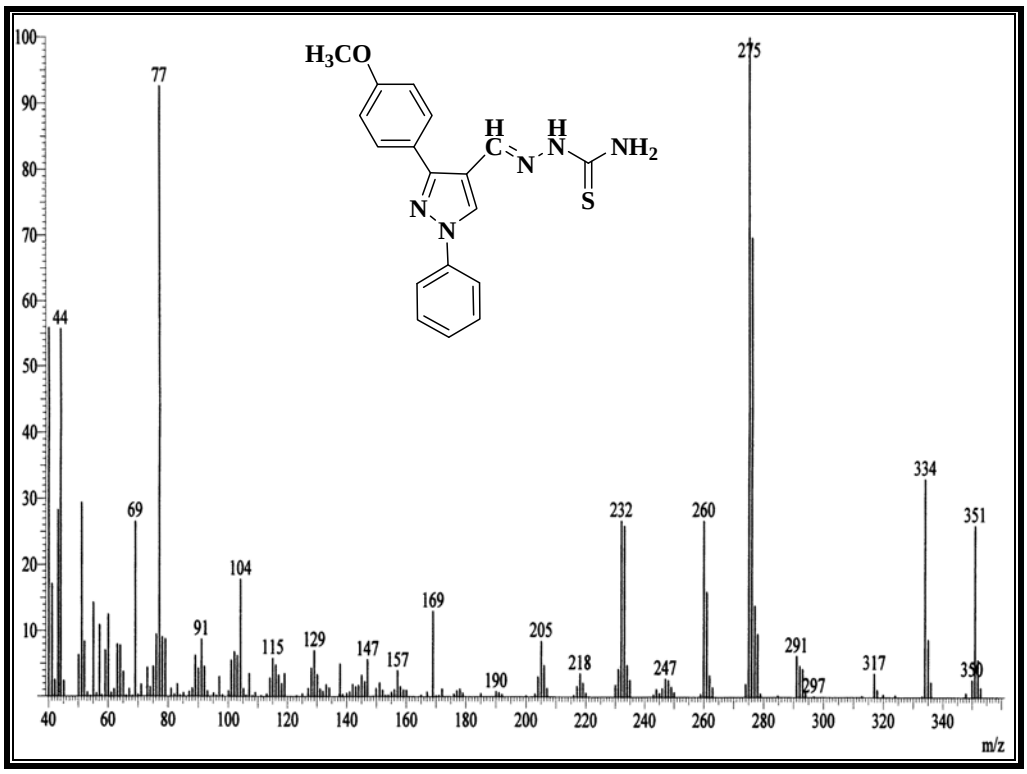
In the ^1H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 9.28 ppm as a singlet. The, -N-NH and NH_2 protons were observed at 11.80 ppm and 8.51 ppm as a singlet, respectively. All the aromatic

protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 136.84 ppm and -C=S carbon, appeared at 178.40 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

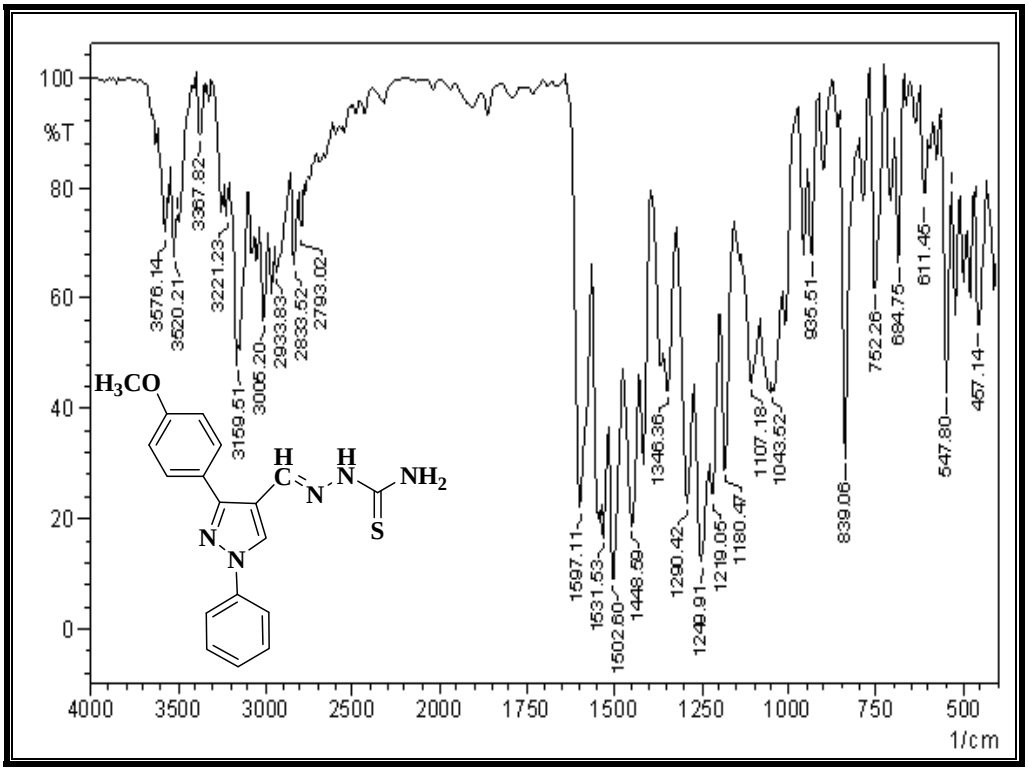
Electronic spectroscopy is a very important tool for the structural identification of synthesized thiosemicarbazone. It is usually measured in the range 200-800 nm. This compound absorb in the region 250-350 nm and the bands are mainly due to at 286 nm $\pi \rightarrow \pi^*$ and 360 nm $n \rightarrow \pi^*$ transitions.

All spectral characterization and elemental analysis confirm the structure of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide(TRM-4).

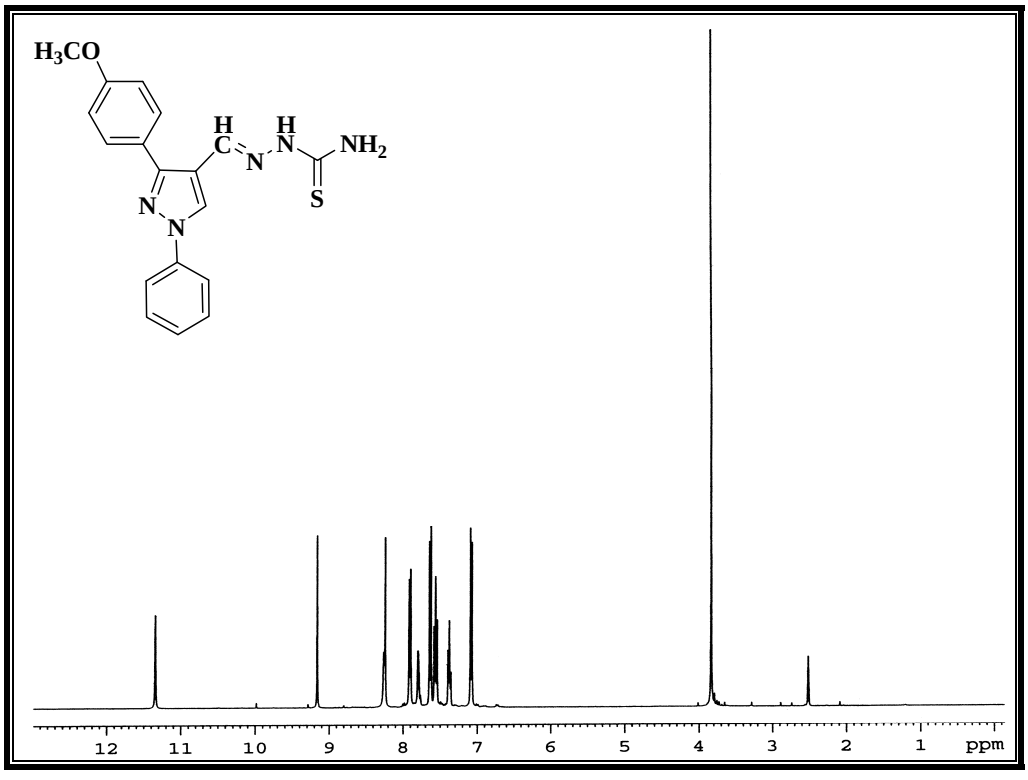
Mass spectrum of TRM-5



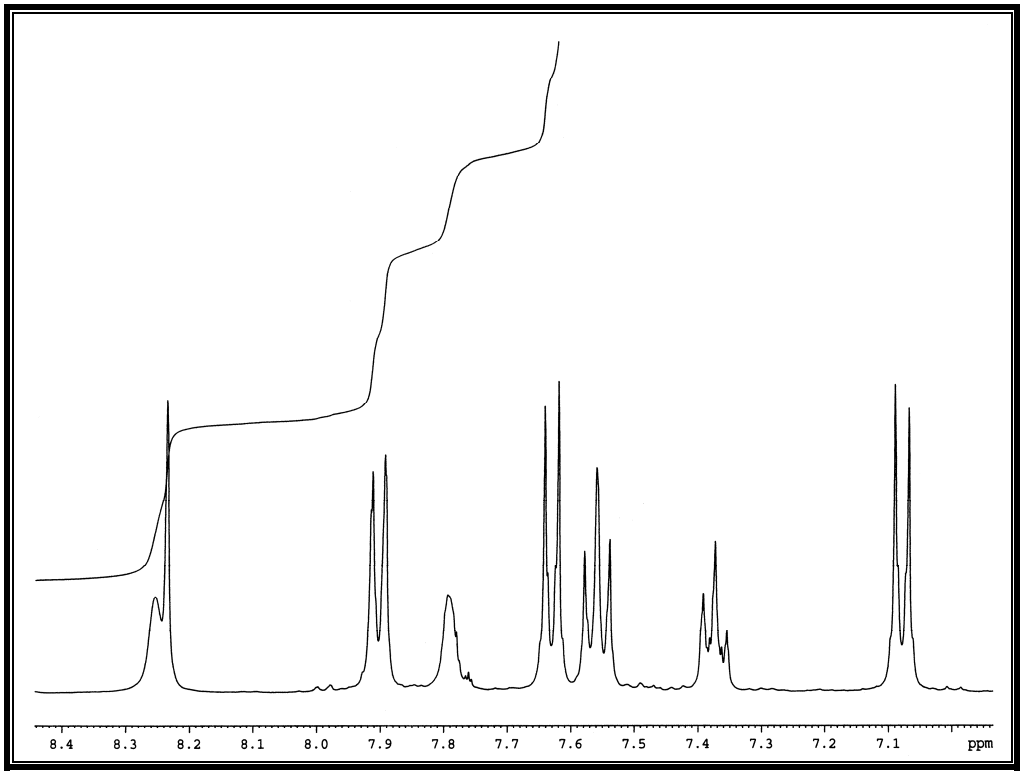
IR spectrum of TRM-5



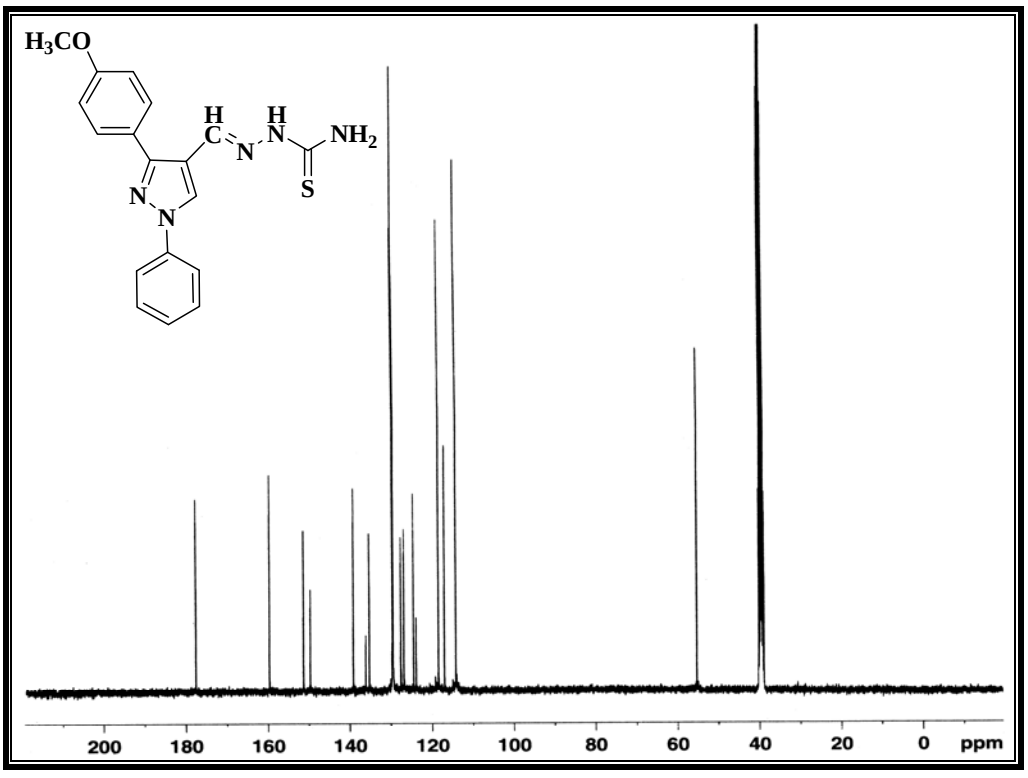
^{1}H NMR spectrum of TRM-5



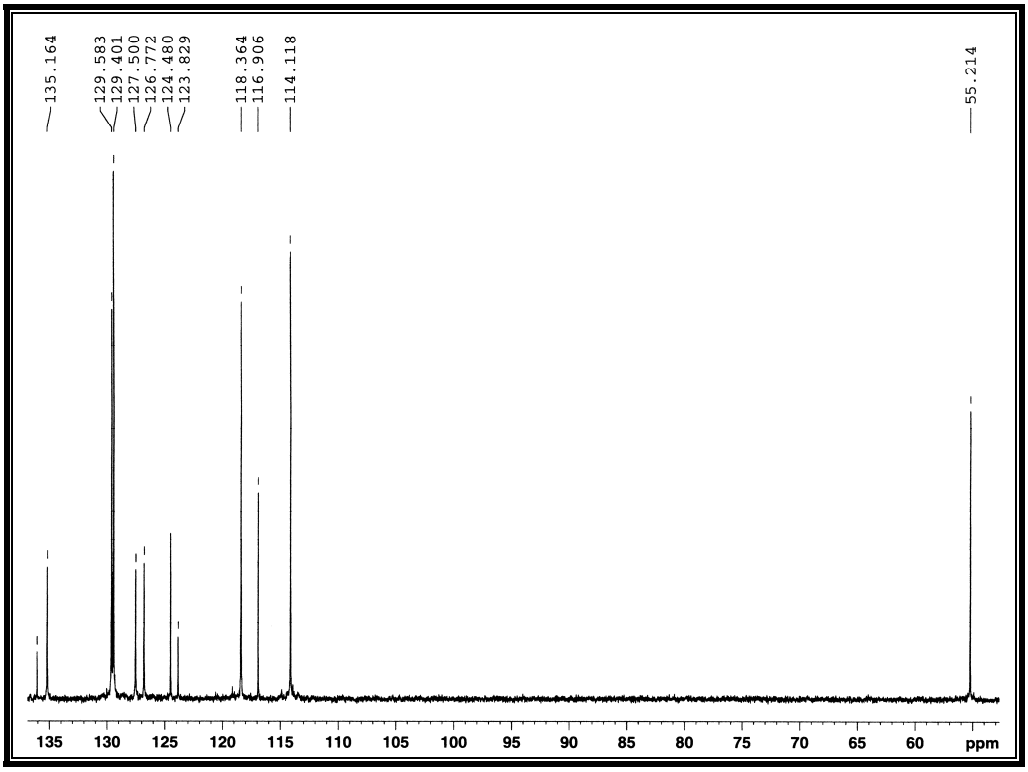
Expanded ^{1}H NMR spectrum of TRM-5



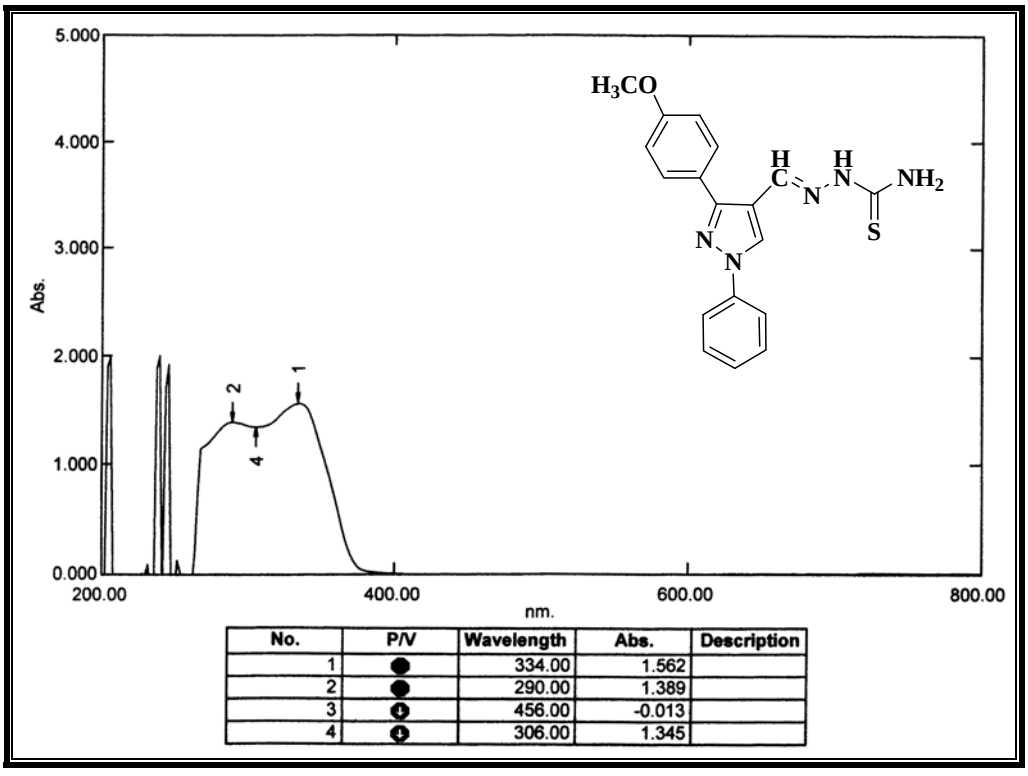
^{13}C NMR spectrum of TRM-5



Expanded ^{13}C NMR spectrum of TRM-5



UV-Visible spectrum of TRM-5



No.	P/V	Wavelength	Abs.	Description
1	●	334.00	1.562	
2	●	290.00	1.389	
3	⊖	456.00	-0.013	
4	⊖	306.00	1.345	

Results & Discussion

In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M+) corresponding to their molecular weight.

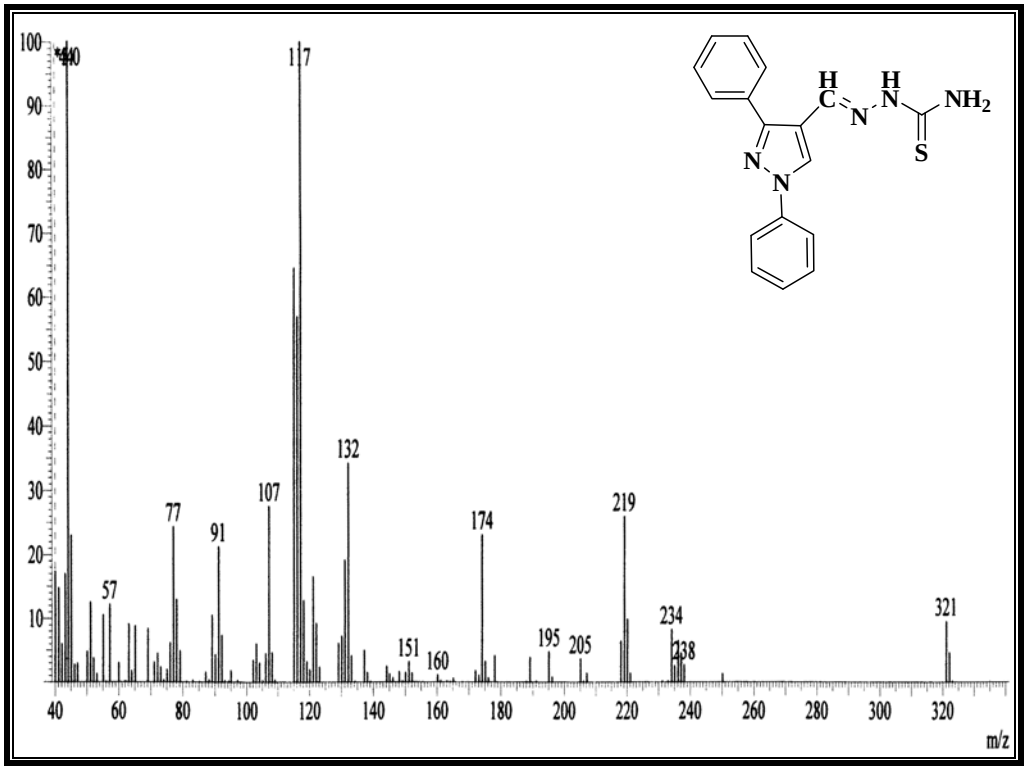
Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3367 cm^{-1}, 1043 cm^{-1} and 1290 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1597 cm^{-1}. The other bands of $-NH_2$ due to at 3221 cm^{-1} and aromatic -C-H and -C=C bands due to at 3159-3005 cm^{-1} and 1502 cm^{-1} respectively.

In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 9.16 ppm as a singlet. The, -N-NH and NH_2 protons were observed at 11.33 ppm and 8.24 ppm as a singlet, respectively. All the aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 139.03 ppm and -C=S carbon, appeared at 177.53 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

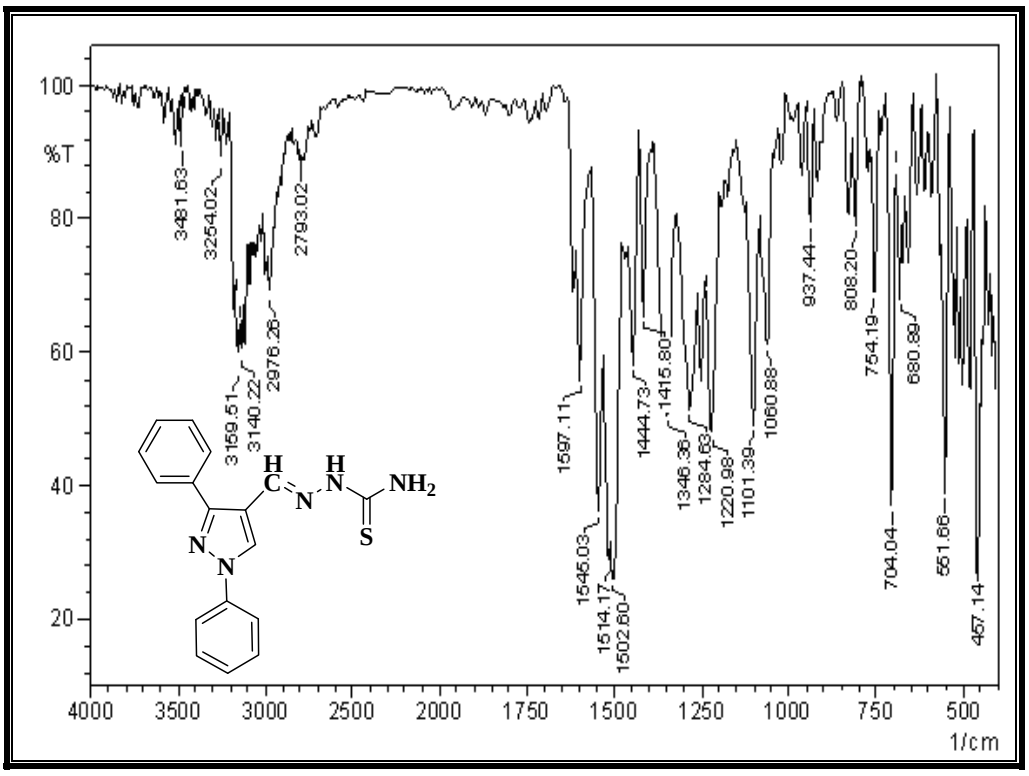
Electronic spectroscopy is a very important tool for the structural identification of synthesized thiosemicarbazone. It is usually measured in the range 200-800 nm. This compound absorb in the region 250-350 nm and the bands are mainly due to at 290 nm $\pi \rightarrow \pi^*$ and 334 nm $n \rightarrow \pi^*$ transitions.

All spectral characterization and elemental analysis confirm the structure of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide (TRM-5).

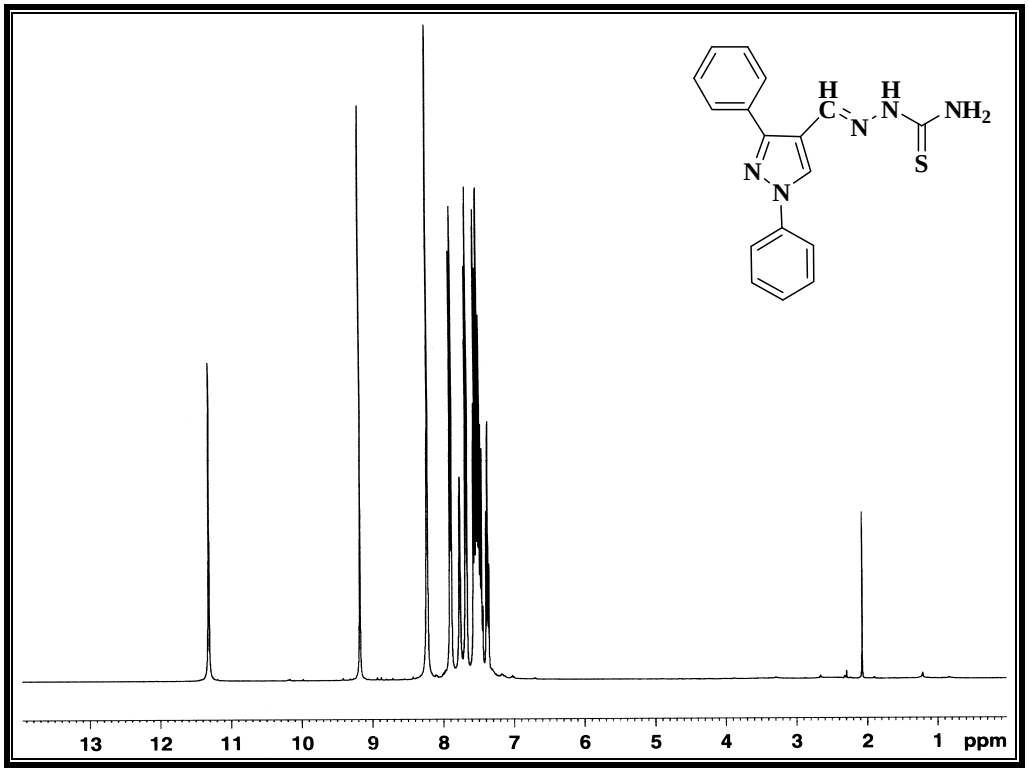
Mass spectrum of TRM-6



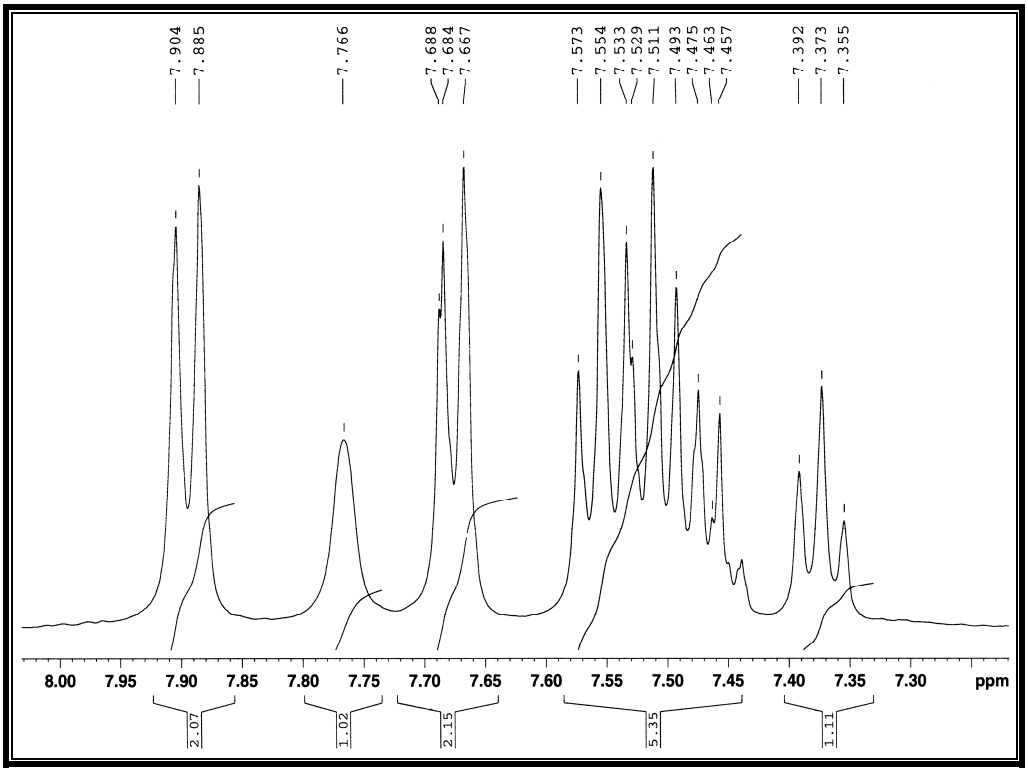
IR spectrum of TRM-6



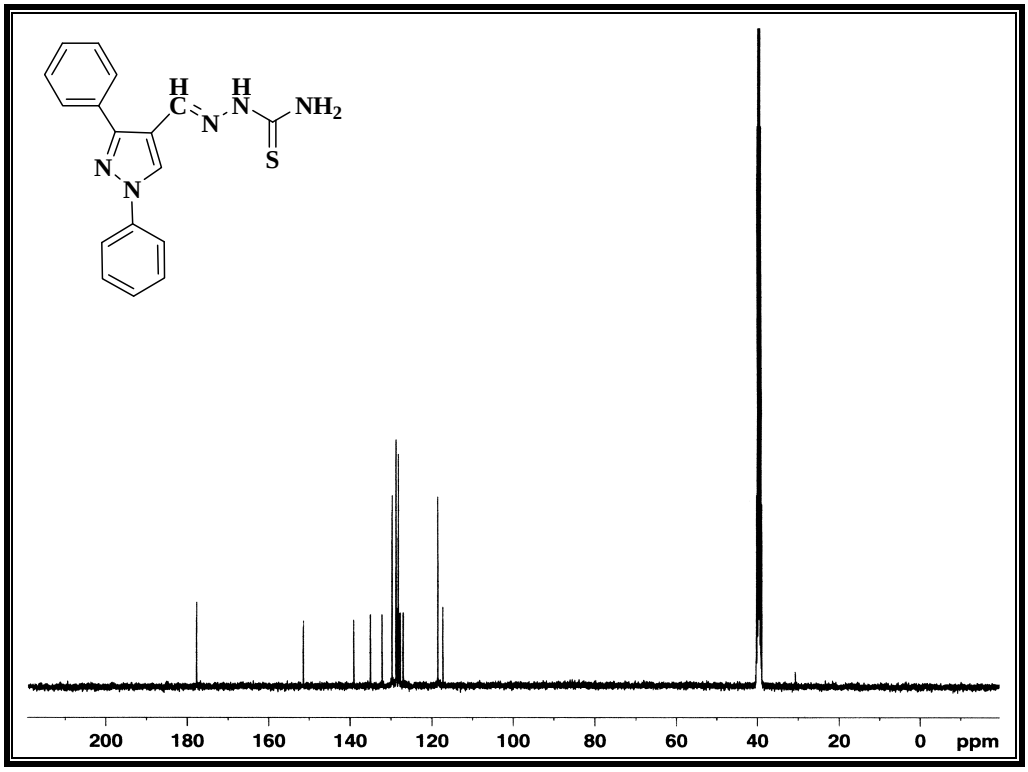
^{1}H NMR spectrum of TRM-6



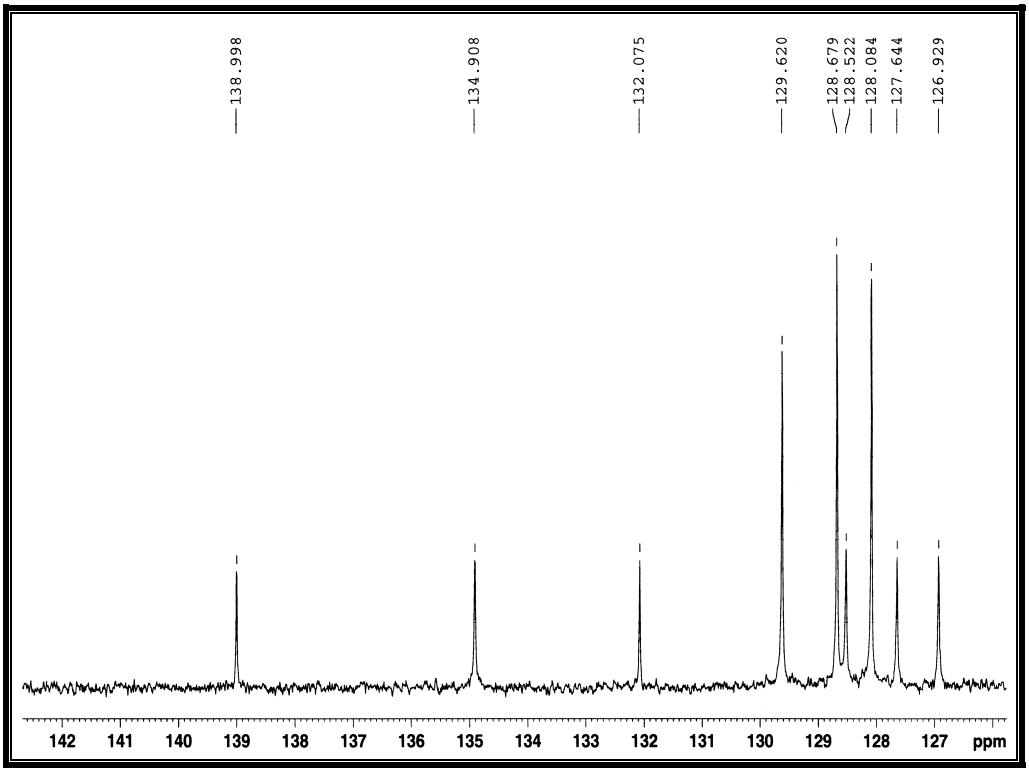
Expanded ^{1}H NMR spectrum of TRM-6



^{13}C NMR spectrum of TRM-6



Expanded ^{13}C NMR spectrum of TRM-6



Results & Discussion

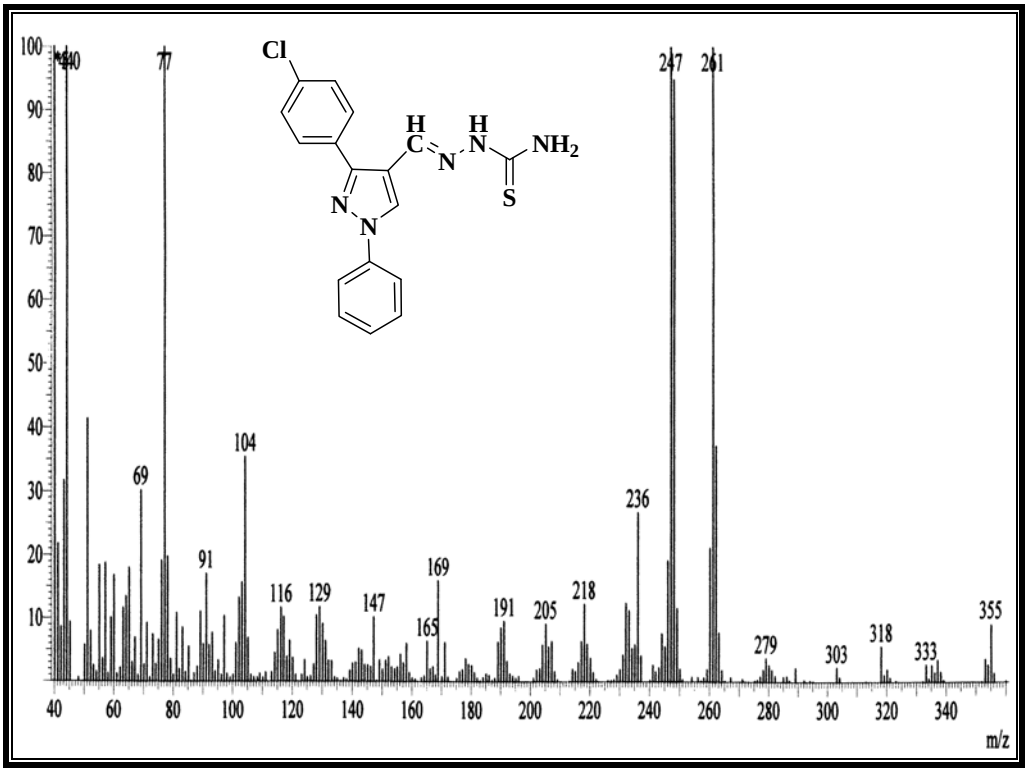
In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M+) corresponding to their molecular weight.

Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3348 cm^{-1}, 1060 cm^{-1} and 1284 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1597 cm^{-1}. The other bands of $-NH_2$ due to at 3254 cm^{-1} and aromatic -C-H and -C=C bands due to at 3140-2976 cm^{-1} and 1502 cm^{-1} respectively.

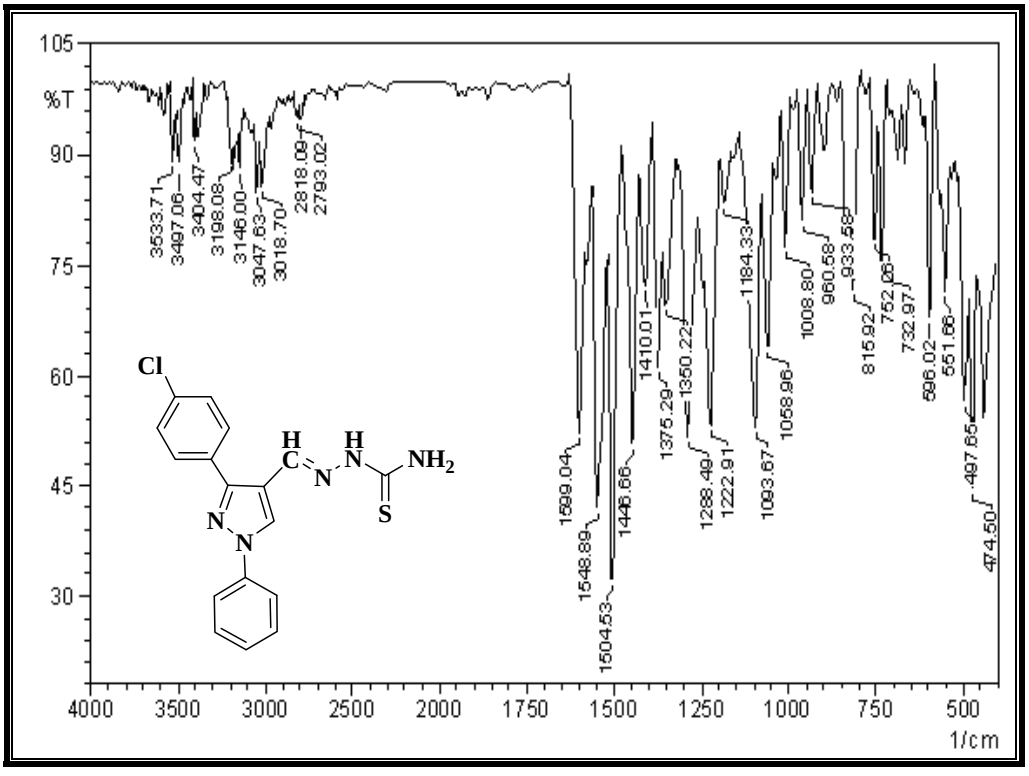
In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 9.17 ppm as a singlet. The, -N-NH and NH_2 protons were observed at 11.31 ppm and 8.22 ppm as a singlet, respectively. All the aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 138.99 ppm and -C=S carbon, appeared at 177.55 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

All spectral characterization and elemental analysis confirm the structure of 1-((1,3-diphenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide(TRM-6).

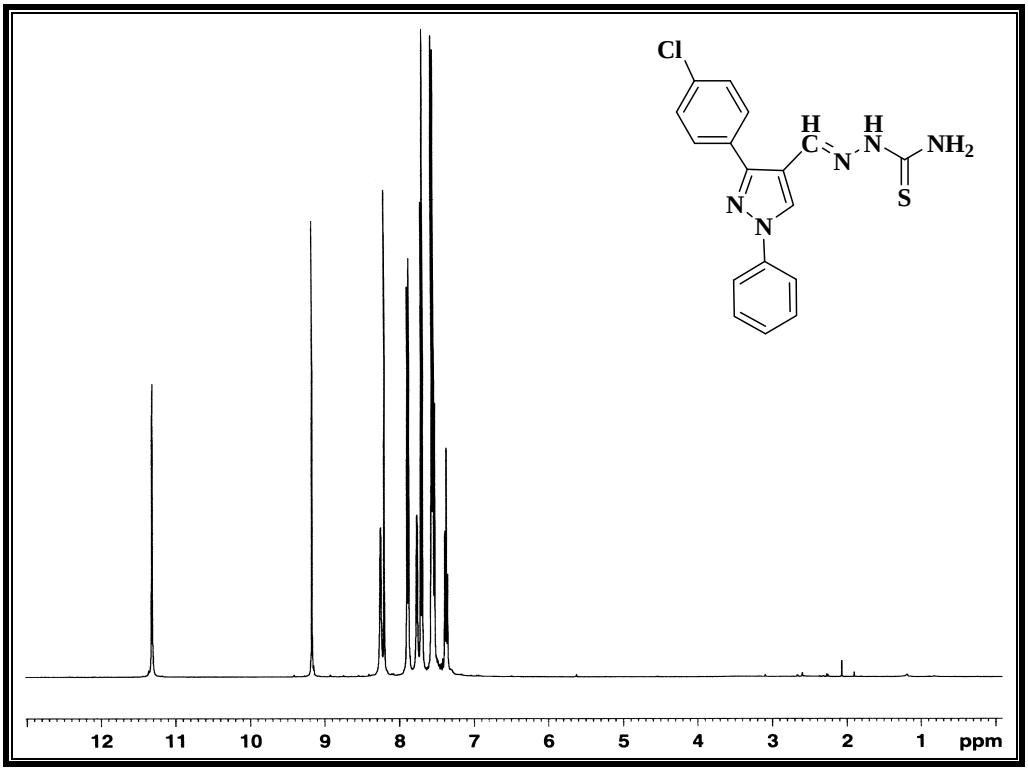
Mass spectrum of TRM-7



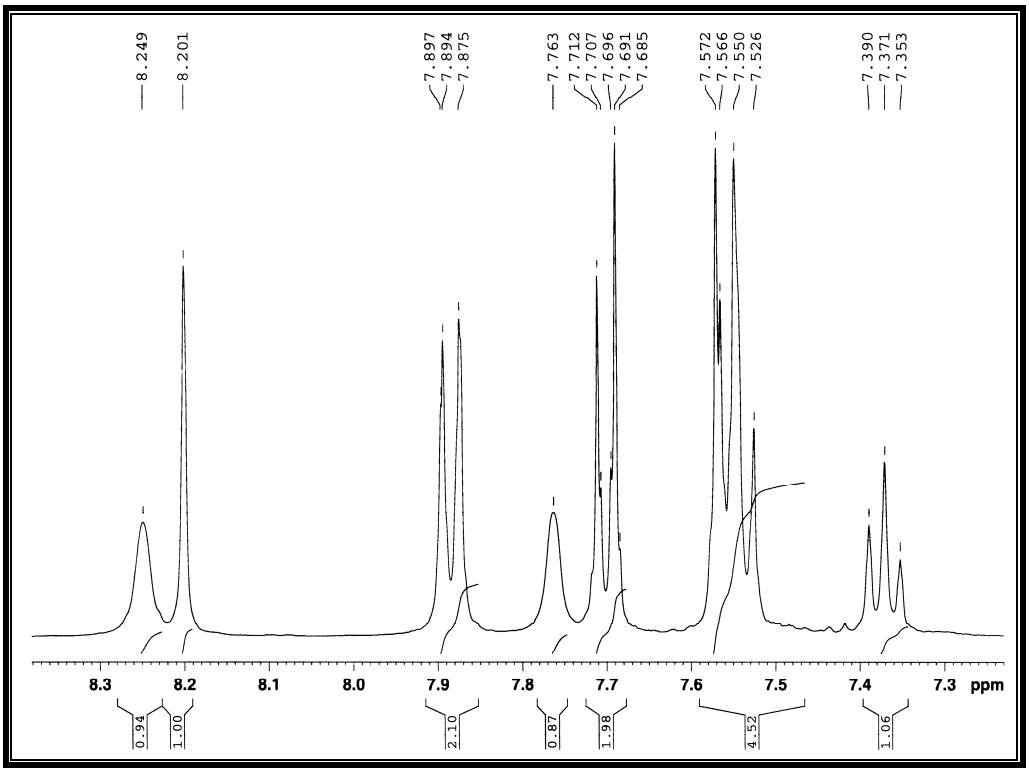
IR spectrum of TRM-7



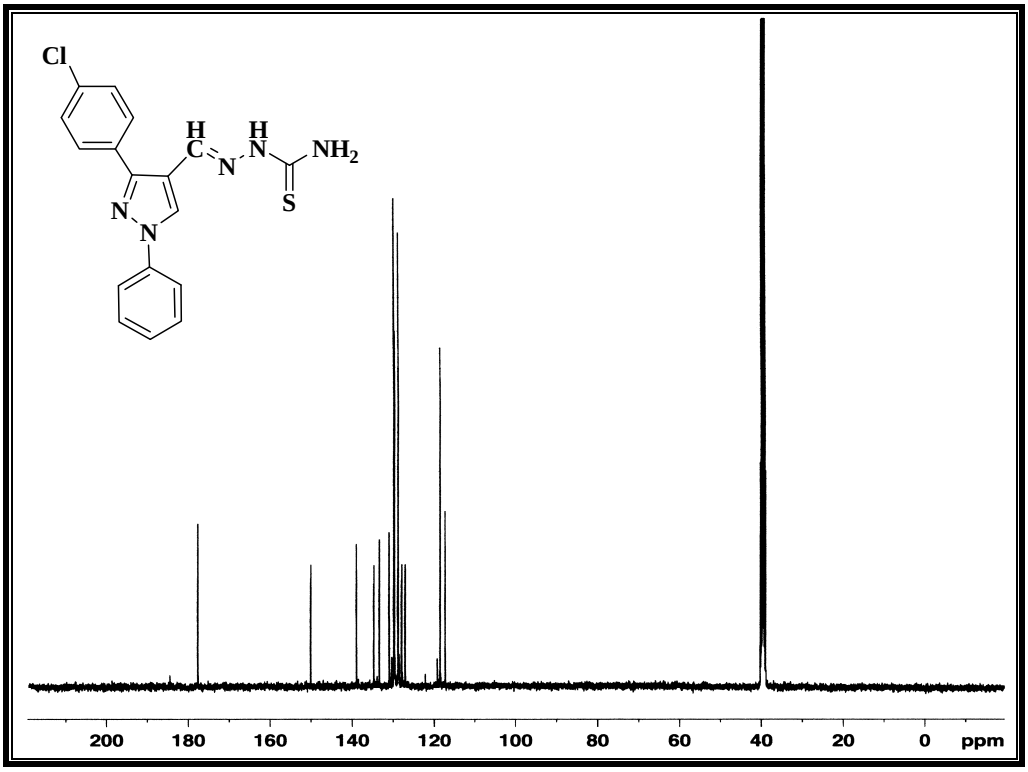
^{1}H NMR spectrum of TRM-7



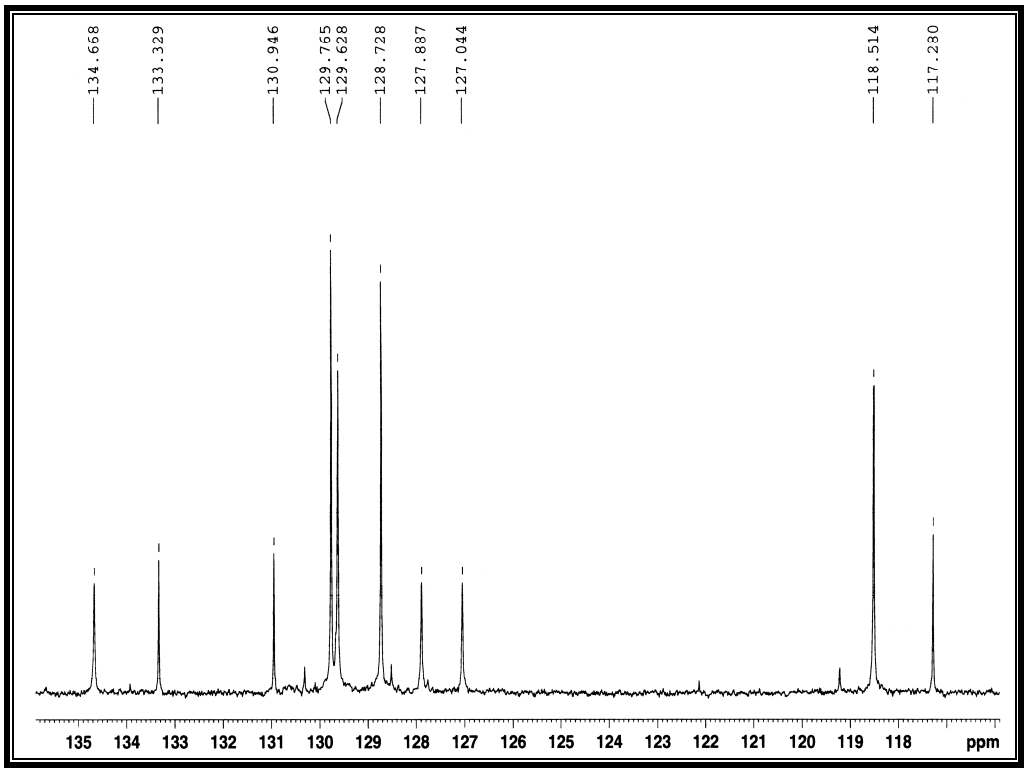
Expanded ^{1}H NMR spectrum of TRM-7



^{13}C NMR spectrum of TRM-7



Expanded ^{13}C NMR spectrum of TRM-7



Results & Discussion

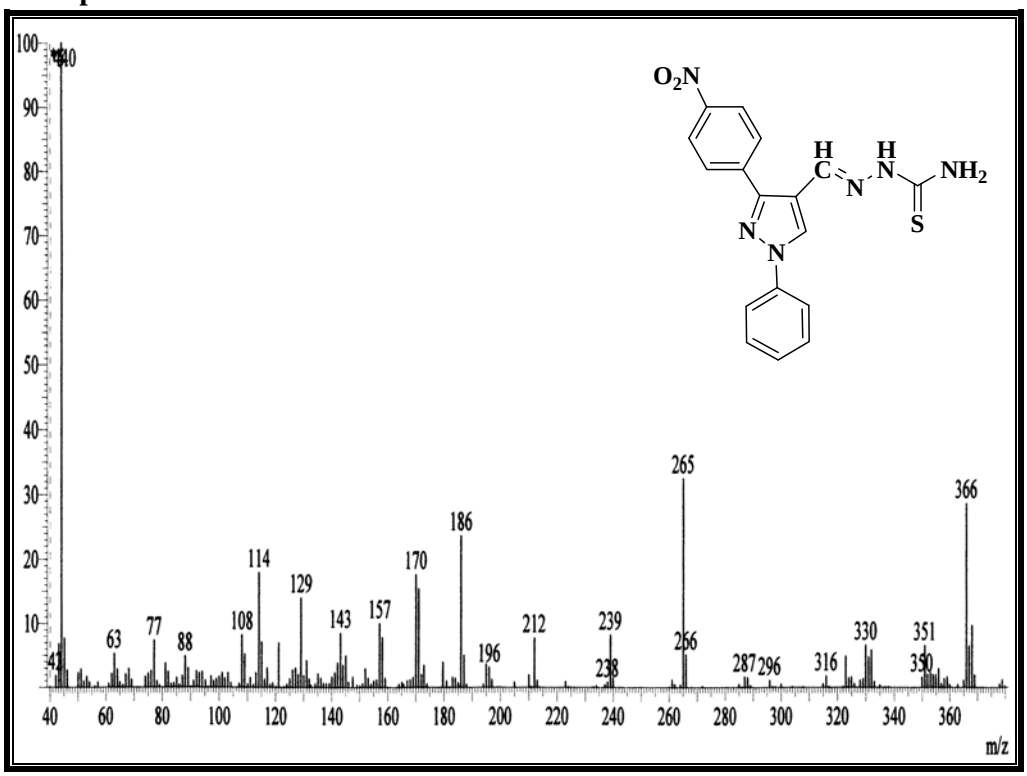
In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M+) corresponding to their molecular weight.

Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3380 cm^{-1}, 1093 cm^{-1} and 1288 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1599 cm^{-1}. The other bands of $-NH_2$ due to at 3198 cm^{-1} and aromatic -C-H and -C=C bands due to at 3146-3018 cm^{-1} and 1504 cm^{-1} respectively.

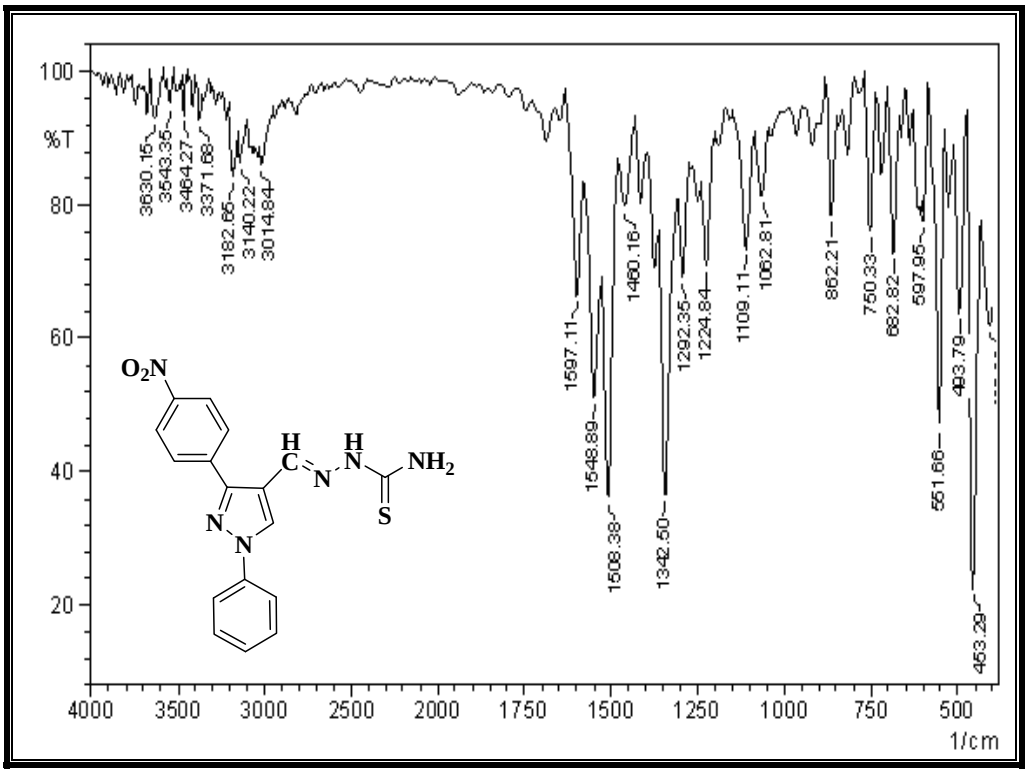
In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 9.16 ppm as a singlet. The, -N-NH and NH_2 protons were observed at 11.31 ppm and 8.24 ppm as a singlet, respectively. All the aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 138.91 ppm and -C=S carbon, appeared at 177.59 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

All spectral characterization and elemental analysis confirm the structure of 1-((3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide(TRM-7).

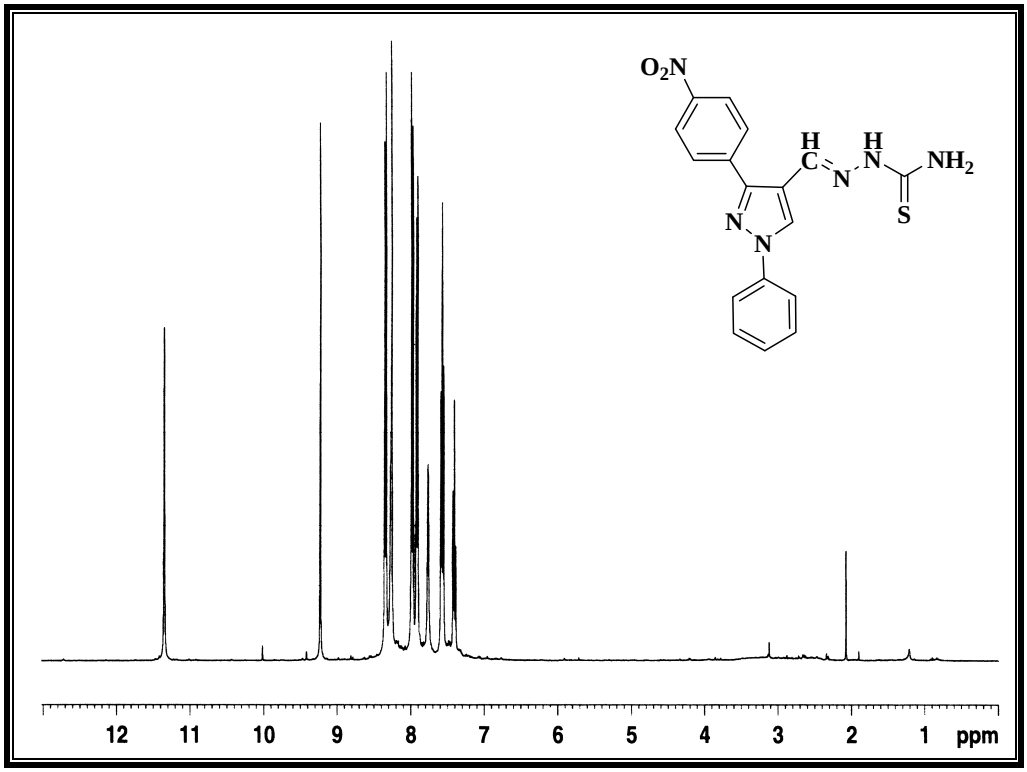
Mass spectrum of TRM-8



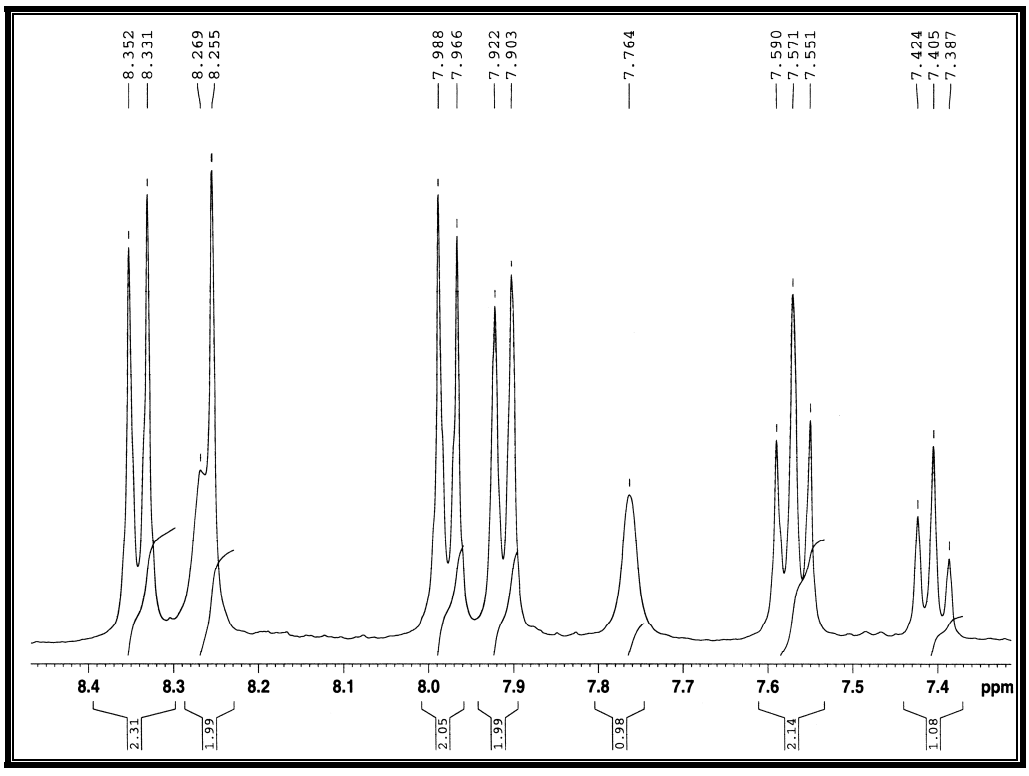
IR spectrum of TRM-8



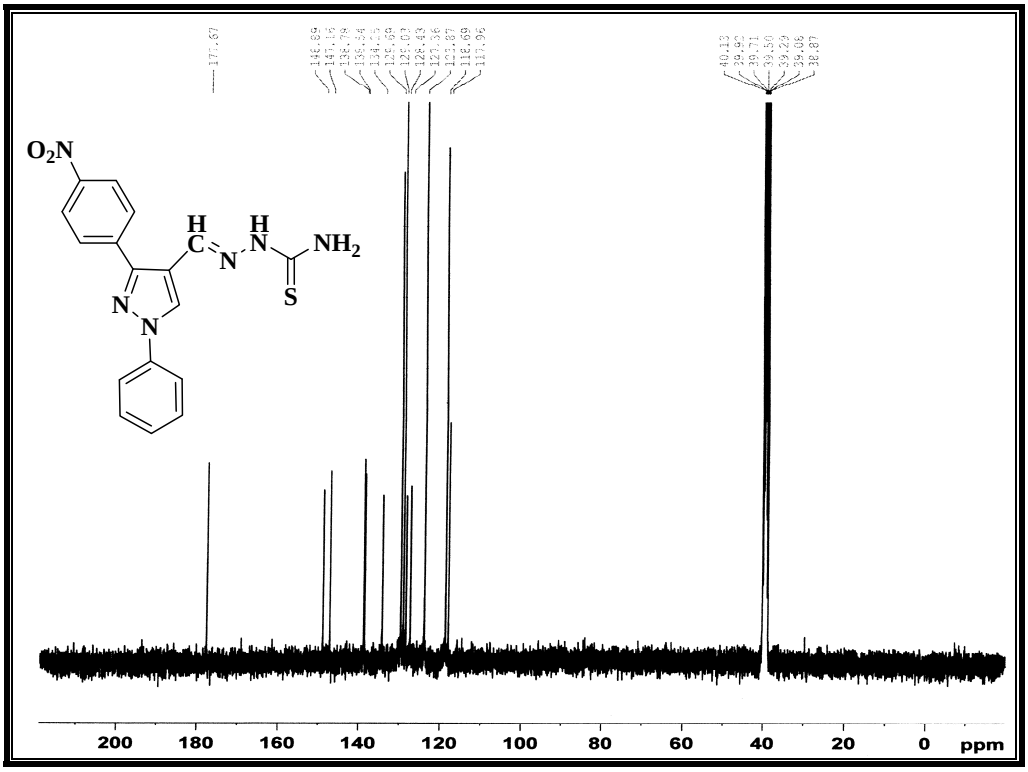
^{1}H NMR spectrum of TRM-8



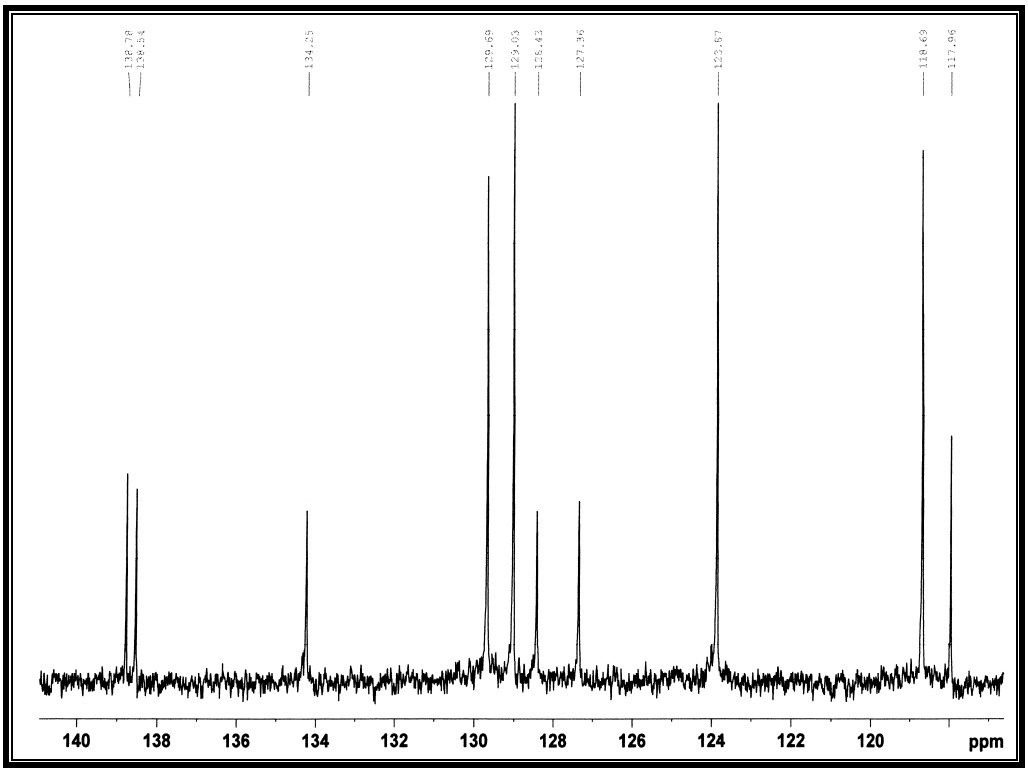
Expanded ^{1}H NMR spectrum of TRM-8



^{13}C NMR spectrum of TRM-8



Expanded ^{13}C NMR spectrum of TRM-8



Results & Discussion

In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M+) corresponding to their molecular weight.

Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3371 cm^{-1}, 1062 cm^{-1} and 1292 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1597 cm^{-1}. The other bands of $-NH_2$ due to at 3182 cm^{-1} and aromatic -C-H and -C=C bands due to at 3140-3014 cm^{-1} and 1508 cm^{-1} respectively.

In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 9.22 ppm as a singlet. The, -N-NH and NH_2 protons were observed at 11.34 ppm and 8.25 ppm as a singlet, respectively. All the aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 138.78 ppm and -C=S carbon, appeared at 177.67 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

All spectral characterization and elemental analysis confirm the structure of 1-((3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide(TRM-8).

CHAPTER-II

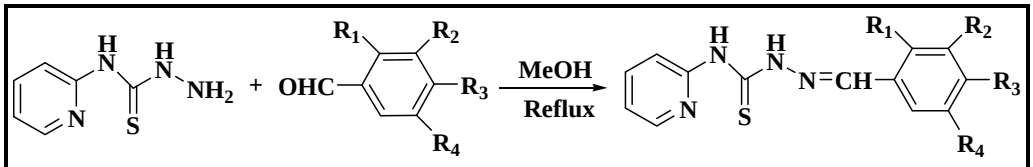
SYNTHESIS AND CHARACTERIZATION OF 1-SUBSTITUTED ARYLIDENE-4-(PYRIDIN-2-YL) THIOSEMICARBAZIDE

1.3.1 EXPERIMENTAL SECTION

Synthesis of Ligands

General procedure for the synthesis of 1-substituted arylidene-4-(pyridin-2-yl) thiosemicarbazide.

The 4-(pyridin-2-yl)thiosemicarbazide (0.01 M) and substituted aromatic aldehyde (0.01 M) were dissolved in 60 ml methanol in a 100 ml round bottom flask, then add 1 ml gl. acetic acid and reflux the resulting reaction mixture for 24 hrs. on boiling water bath, reaction was monitored by TLC. After completion of the reaction, reaction mixture was poured into crushed ice (250 gm). The separated product was filtered wash with sodium bisulphite solution and dried at room temperature.



SCHEME - 4 **TRM - 9 to 13**

Table - IV

Comp. Code	R_1	R_2	R_3	R_4	Yield %	M. P. °C	R_f
TRM-9	-H	$-OCH_3$	-OH	-Br	69	140	0.47
TRM-10	-Cl	-H	-Cl	-H	76	84	0.84
TRM-11	-H	-H	$-OCH_3$	-H	66	128	0.69
TRM-12	-H	$-OCH_3$	$-OCH_3$	-H	70	110	0.50
TRM-13	-H	-OH	-H	-H	63	134	0.53

TLC solvent system - benzene:acetone **(**8:2)

1.3.2 SPECTRAL DATA OF THE SYNTHESIZED LIGANDS

[1] 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(TRM-9).

Colour: Brown; **Anal. Calcd**. For $C_{14}H_{13}BrN_4O_2S$ (381.25 g/mol): C, 44.11%; H, 3.44%; N, 14.70%; S, 8.41%. **Found:** C, 44.02%; H, 3.31%; N, 14.62%; S, 8.30%; **MS** (m/z): 380 (M-1); **IR (KBr, cm^{-1}):** *v*(OH) 3439; *v*(NH) 3339; *v*(C=N) 1599; *v*(N-N) 1045; *v*(C=S) 1288; δ(C=S) 852; *v*(Ar–C-H) 3101-2935; *v*(Ar–C=C) 1529; *v*(C-Br) 617; **^{1}H-NMR (DMSO-d_6):** δppm 3.89 (s, 3H, OMe); 7.04, (tri, 1H, Ar-H); 7.15, (m, 1H, Ar-H); 7.42, (m, 1H, Ar-H); 7.84, (m, 1H, Ar-H); 8.07 (s, 1H, HC=N); 8.36, (m, 1H, Ar-H); 8.62, (d, 1H, *J* = 6.0 Hz, Ar-H); 9.76 (s, 1H, OH); 10.12 (s, 1H, NH); 12.02 (s, 1H, NH); **^{13}C-NMR (DMSO-d_6):** δppm 56.41, (O-CH_3); 109.18, 109.57, 114.38, 117.81, 124.17, 128.62, 138.51, 148.61, 149.77, 152.67, 155.44 (Ph); 142.98 (HC=N); 177.01 (C=S); **UV-Vis:(DMF)** (λ_{max}/ nm): 274, 320.

[2] 1-(2,4-dichlorobenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(TRM-10).

Colour: Cream; **Anal. Calcd**. For $C_{13}H_{10}Cl_2N_4S$ (325.22 g/mol): C, 48.01%; H, 3.10%; N, 17.23%; S, 9.86%. **Found:** C, 47.92%; H, 3.03%; N, 17.11%; S, 9.75%; **MS** (m/z): 324 (M-1); **IR (KBr, cm^{-1}):** *v*(NH) 3282; *v*(C=N) 1593; *v*(N-N) 1049; *v*(C=S) 1311; δ(C=S) 864; *v*(Ar–C-H) 3146-2958; *v*(Ar–C=C) 1519; *v*(C-Cl) 777; **^{1}H-NMR (DMSO-d_6):** δppm 7.04, (m, 1H, Ar-H); 7.15, (m, 1H, Ar-H); 7.42, (m, 1H, Ar-H); 7.84, (m, 2H, Ar-H); 8.30 (s, 1H, HC=N); 8.36, (m, 1H, Ar-H); 8.62, (d, 1H, *J* = 5.6 Hz, Ar-H); 10.26 (s, 1H, NH); 12.27 (s, 1H, NH); **^{13}C-NMR (DMSO-d_6):** δppm 112.36, 114.34, 127.83, 129.31, 130.08, 133.45, 135.03, 138.39, 138.49, 152.66, 155.46 (Ph); 143.64 (HC=N); 177.00 (C=S).

[3] 1-(4-methoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(TRM-11).

Colour: Cream; **Anal. Calcd**. For $C_{14}H_{14}N_4OS$ (286.35 g/mol): C, 58.72%; H, 4.93%; N, 19.57%; S, 11.20%. **Found:** C, 58.61%; H, 4.85%; N, 19.49%; S, 11.06%; **MS** (m/z): 286 (M); **IR (KBr, cm^{-1}):** *v*(NH) 3304; *v*(C=N) 1599; *v*(N-N) 1022; *v*(C=S) 1267; δ(C=S) 858; *v*(Ar–C-H) 3163-2964; *v*(Ar–C=C) 1510;

^{1}H-NMR (DMSO-d_6): δppm 3.80 (s, 3H, OMe); 7.04, (d, 1H, *J* = 2.0 Hz, Ar-H); 7.16, (m, 2H, Ar-H); 7.74, (d, 1H, *J* = 8.8 Hz, Ar-H); 7.84, (m, 2H, Ar-H); 8.16 (s, 1H, HC=N); 8.36, (d, 1H, *J* = 4.8 Hz, Ar-H); 8.55, (d, 1H, *J* = 8.4 Hz, Ar-H); 10.03 (s, 1H, NH); 12.03 (s, 1H, NH); **^{13}C-NMR (DMSO-d_6):** δppm 55.29, (O-CH_3); 114.35, 114.47, 116.15, 117.75, 126.01, 129.08, 129.90, 138.56, 148.07, 152.67, 161.13 (Ph); 143.86 (HC=N); 177.01 (C=S); **UV-Vis:(DMF)** (λ_{max}/ nm): 298, 364.

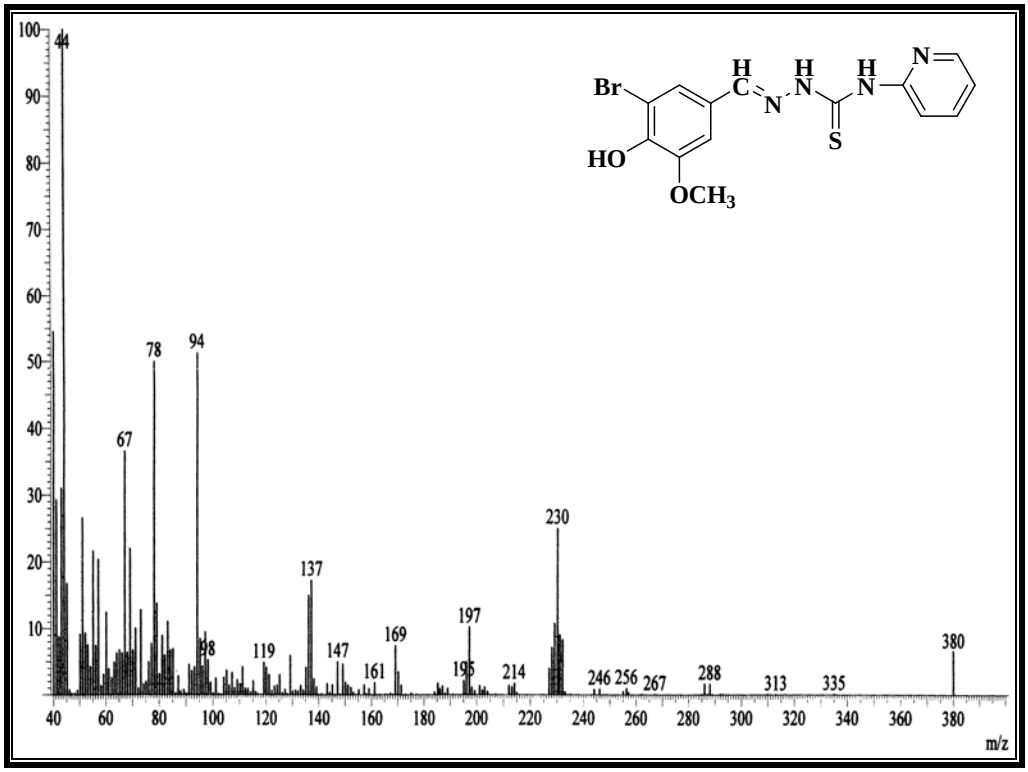
[4] 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(TRM-12).

Colour: White; **Anal. Calcd**. For $C_{15}H_{16}N_4O_2S$ (316.38 g/mol): C, 56.94%; H, 5.10%; N, 17.71%; S, 10.14%. **Found:** C, 56.80%; H, 5.00%; N, 17.59%; S, 10.03%; **MS** (m/z): 316 (M); **IR (KBr, cm^{-1}):** *ν*(NH) 3282; *ν*(C=N) 1608; *ν*(N-N) 1028; *ν*(C=S) 1303; δ(C=S) 878; *ν*(Ar–C-H) 3173-2955; *ν*(Ar–C=C) 1512; **^{1}H-NMR (DMSO-d_6):** δppm 3.80 (s, 3H, OMe); 3.81 (s, 3H, OMe); 7.02, (d, 1H, *J* = 8.4 Hz, Ar-H); 7.22, (m, 2H, Ar-H); 7.45, (s, 1H, Ar-H); 7.83, (tri, 1H, Ar-H); 8.13 (s, 1H, HC=N); 8.40, (tri, 2H, Ar-H); 10.05 (s, 1H, NH); 12.01 (s, 1H, NH); **^{13}C-NMR (DMSO-d_6):** δppm 55.56, 55.66 (O-CH_3); 109.34, 111.57, 117.24, 120.59, 122.05, 126.20, 137.29, 148.09, 149.06, 151.05, 151.73 (Ph); 144.22 (HC=N); 174.13 (C=S); **UV-Vis:(DMF)** (λ_{max}/ nm): 298, 364.

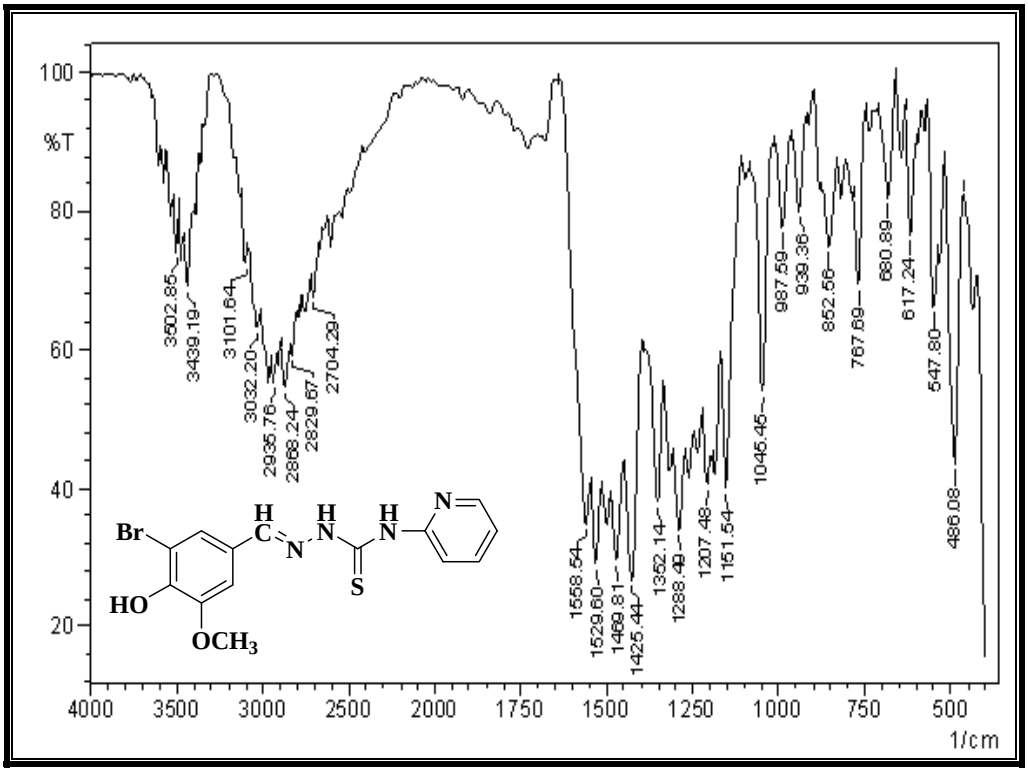
[5] 1-(3-hydroxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(TRM-13).

Colour: Cream; **Anal. Calcd**. For $C_{13}H_{12}N_4OS$ (272.33 g/mol): C, 57.34%; H, 4.44%; N, 20.57%; S, 11.77%. **Found:** C, 57.22%; H, 4.33%; N, 20.50%; S, 11.68%; **MS** (m/z): 272 (M); **IR (KBr, cm^{-1}):** *ν*(OH) 3417; *ν*(NH) 3281; *ν*(C=N) 1626; *ν*(N-N) 1049; *ν*(C=S) 1288; δ(C=S) 860; *ν*(Ar–C-H) 3144-2953; *ν*(Ar–C=C) 1467; **^{1}H-NMR (DMSO-d_6):** δppm 6.86, (m, 1H, Ar-H); 7.15, (m, 2H, Ar-H); 7.25, (tri, 1H, Ar-H); 7.83, (m, 2H, Ar-H); 8.14 (s, 1H, HC=N); 8.36, (d, 1H, *J* = 4.8 Hz, Ar-H); 8.62, (tri, 1H, Ar-H); 9.67 (s, 1H, OH); 10.01 (s, 1H, NH); 12.11 (s, 1H, NH); **^{13}C-NMR (DMSO-d_6):** δppm 112.84, 114.43, 117.76, 117.85, 119.54, 129.90, 134.69, 138.52, 148.08, 152.67, 157.69 (Ph); 144.12 (HC=N); 177.01 (C=S).

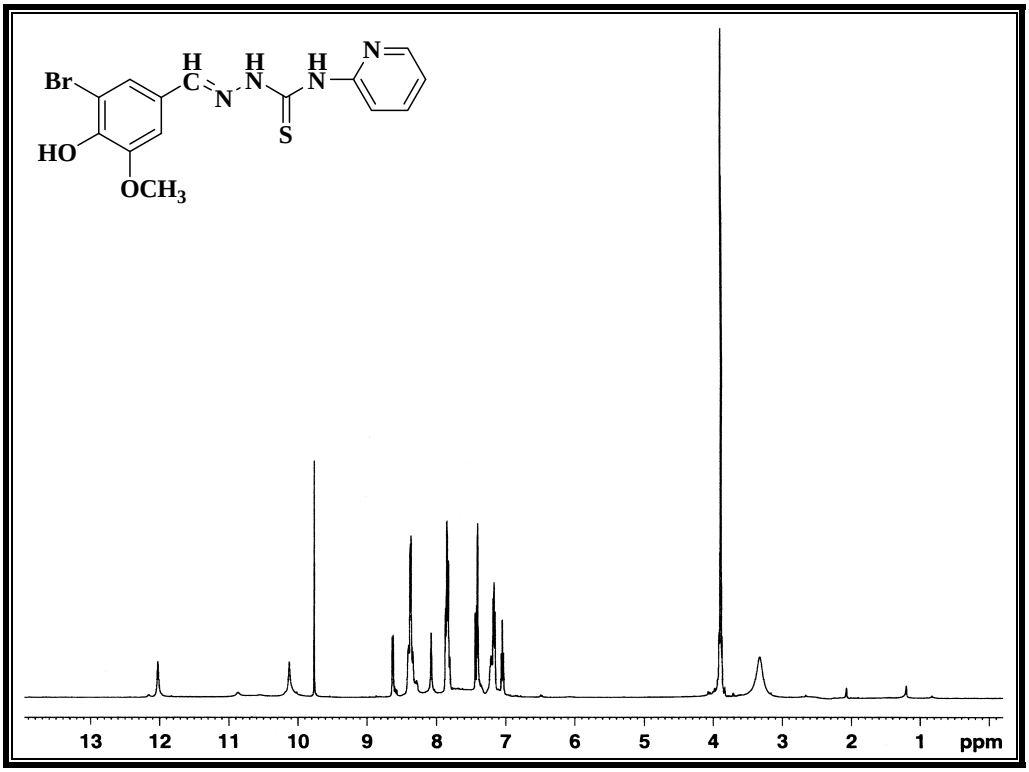
Mass spectrum of TRM-9



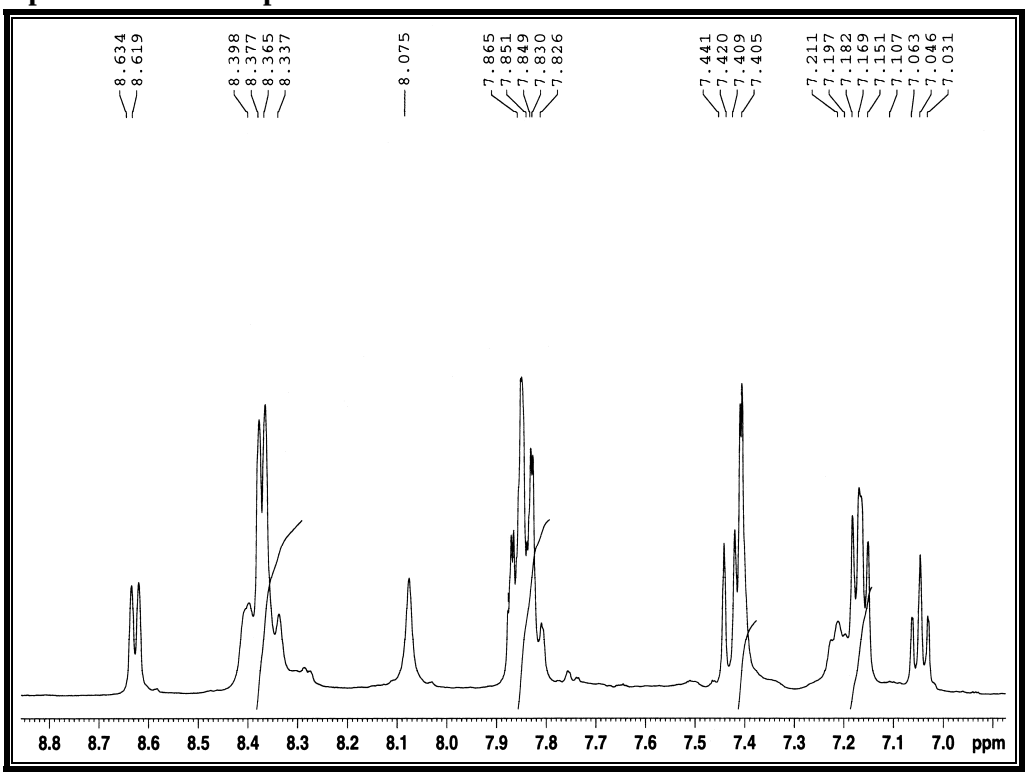
IR spectrum of TRM-9



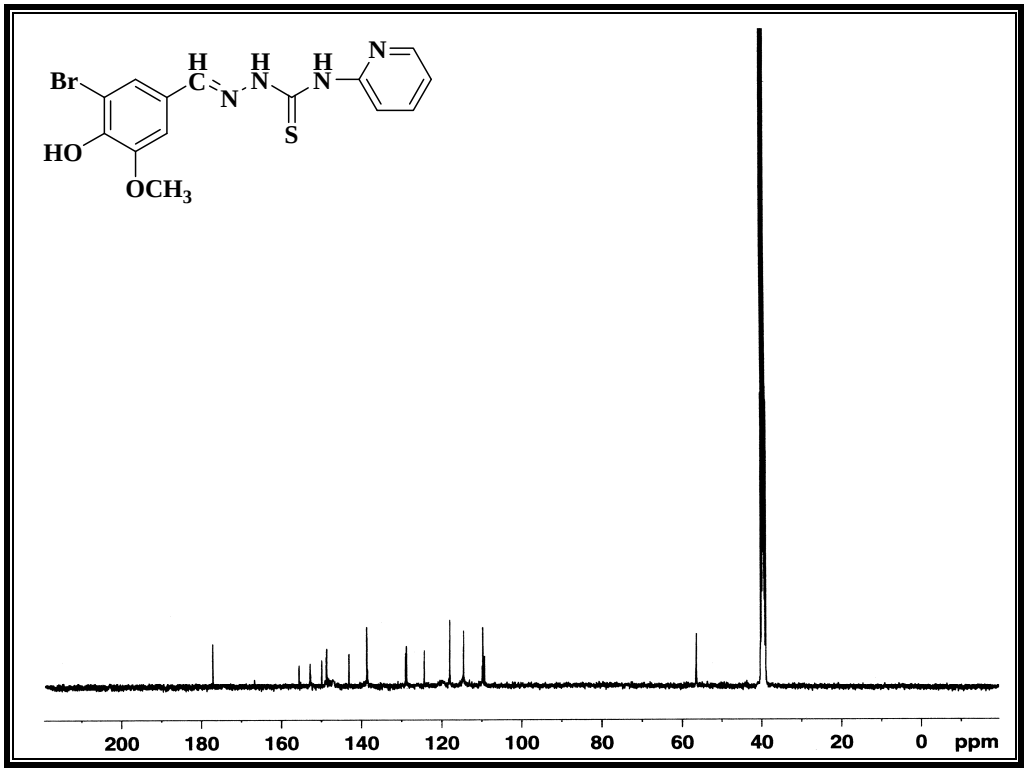
^{1}H NMR spectrum of TRM-9



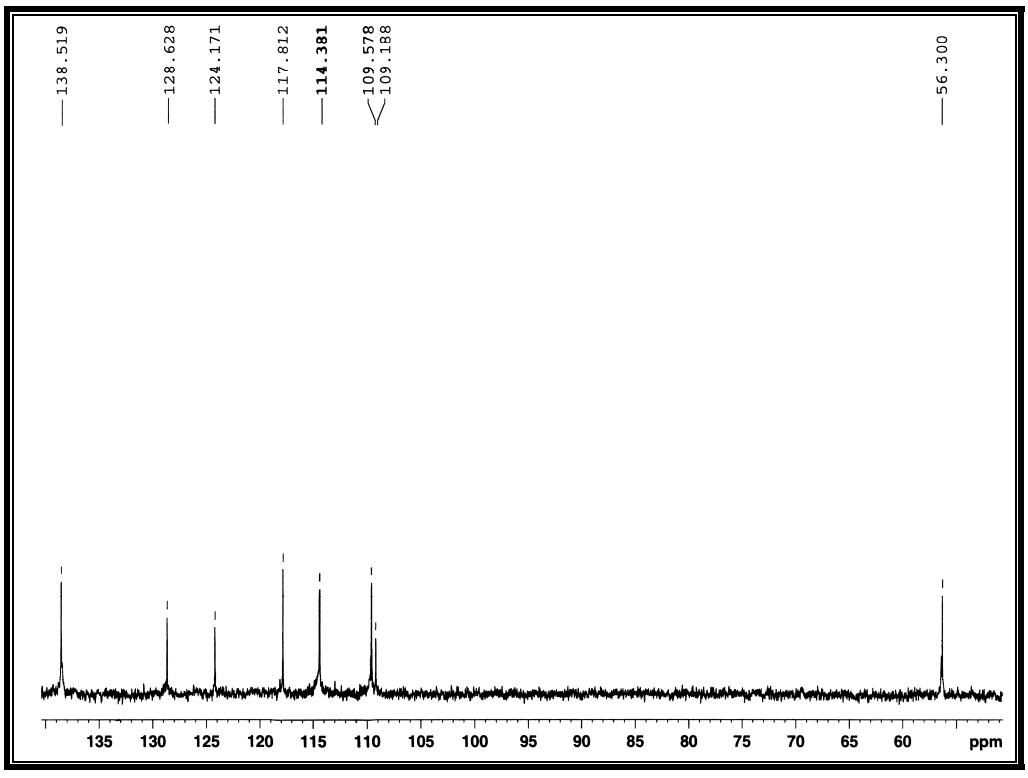
Expanded ^{1}H NMR spectrum of TRM-9



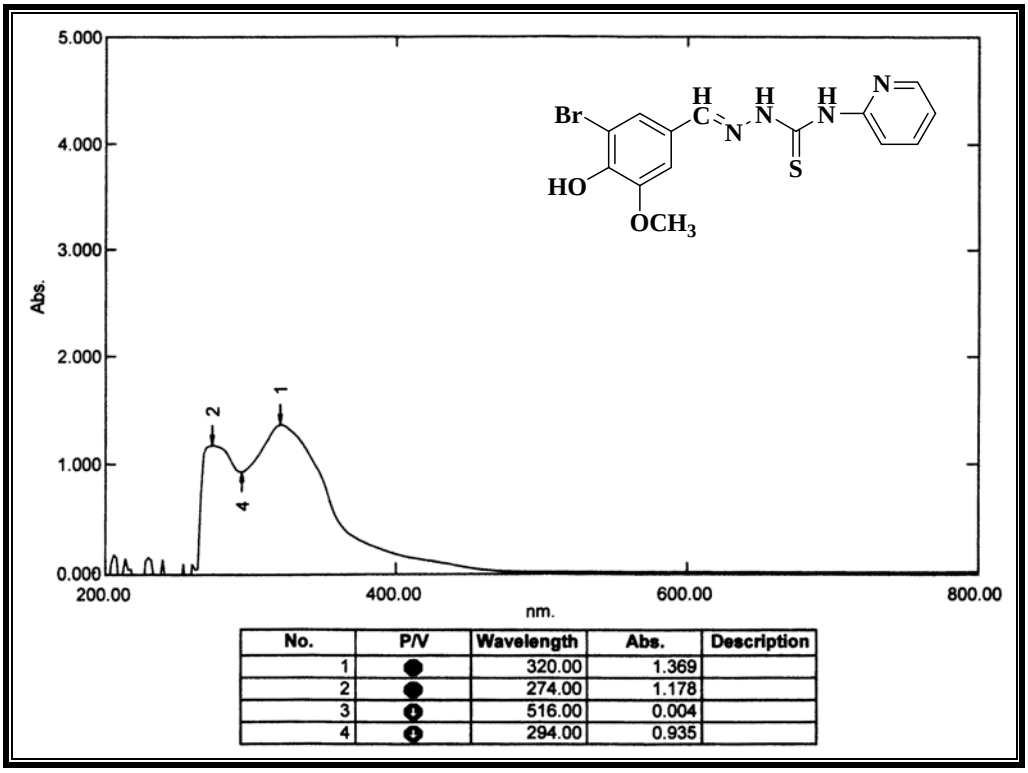
^{13}C NMR spectrum of TRM-9



Expanded ^{13}C NMR spectrum of TRM-9



UV-Visible spectrum of TRM-9



No.	P/V	Wavelength	Abs.	Description
1	●	320.00	1.369	
2	●	274.00	1.178	
3	●	516.00	0.004	
4	●	294.00	0.935	

Results & Discussion

In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M-1) corresponding to their molecular weight.

Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3339 cm^{-1}, 1045 cm^{-1} and 1288 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1599 cm^{-1}. The other bands of -OH due to at 3439 cm^{-1} and aromatic -C-H and -C=C bands due to at 3101-2935 cm^{-1} and 1529 cm^{-1} respectively.

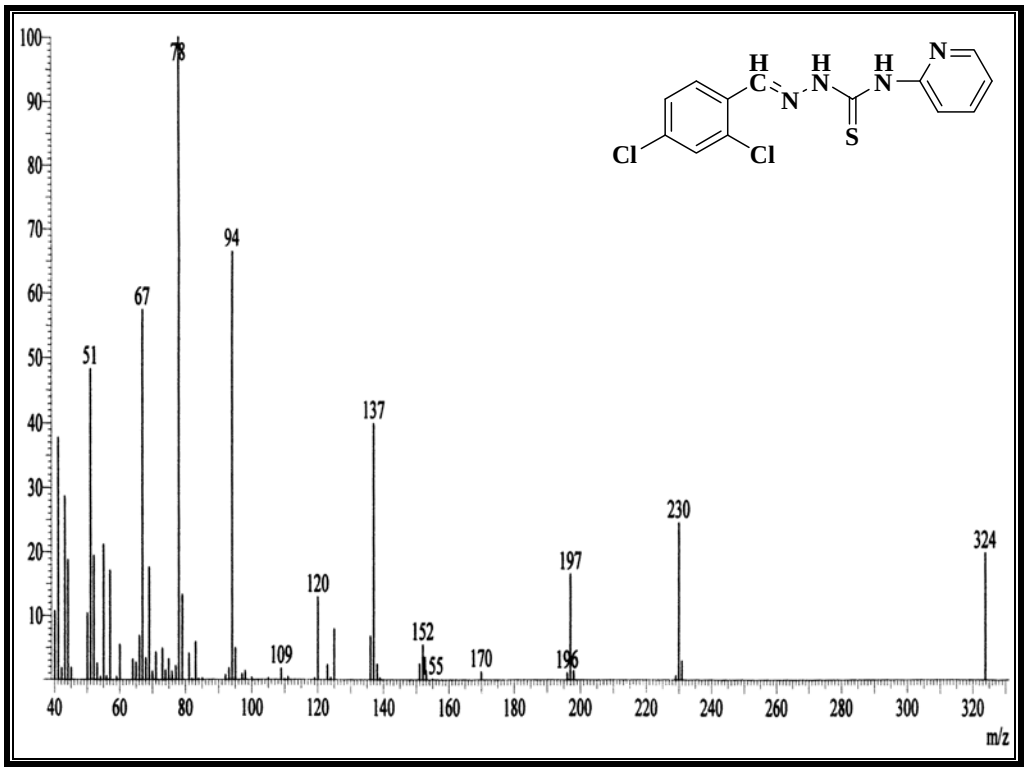
In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 8.07 ppm as a singlet. The, -C-NH, -N-NH and -OH protons were observed at 10.12 ppm, 12.02 ppm and 9.76 ppm as a singlet, respectively. All

the aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 142.98 ppm and -C=S carbon, appeared at 177.01 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

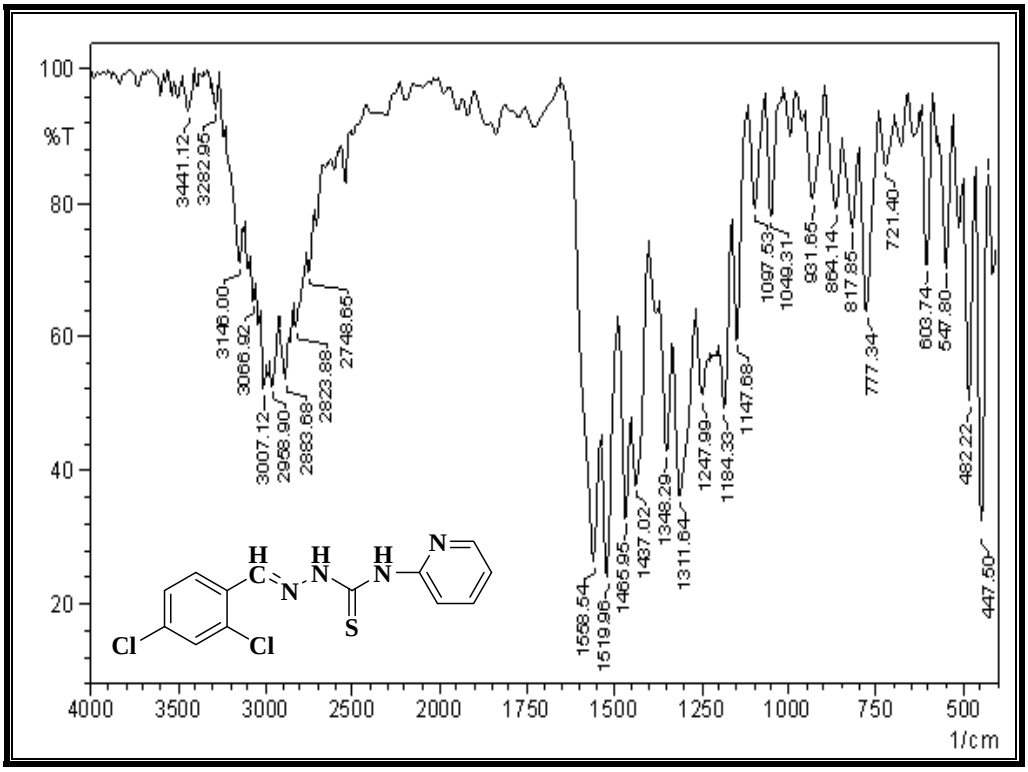
Electronic spectroscopy is a very important tool for the structural identification of synthesized thiosemicarbazone. It is usually measured in the range 200-800 nm. This compound absorb in the region 250-350 nm and the bands are mainly due to at 274 nm $\pi \rightarrow \pi^*$ and 320 nm $n \rightarrow \pi^*$ transitions.

All spectral characterization and elemental analysis confirm the structure of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide (TRM-9).

Mass spectrum of TRM-10



IR spectrum of TRM-10



Results & Discussion

In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M-1) corresponding to their molecular weight.

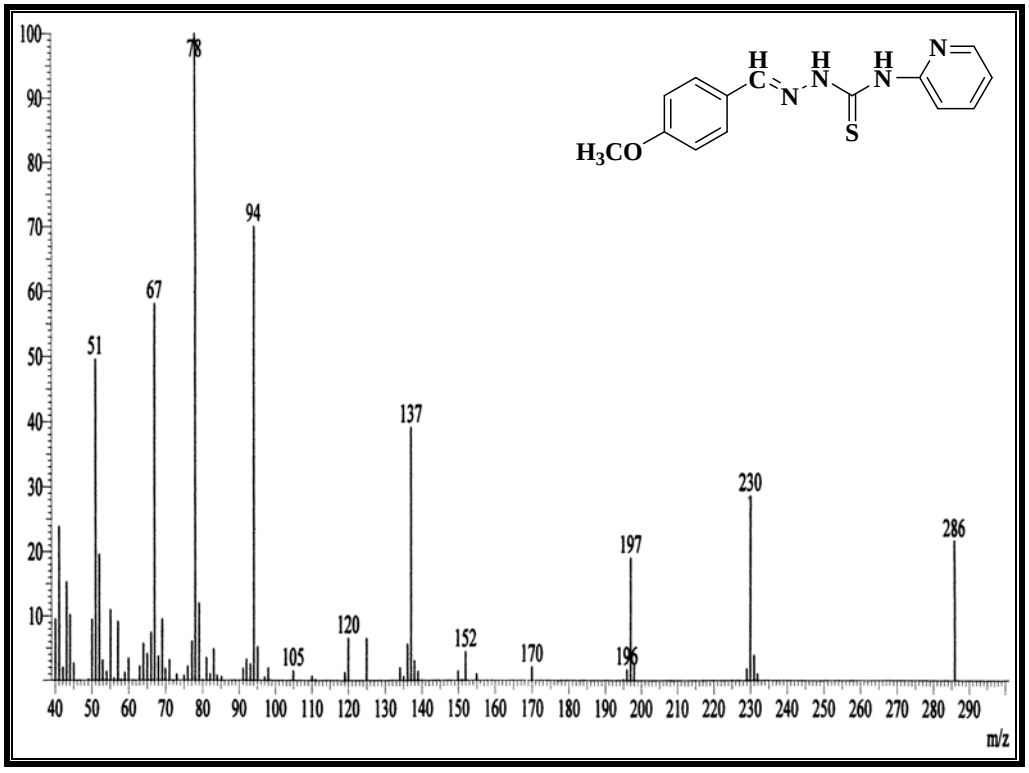
Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3282 cm^{-1}, 1049 cm^{-1} and 1311 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1593 cm^{-1}. The aromatic -C-H and -C=C bands due to at 3146-2958 cm^{-1} and 1519 cm^{-1} respectively.

In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 8.30 ppm as a singlet. The, -C-NH and -N-NH protons were observed at 10.26 ppm and 12.27 ppm as a singlet, respectively. All the aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due

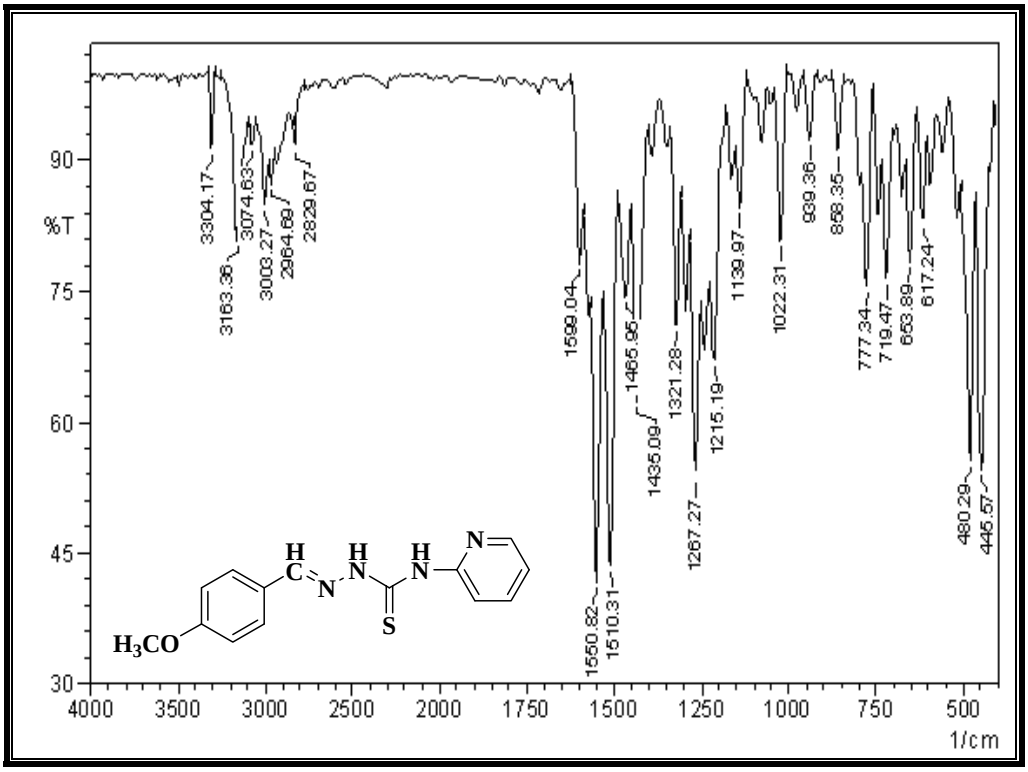
to (-CH=N-) carbon, appeared at 143.64 ppm and -C=S carbon, appeared at 177.00 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

All spectral characterization and elemental analysis confirm the structure of 1-(2,4-dichlorobenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(TRM-10).

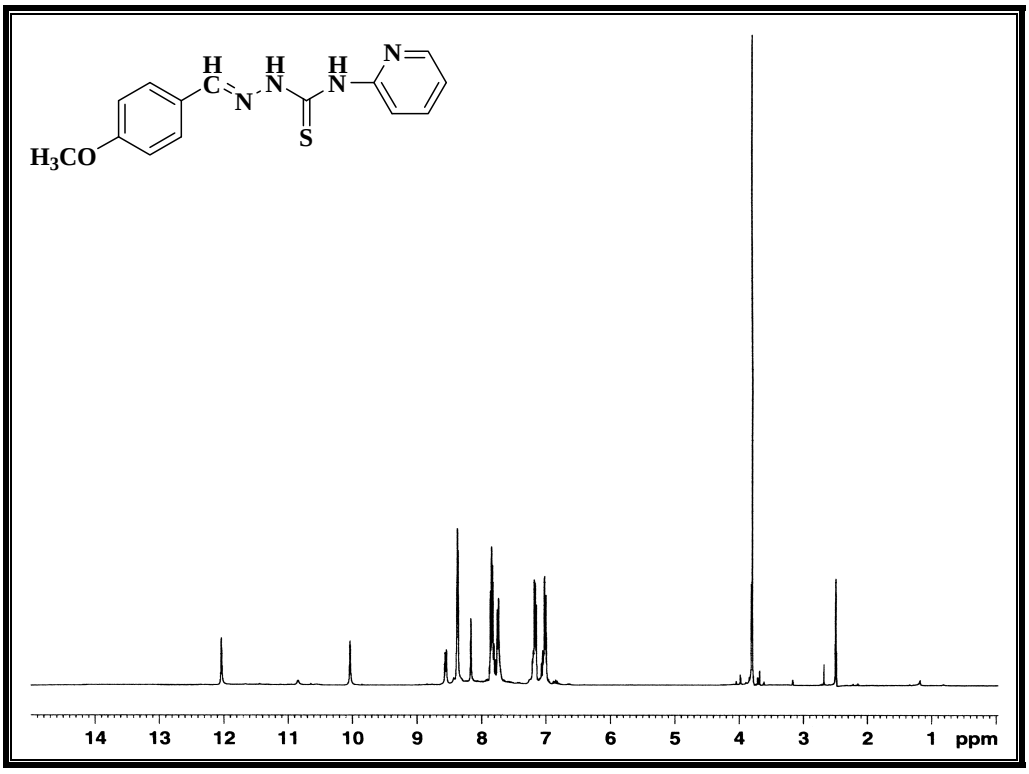
Mass spectrum of TRM-11



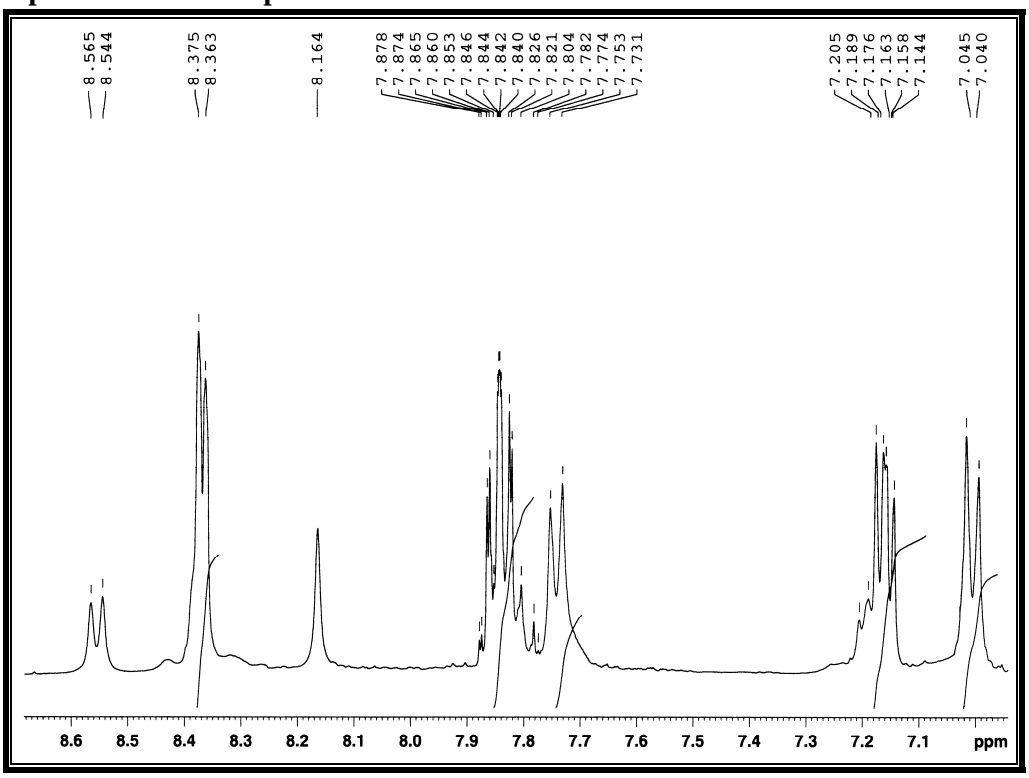
IR spectrum of TRM-11



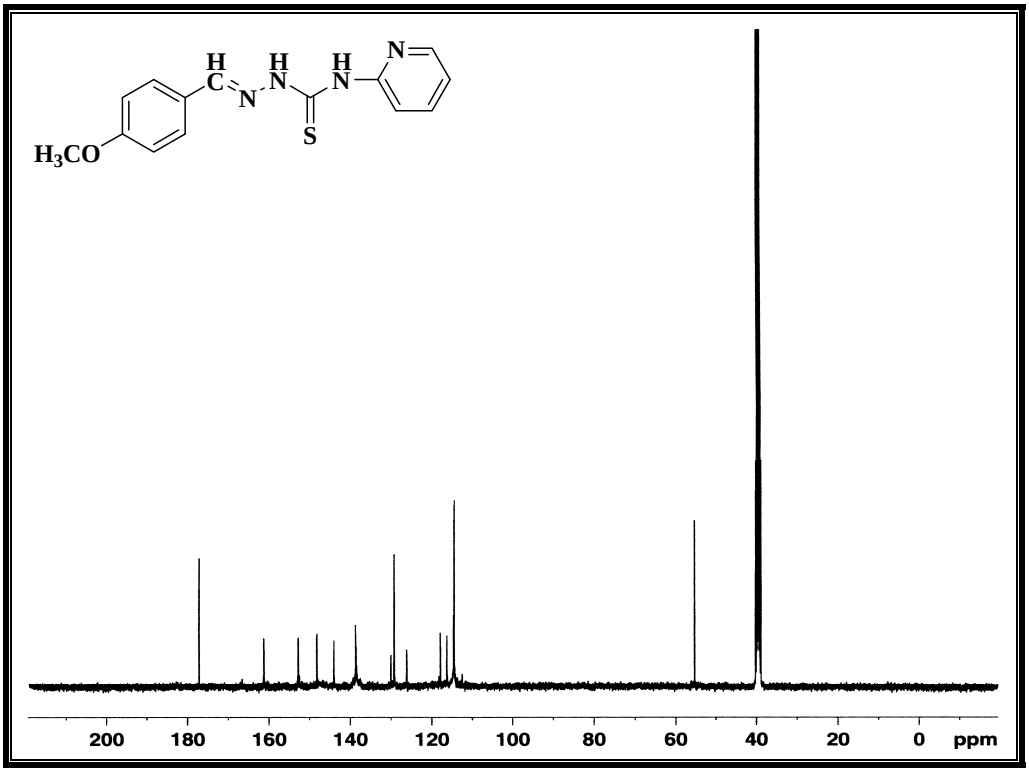
^{1}H NMR spectrum of TRM-11



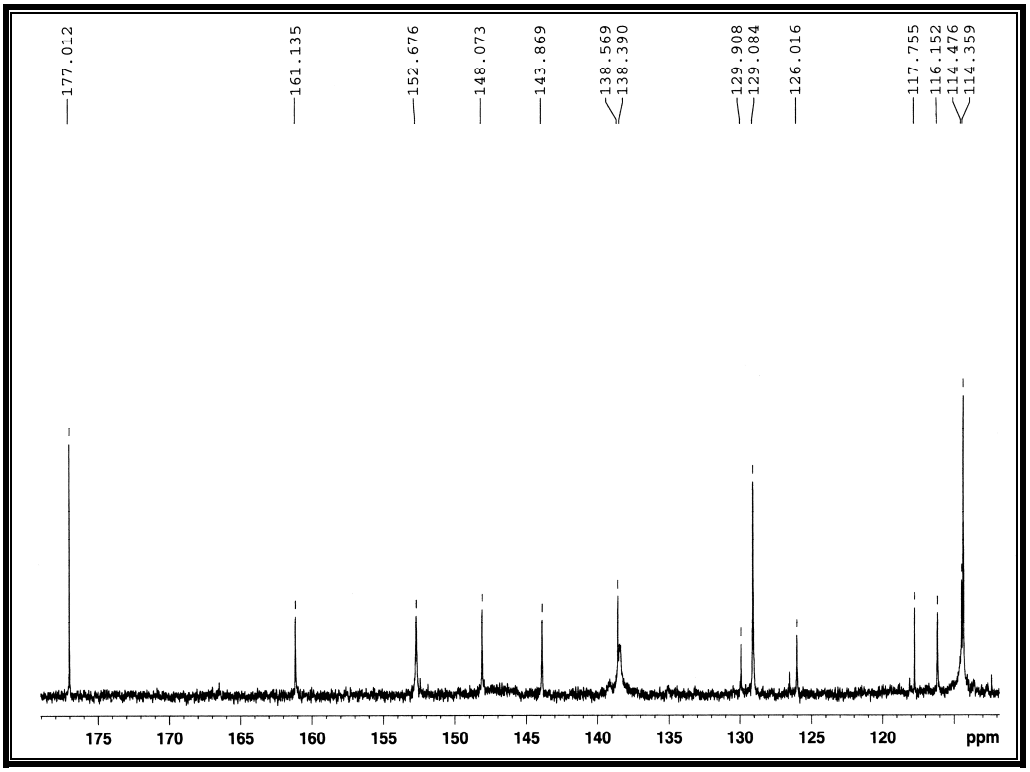
Expanded ^{1}H NMR spectrum of TRM-11



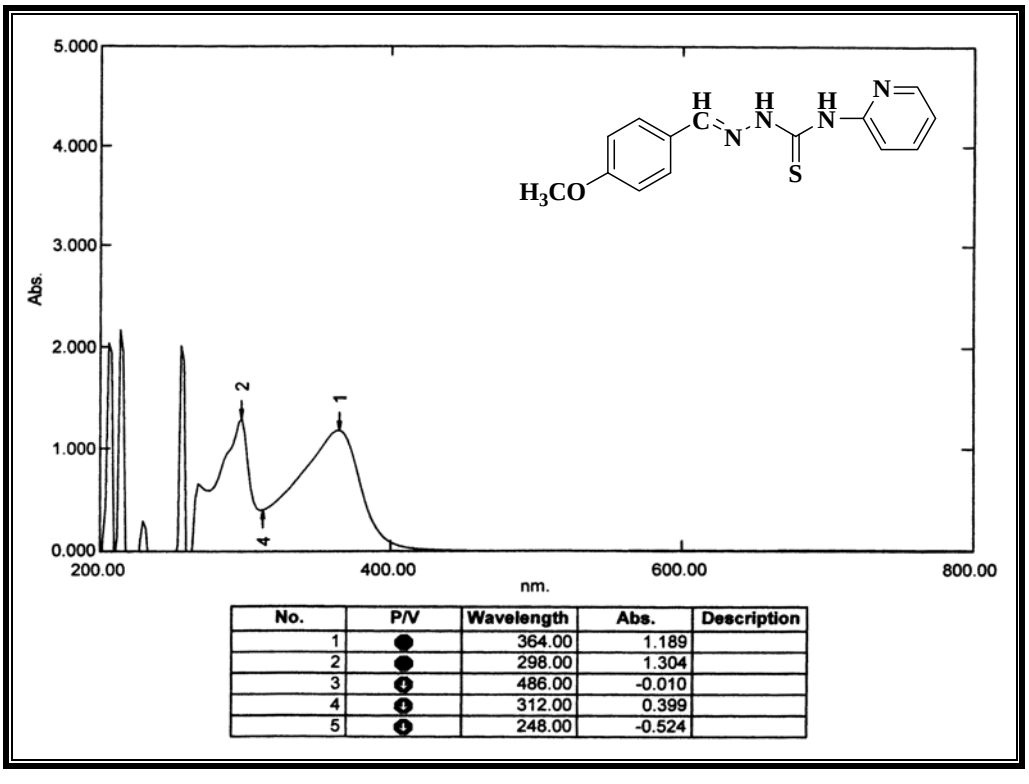
^{13}C NMR spectrum of TRM-11



Expanded ^{13}C NMR spectrum of TRM-11



UV-Visible spectrum of TRM-11



No.	P/V	Wavelength	Abs.	Description
1	●	364.00	1.189	
2	●	298.00	1.304	
3	⊕	486.00	-0.010	
4	⊕	312.00	0.399	
5	⊕	248.00	-0.524	

Results & Discussion

In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M+) corresponding to their molecular weight.

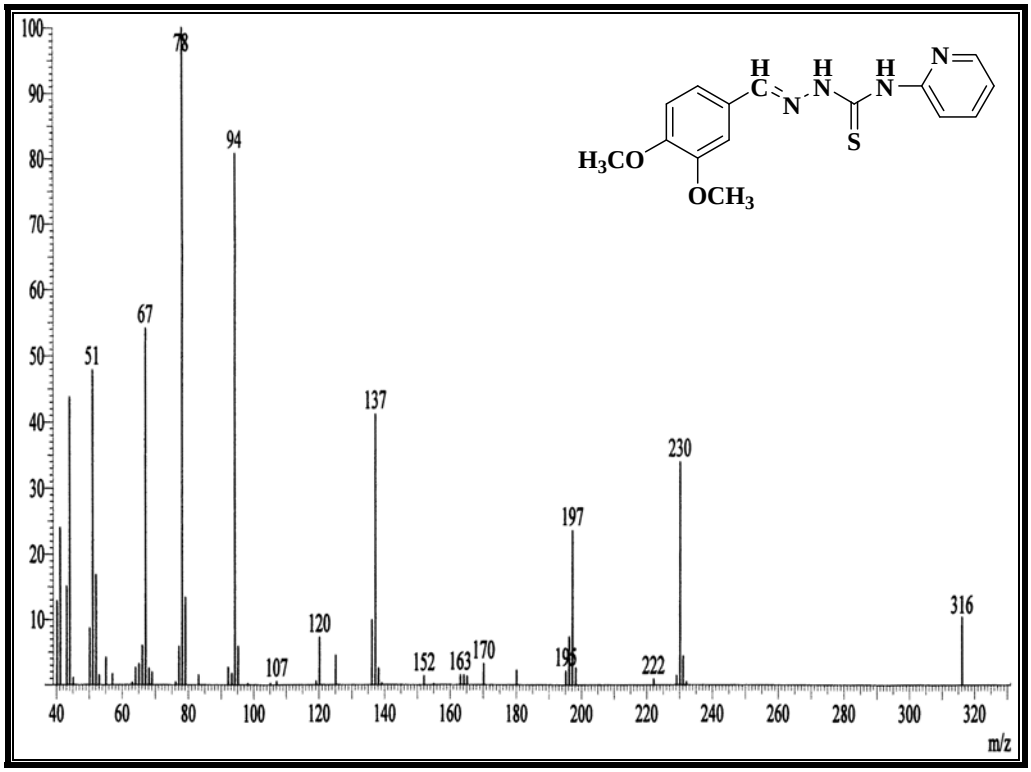
Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3304 cm^{-1}, 1022 cm^{-1} and 1267 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1599 cm^{-1}. The aromatic -C-H and -C=C bands due to at 3163-2964 cm^{-1} and 1510 cm^{-1} respectively.

In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 8.16 ppm as a singlet. The, -C-NH, -N-NH and -O-CH_3 protons were observed at 10.03 ppm, 12.03 ppm and 3.80 ppm as a singlet, respectively. All the aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 143.86 ppm and -C=S carbon, appeared at 177.01 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

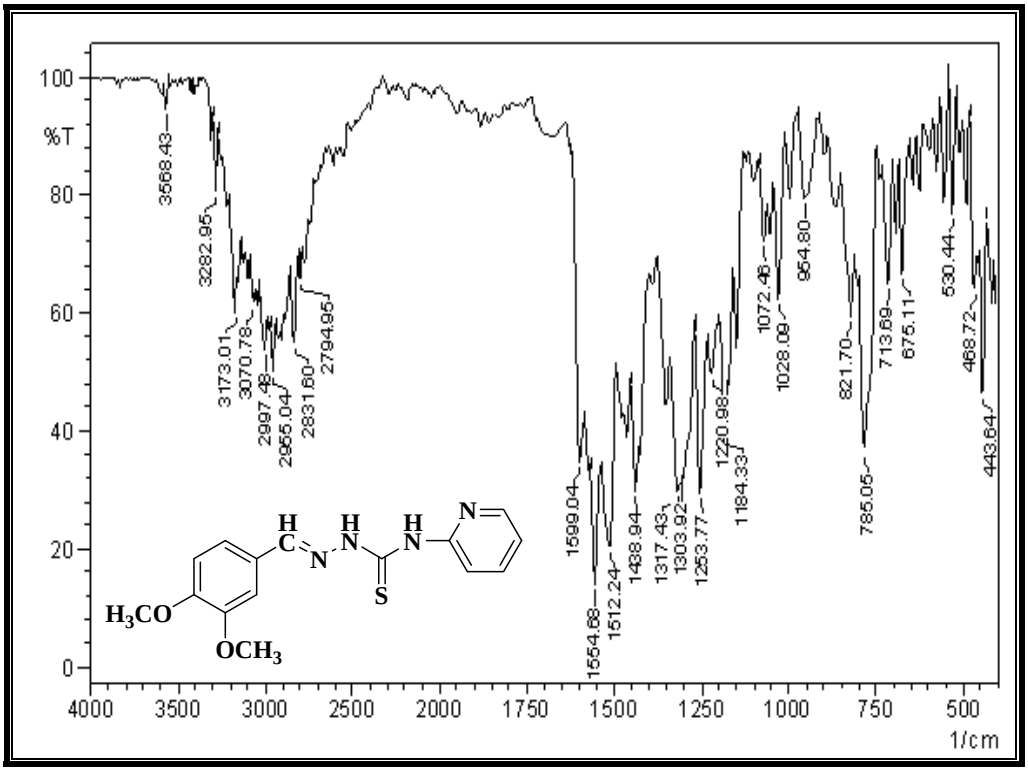
Electronic spectroscopy is a very important tool for the structural identification of synthesized thiosemicarbazone. It is usually measured in the range 200-800 nm. This compound absorb in the region 250-350 nm and the bands are mainly due to at 298 nm $\pi \rightarrow \pi^*$ and 364 nm $n \rightarrow \pi^*$ transitions.

All spectral characterization and elemental analysis confirm the structure of 1-(4-methoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(TRM-11).

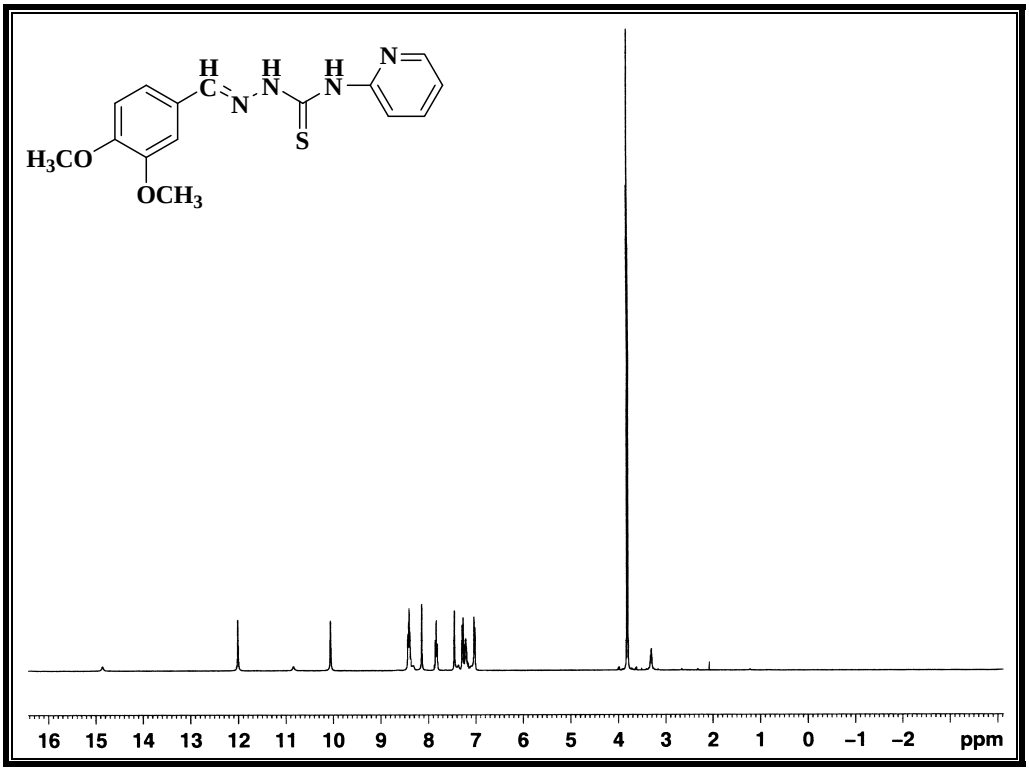
Mass spectrum of TRM-12



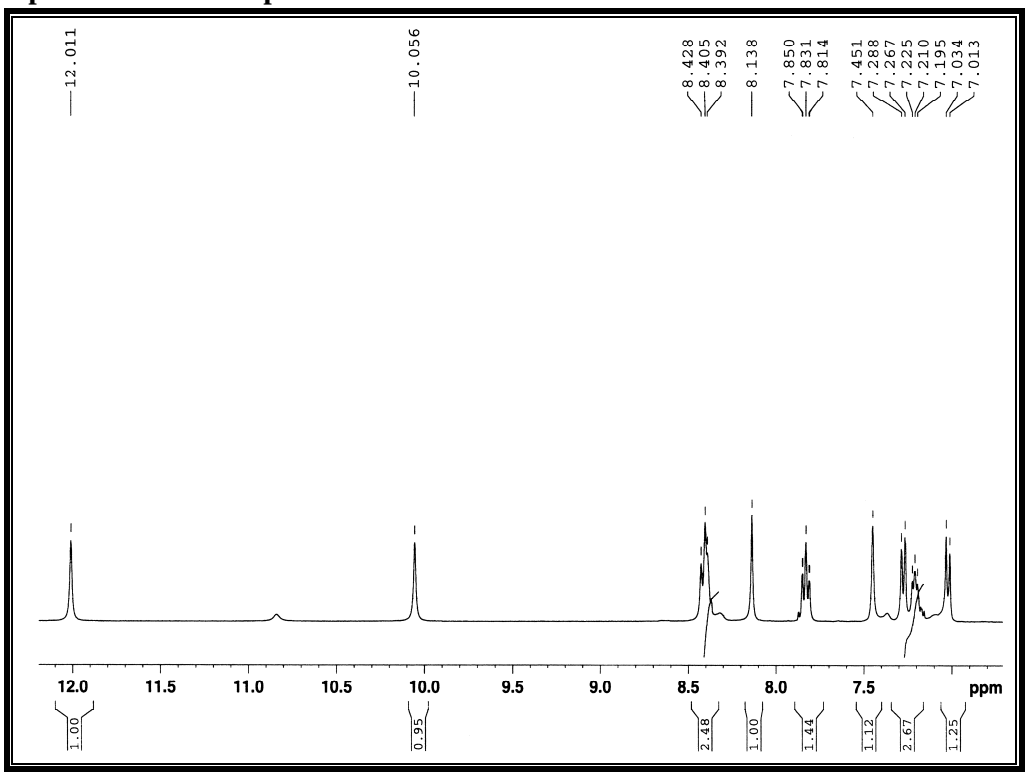
IR spectrum of TRM-12



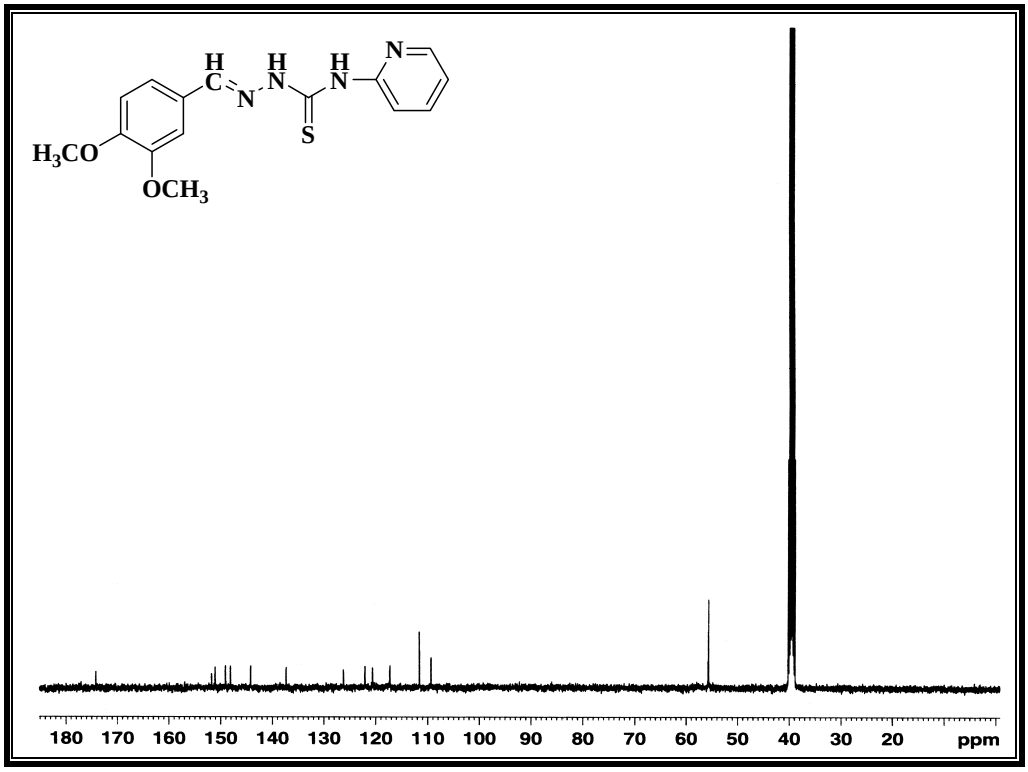
^{1}H NMR spectrum of TRM-12



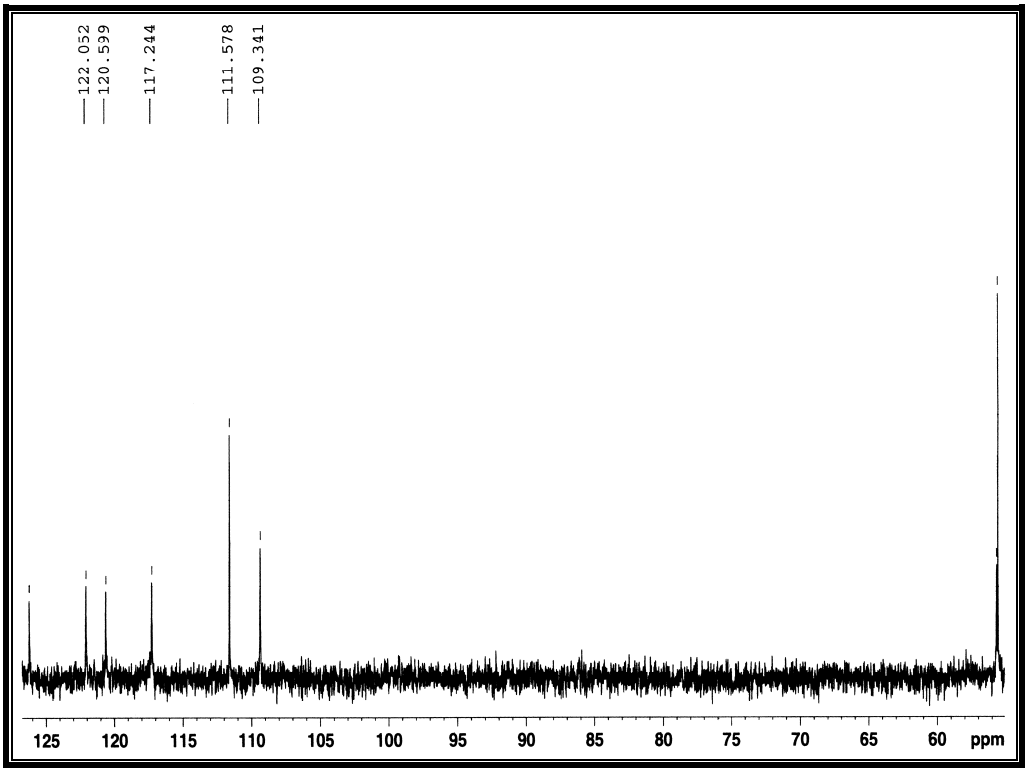
Expanded ^{1}H NMR spectrum of TRM-12



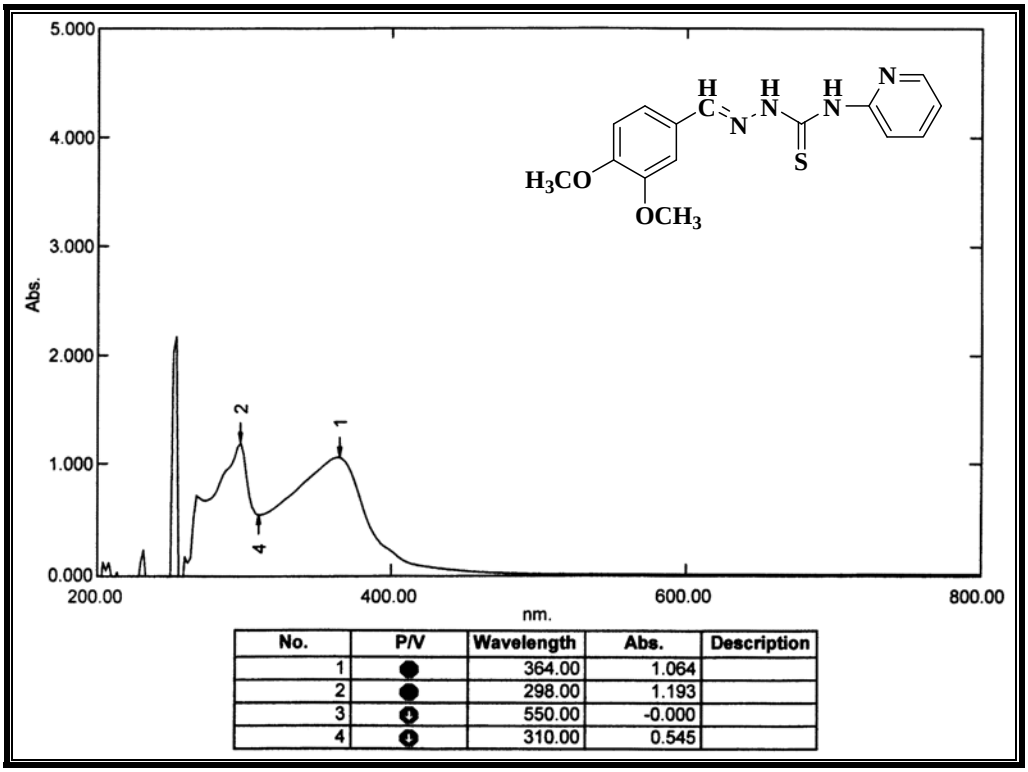
^{13}C NMR spectrum of TRM-12



Expanded ^{13}C NMR spectrum of TRM-12



UV-Visible spectrum of TRM-12



No.	P/V	Wavelength	Abs.	Description
1	●	364.00	1.064	
2	●	298.00	1.193	
3	▲	550.00	-0.000	
4	▲	310.00	0.545	

Results & Discussion

In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M+) corresponding to their molecular weight.

Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3282 cm^{-1}, 1028 cm^{-1} and 1303 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1608 cm^{-1}. The aromatic -C-H and -C=C bands due to at 3173-2955 cm^{-1} and 1512 cm^{-1} respectively.

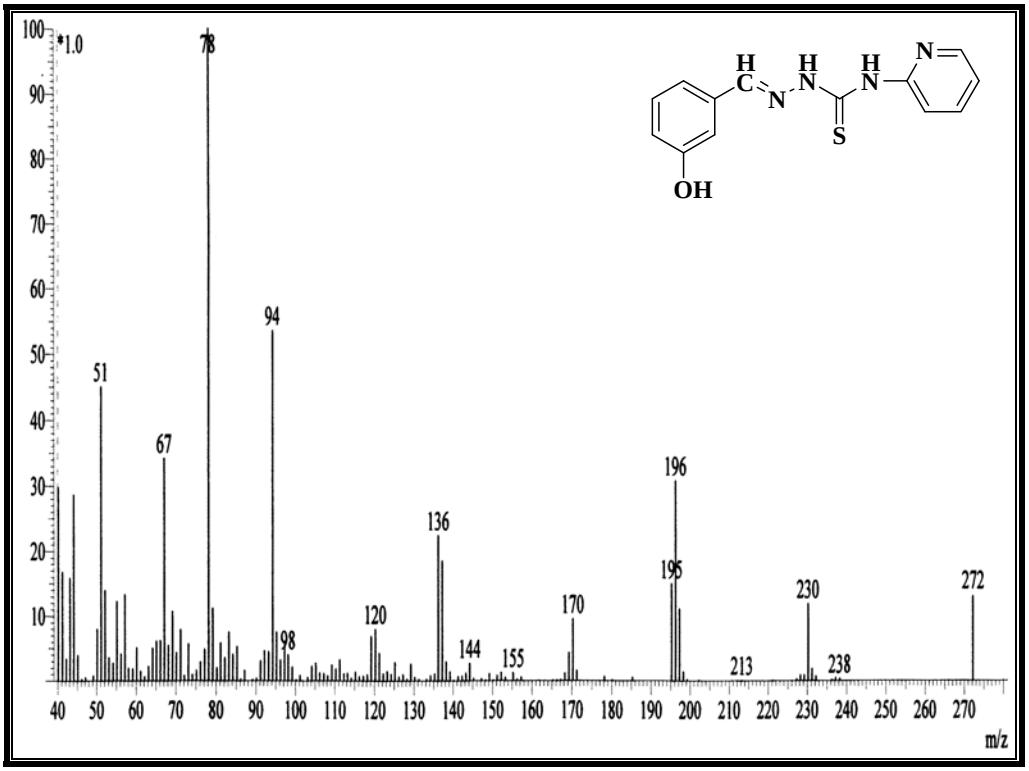
In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 8.13 ppm as a singlet. The, -C-NH, -N-NH and -O-CH_3 protons were observed at 10.05 ppm, 12.01 ppm and 3.80 ppm as a singlet, respectively. All the aromatic protons were observed in the expected regions. In the

^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 144.22 ppm and -C=S carbon, appeared at 174.13 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

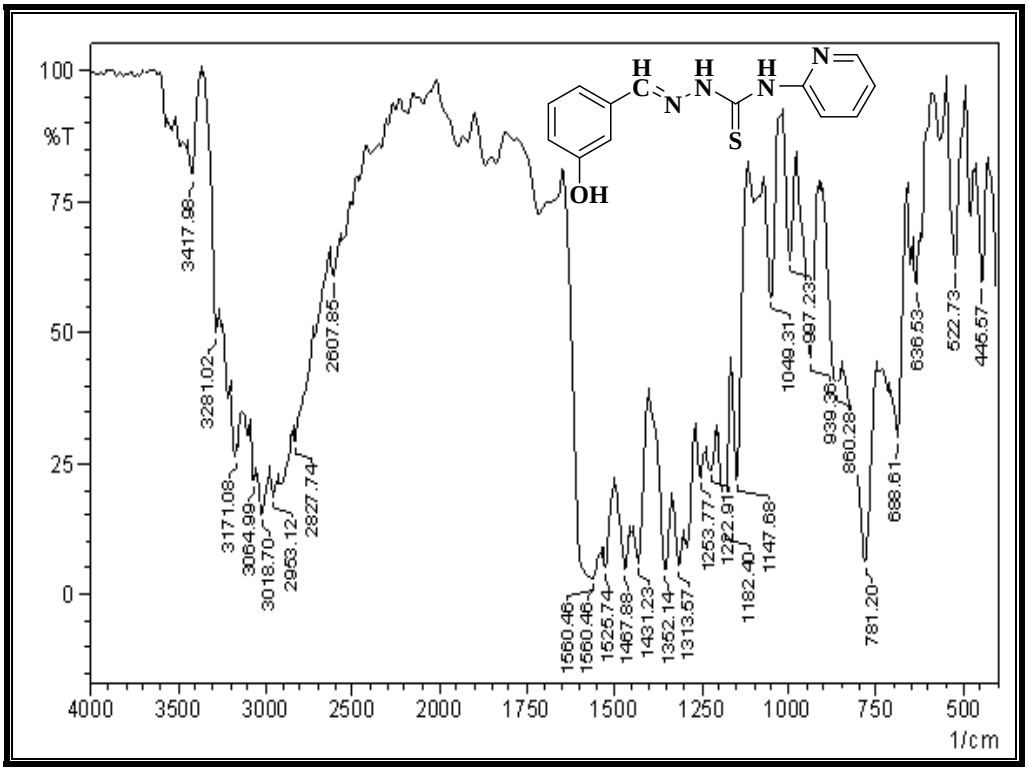
Electronic spectroscopy is a very important tool for the structural identification of synthesized thiosemicarbazone. It is usually measured in the range 200-800 nm. This compound absorb in the region 250-350 nm and the bands are mainly due to at 298 nm $\pi \rightarrow \pi^*$ and 364 nm $n \rightarrow \pi^*$ transitions.

All spectral characterization and elemental analysis confirm the structure of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(TRM-12).

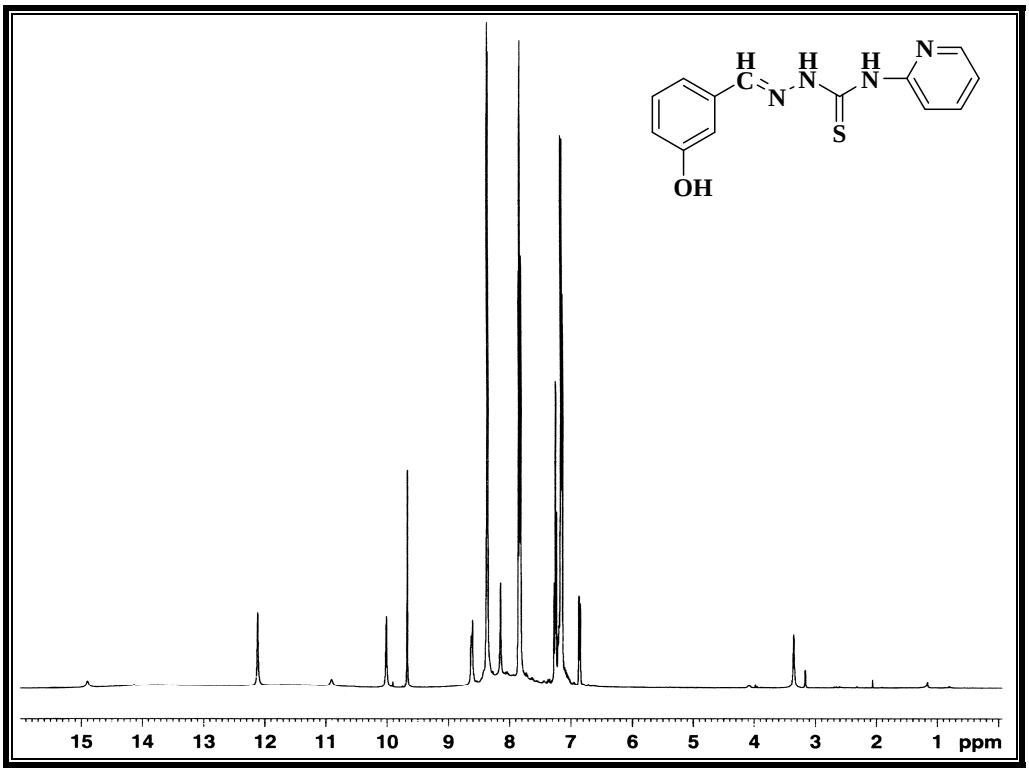
Mass spectrum of TRM-13



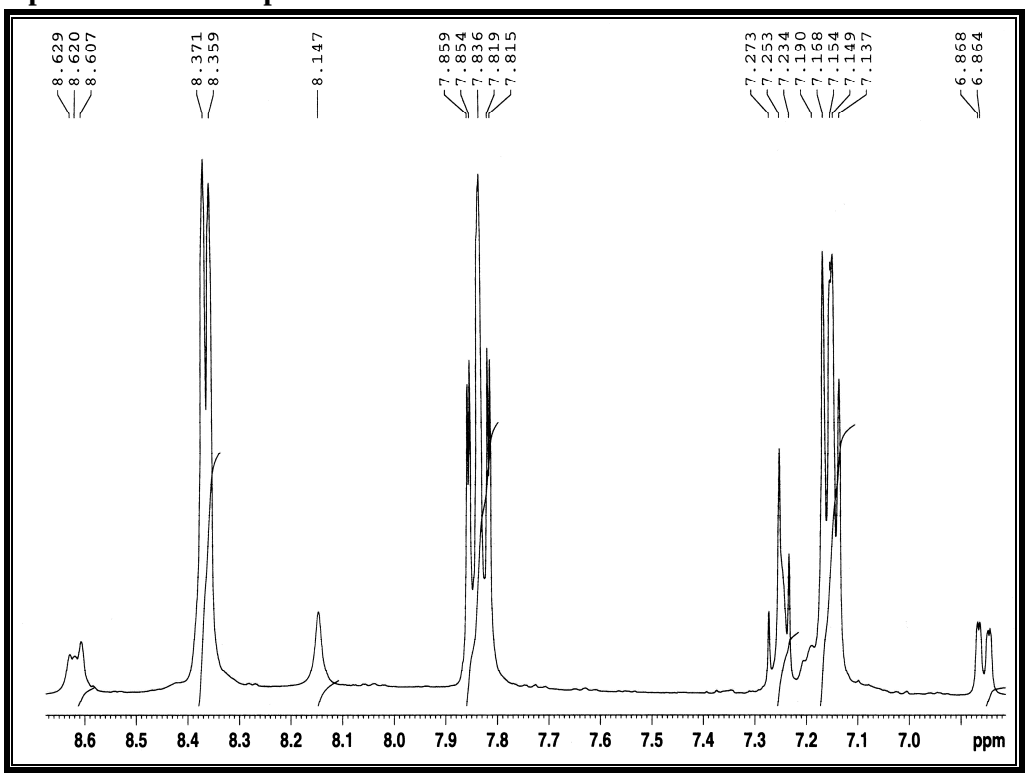
IR spectrum of TRM-13



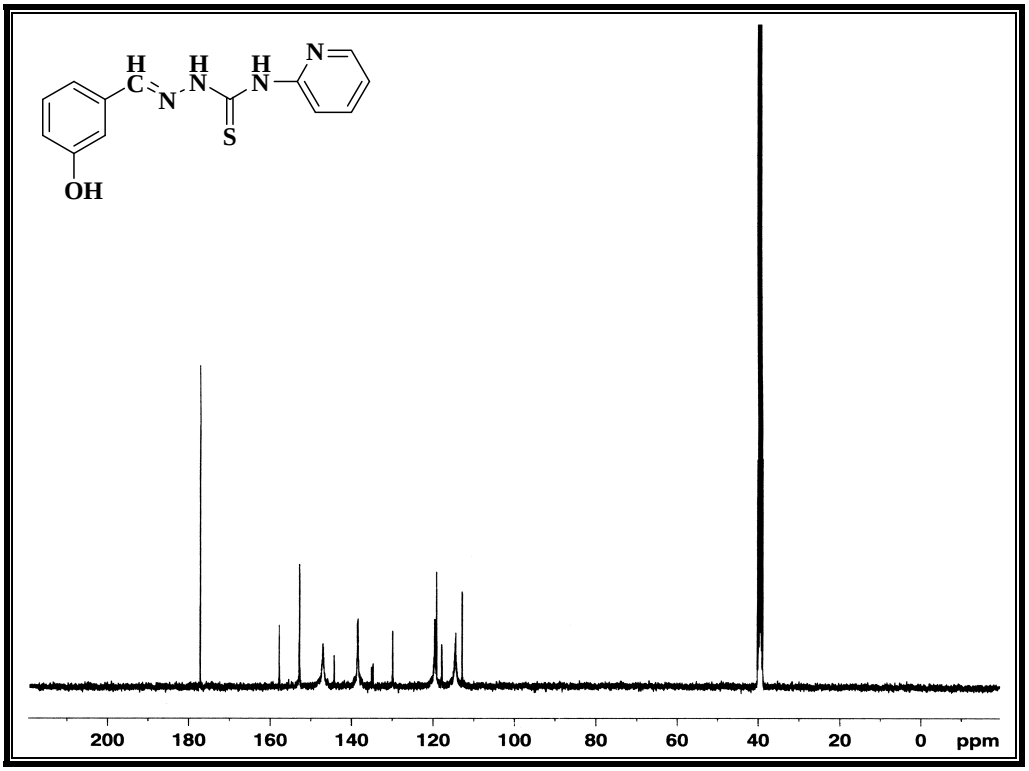
^{1}H NMR spectrum of TRM-13



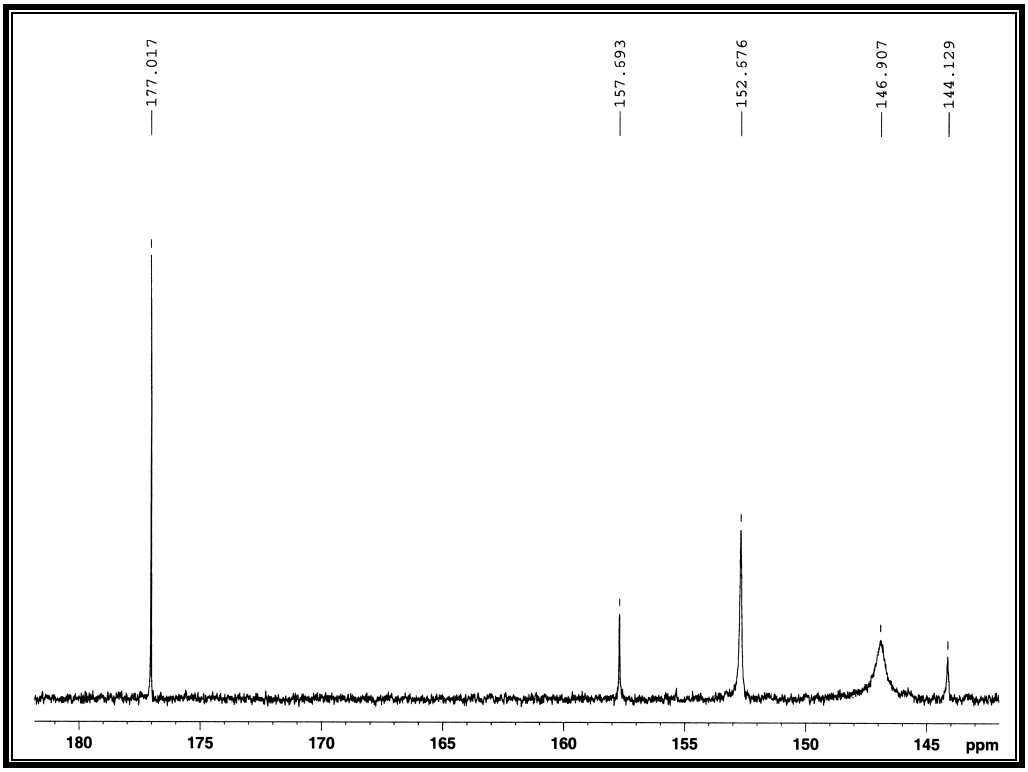
Expanded ^{1}H NMR spectrum of TRM-13



^{13}C NMR spectrum of TRM-13



Expanded ^{13}C NMR spectrum of TRM-13



Results & Discussion

In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M+) corresponding to their molecular weight.

Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3281 cm^{-1}, 1049 cm^{-1} and 1288 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1626 cm^{-1}. The other bands of -OH due to at 3417 cm^{-1} and aromatic -C-H and -C=C bands due to at 3144-2953 cm^{-1} and 1467 cm^{-1} respectively.

In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 8.14 ppm as a singlet. The, -C-NH, -N-NH and -OH protons were observed at 10.01 ppm, 12.11 ppm and 9.67 ppm as a singlet, respectively. All

the aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 144.12 ppm and -C=S carbon, appeared at 177.01 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

All spectral characterization and elemental analysis confirm the structure of 1-(3-hydroxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(TRM-13).

CHAPTER-III

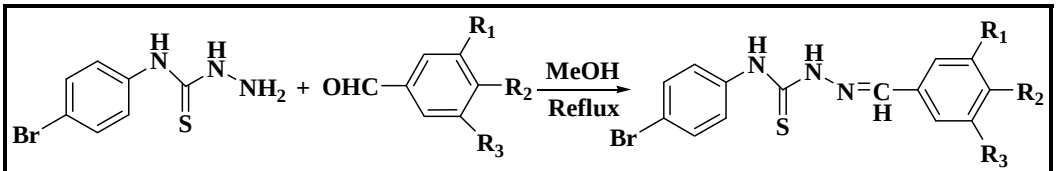
SYNTHESIS AND CHARACTERIZATION OF 1-SUBSTITUTED ARYLIDENE-4-(4-BROMO-PHENYL)THIOSEMICARBAZIDE

1.4.1 EXPERIMENTAL SECTION

Synthesis of Ligands

General procedure for the synthesis of 1-substituted arylidene-4-(4-bromophenyl)thiosemicarbazide.

The methanolic solution of 4-(4-bromophenyl)thiosemicarbazide (0.01 M) and substituted aldehyde (0.01 M) were refluxed on a boiling water bath for 24 hours with catalytic amount of gl. acetic acid, reaction was monitored by TLC. After completion of the reaction, reaction mixture was poured into crushed ice. The separated product was filtered wash with sodium bisulphite solution and dried at room temperature.



SCHEME - 5 **TRM - 14 & 15**

Table - 5

Comp. Code	R_1	R_2	R_3	Yield %	M. P. °C	R_f
TRM-14	$-OCH_3$	-OH	-Br	79	220	0.48
TRM-15	$-OCH_3$	$-OCH_3$	-H	82	176	0.64

TLC solvent system - benzene:acetone **(**8:2)

1.4.2 SPECTRAL DATA OF THE SYNTHESIZED LIGANDS

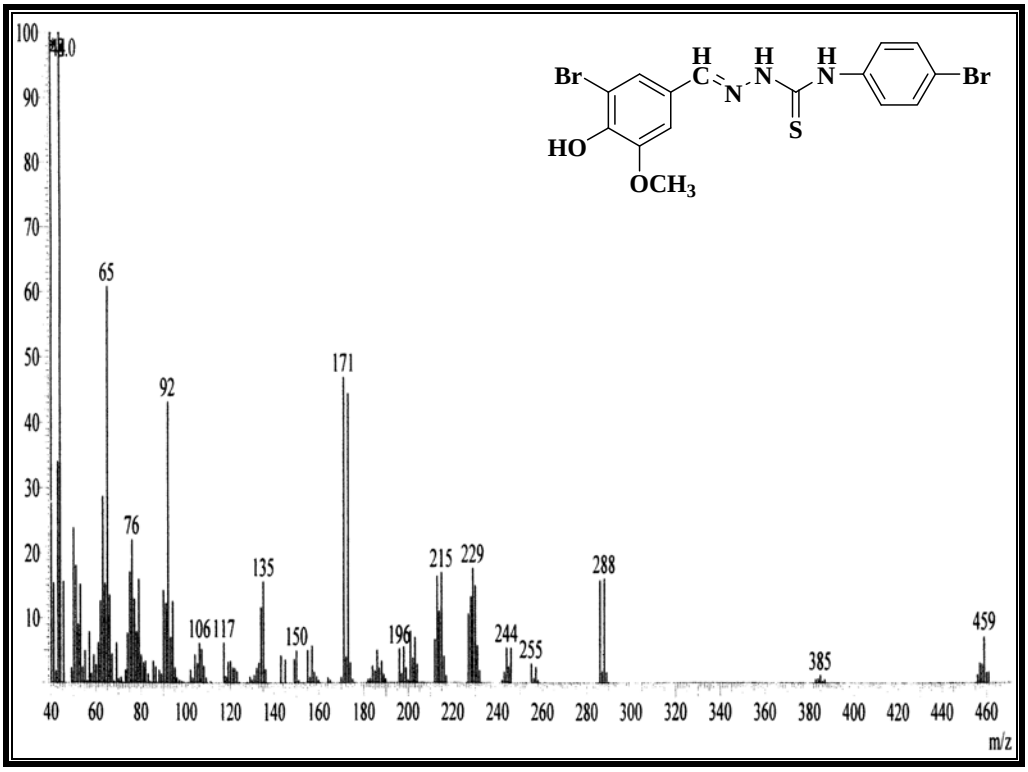
[1] 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide(TRM-14)

Colour: Yellow; **Anal. Calcd**. For $C_{15}H_{13}Br_2N_3O_2S$ (459.16 g/mol): C, 39.24%; H, 2.85%; N, 9.15%; S, 6.98%. **Found:** C, 39.16%; H, 2.97%; N, 9.05%; S, 6.90%; **MS** (m/z): 459 (M); **IR (KBr, cm^{-1}):** *v*(OH) 3495; *v*(NH) 3315; *v*(C=N) 1678; *v*(N-N) 1047; *v*(C=S) 1288; δ(C=S) 823; *v*(Ar–C-H) 3147-2983; *v*(Ar–C=C) 1494; *v*(C-Br) 628; **^{1}H-NMR (DMSO-d_6):** δppm 3.91 (s, 3H, OMe); 7.31 (m, 1H, Ar-H); 7.46, (d, 2H, *J* = 8.7 Hz, Ar-H); 7.53, (d, 1H, *J* = 1.6 Hz, Ar-H); 7.58 (m, 2H, Ar-H); 8.01 (s, 1H, HC=N); 9.31 (s, br, 1H, OH); 9.74 (s, 1H, NH); 11.69 (s, 1H, NH); **^{13}C-NMR (DMSO-d_6):** δppm 56.26 (O-CH_3); 109.11, 109.36, 117.61, 124.46, 125.93, 127.40, 128.68, 130.63, 138.22, 145.74, 148.19, 149.81 (Ph); 142.27 (HC=N); 175.42 (C=S); **UV-Vis:(DMF)** (λ_{max}/ nm): 232, 270, 312.

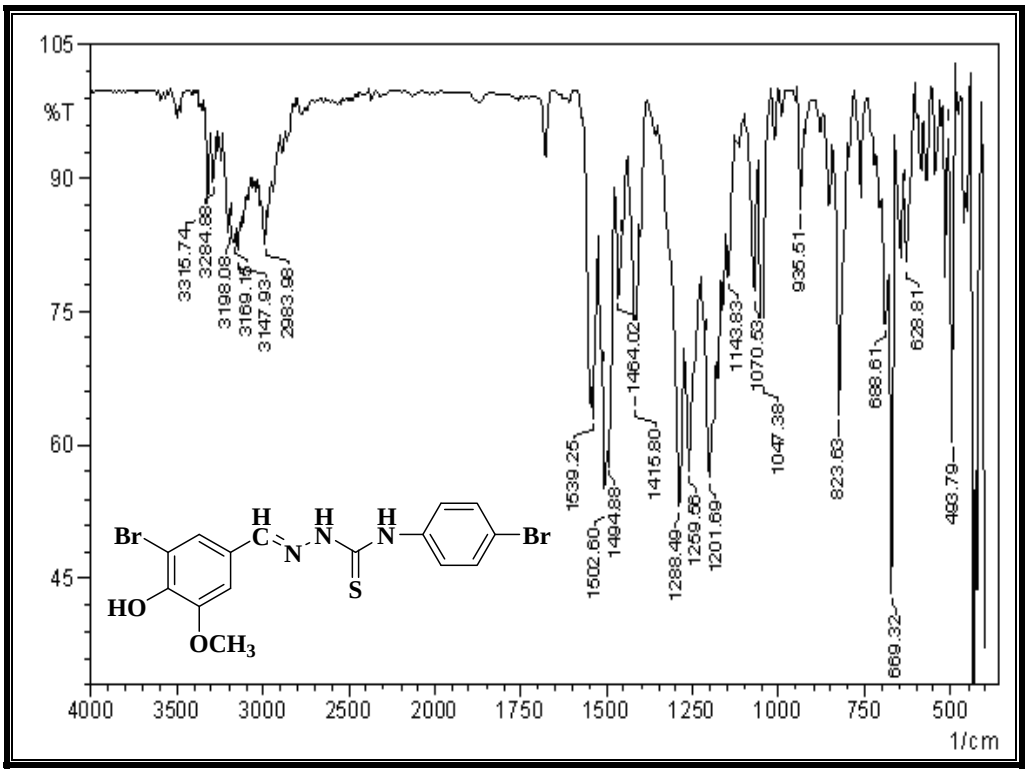
[2] 1-(3,4-dimethoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide(TRM-15)

Colour: Cream; **Anal. Calcd**. For $C_{16}H_{16}BrN_3O_2S$ (394.29 g/mol): C, 48.74%; H, 4.09%; N, 10.66%; S, 8.13%. **Found:** C, 48.81%; H, 4.01%; N, 10.75%; S, 8.06%; **MS** (m/z): 393 (M-1); **IR (KBr, cm^{-1}):** *v*(NH) 3332; *v*(C=N) 1600; *v*(N-N) 1020; *v*(C=S) 1267; δ(C=S) 831; *v*(Ar–C-H) 3151-2998; *v*(Ar–C=C) 1509; *v*(C-Br) 610; **^{1}H-NMR (DMSO-d_6):** δppm 3.88 (s, 3H, OMe); δ 3.93 (s, 3H, OMe); 6.91, (m, 1H, Ar-H); 7.24, (m, 1H, Ar-H); 7.28, (m, 1H, Ar-H); 7.45, (m, 2H, Ar-H); 7.62, (d, 2H, *J* = 8.6 Hz, Ar-H); 8.09 (s, 1H, HC=N); 9.65 (s, 1H, NH); 11.67 (s, 1H, NH); **^{13}C-NMR (DMSO-d_6):** δppm 55.44, 55.49 (O-CH_3); 108.80, 110.64, 117.55, 122.25, 125.20, 126.48, 126.81, 130.67, 138.02, 148.85, 150.63, 160.46 (Ph); 143.45 (HC=N); 175.19 (C=S); **UV-Vis:(DMF)** (λ_{max}/ nm): 286, 366.

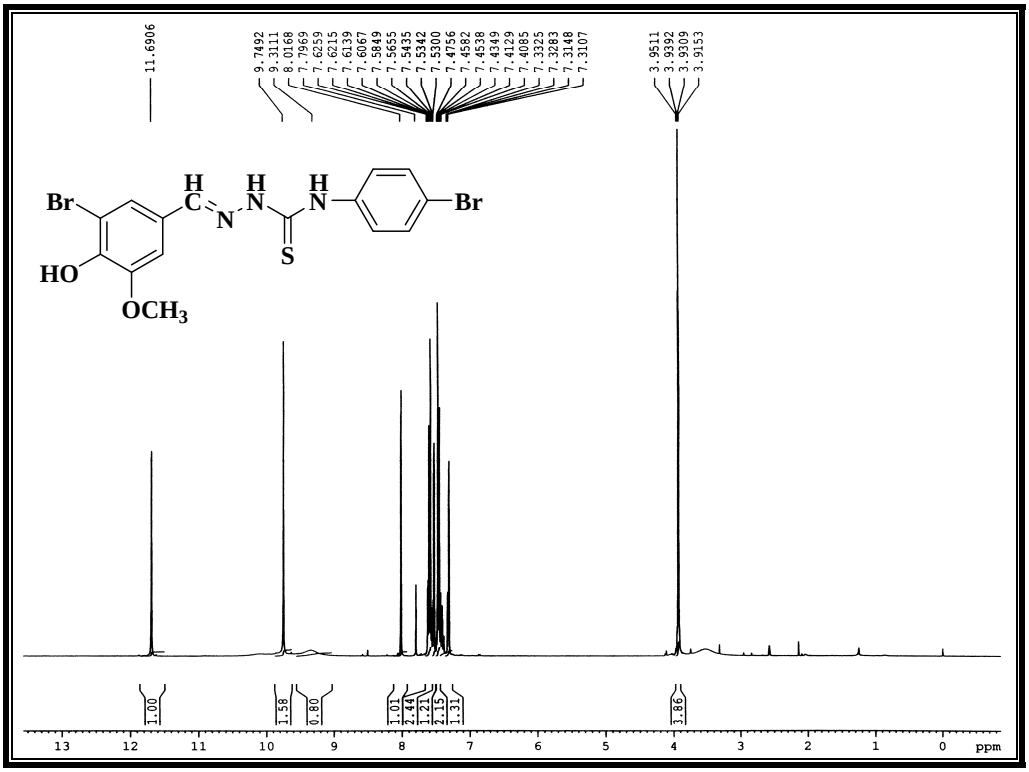
Mass spectrum of TRM-14



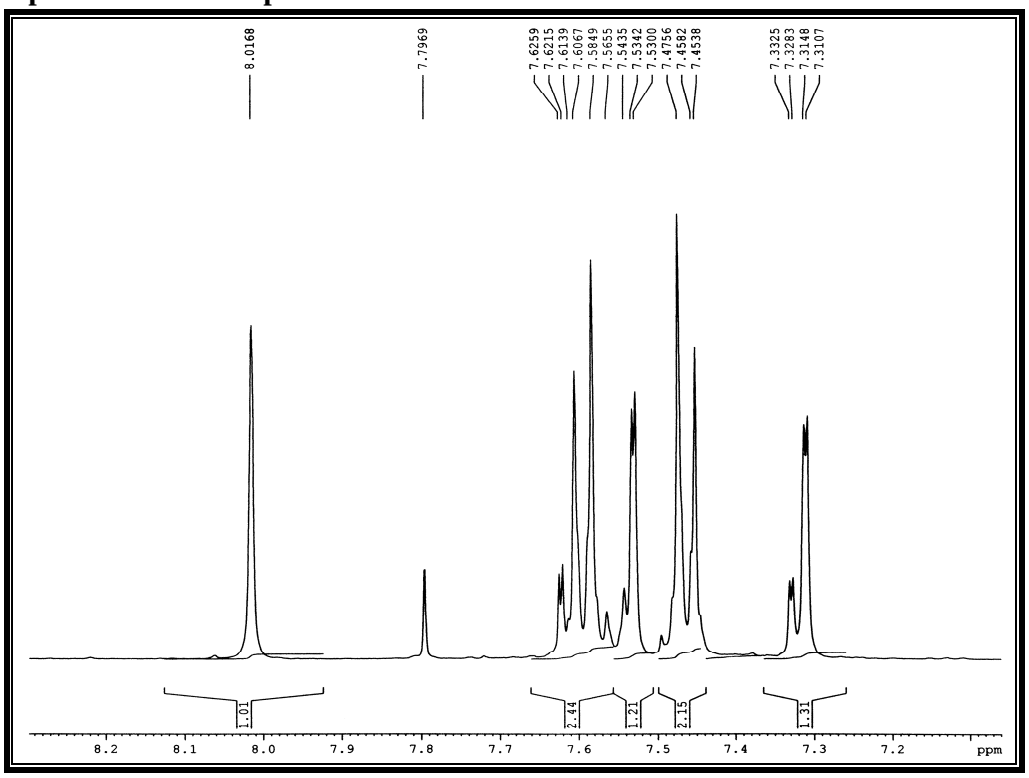
IR spectrum of TRM-14



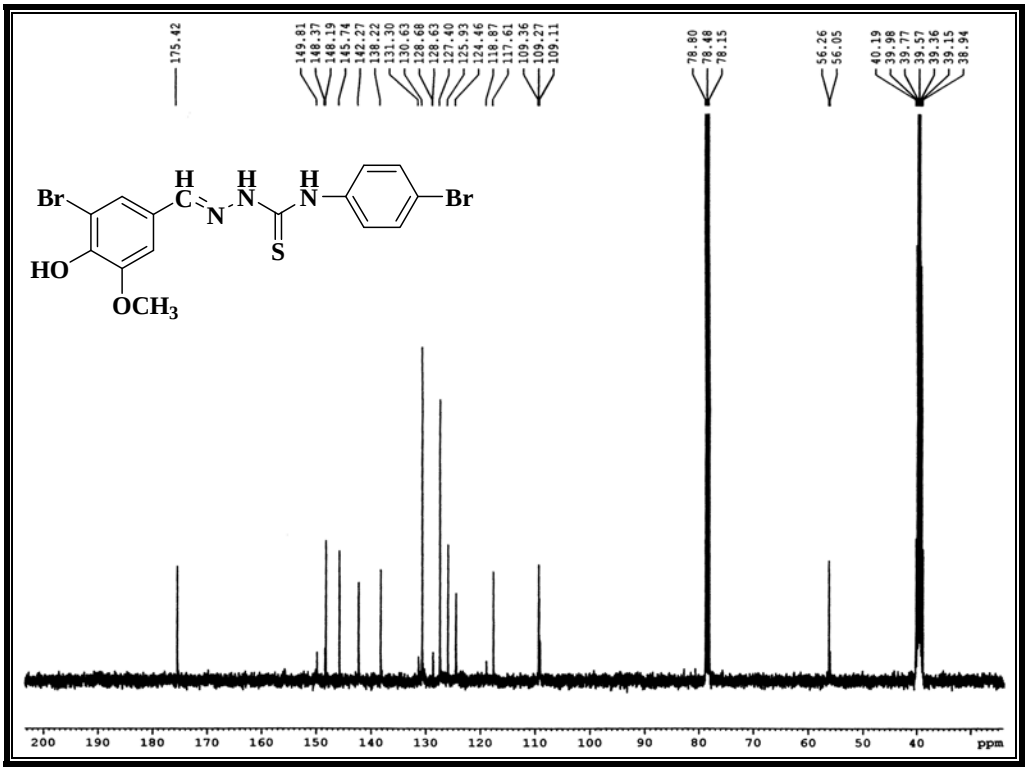
^{1}H NMR spectrum of TRM-14



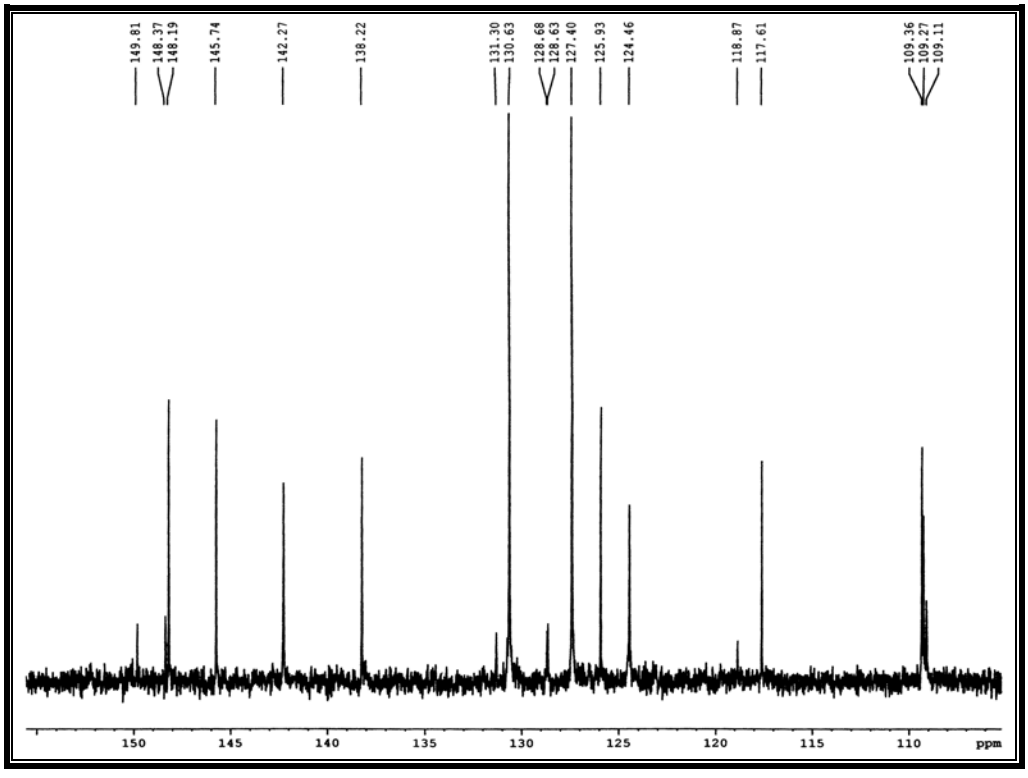
Expanded ^{1}H NMR spectrum of TRM-14



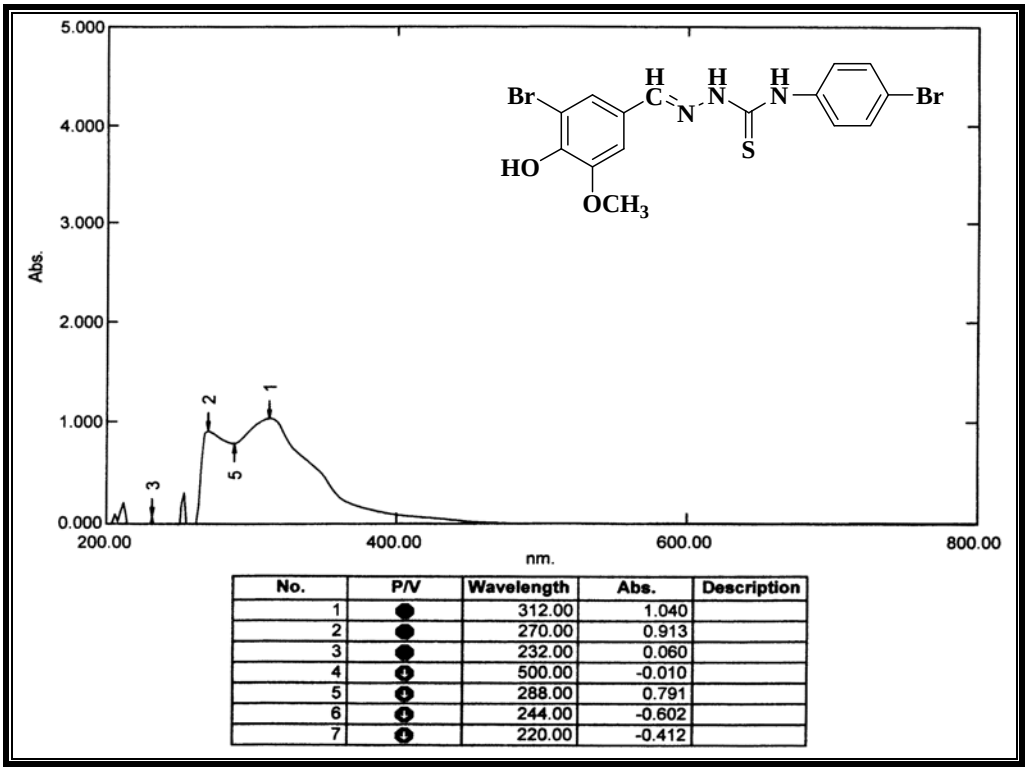
^{13}C NMR spectrum of TRM-14



Expanded ^{13}C NMR spectrum of TRM-14



UV-Visible spectrum of TRM-14



No.	P/V	Wavelength	Abs.	Description
1	●	312.00	1.040	
2	●	270.00	0.913	
3	●	232.00	0.060	
4	●	500.00	-0.010	
5	●	288.00	0.791	
6	●	244.00	-0.602	
7	●	220.00	-0.412	

Results & Discussion

In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M+) corresponding to their molecular weight.

Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3315 cm^{-1}, 1047 cm^{-1} and 1288 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1678 cm^{-1}. The other bands of -OH due to at 3495 cm^{-1} and aromatic -C-H and -C=C bands due to at 3147-2983 cm^{-1} and 1494 cm^{-1} respectively.

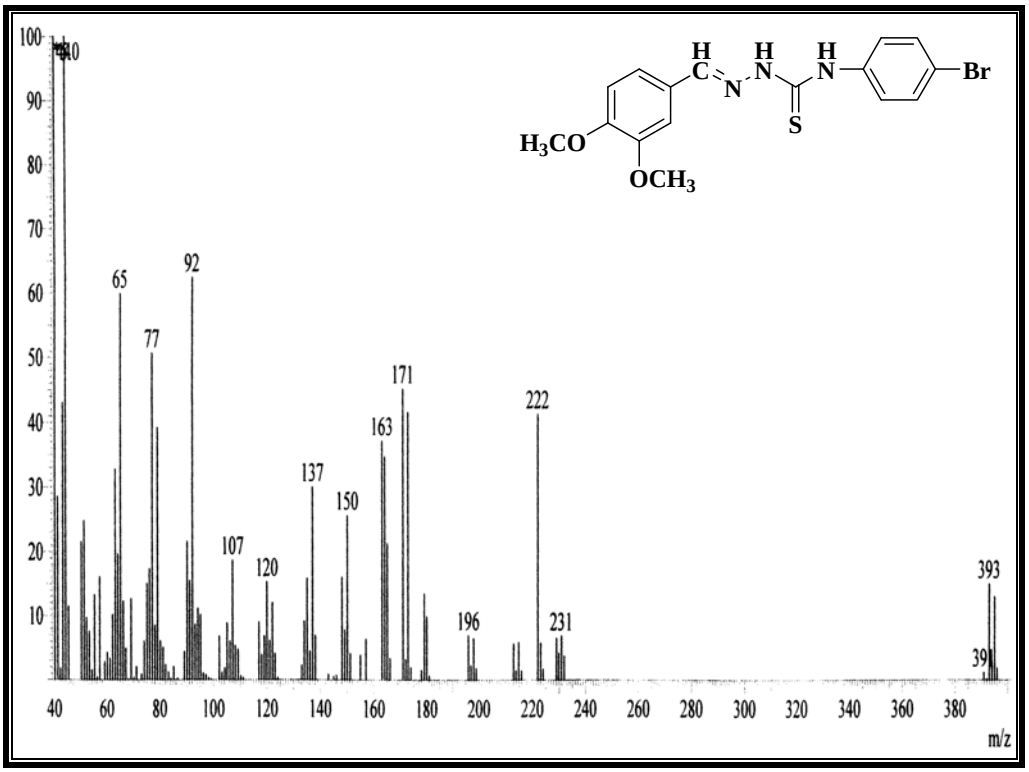
In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 8.01 ppm as a singlet. The, -C-NH, -N-NH and -OH protons were observed at 9.74 ppm, 11.69 ppm and 9.31 ppm as a singlet, respectively. All the

aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 142.27 ppm and -C=S carbon, appeared at 175.42 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

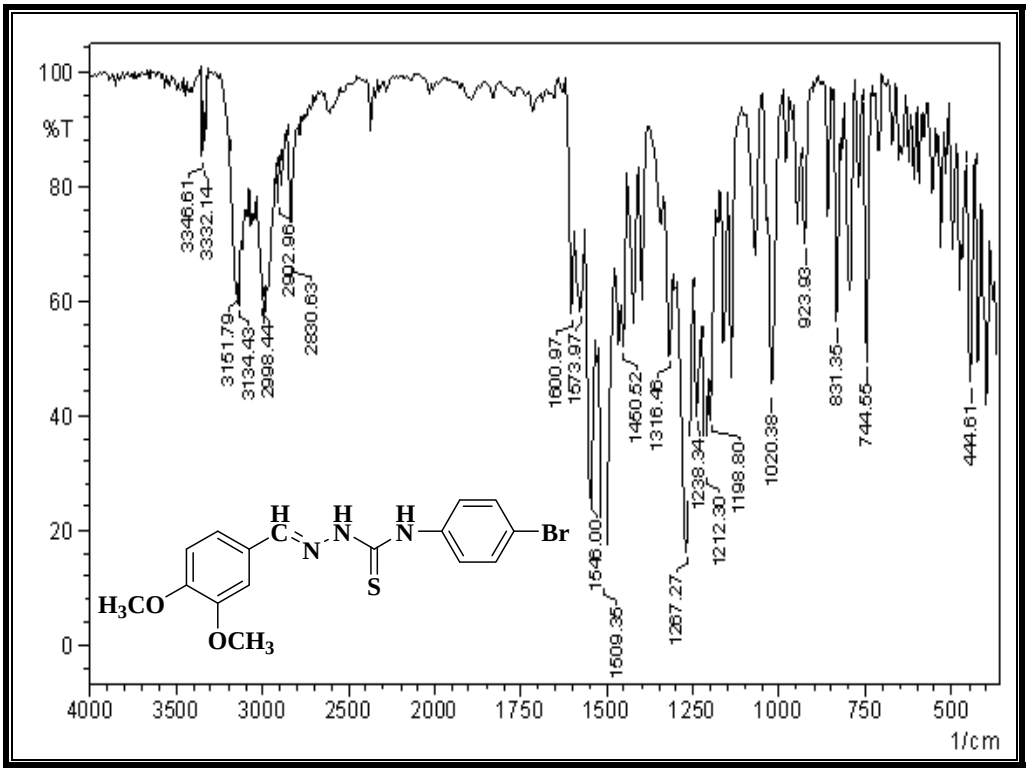
Electronic spectroscopy is a very important tool for the structural identification of synthesized thiosemicarbazone. It is usually measured in the range 200-800 nm. This compound absorb in the region 250-350 nm and the bands are mainly due to at 232, 270 nm $\pi \rightarrow \pi^*$ and 312 nm $n \rightarrow \pi^*$ transitions.

All spectral characterization and elemental analysis confirm the structure of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide (TRM-14).

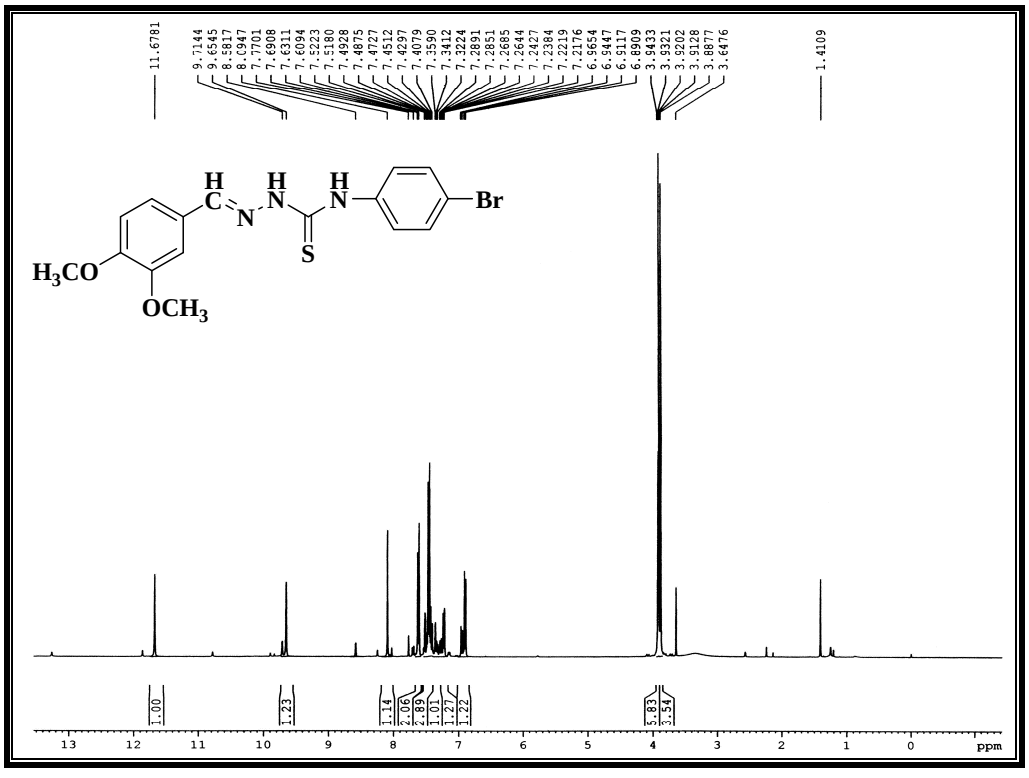
Mass spectrum of TRM-15



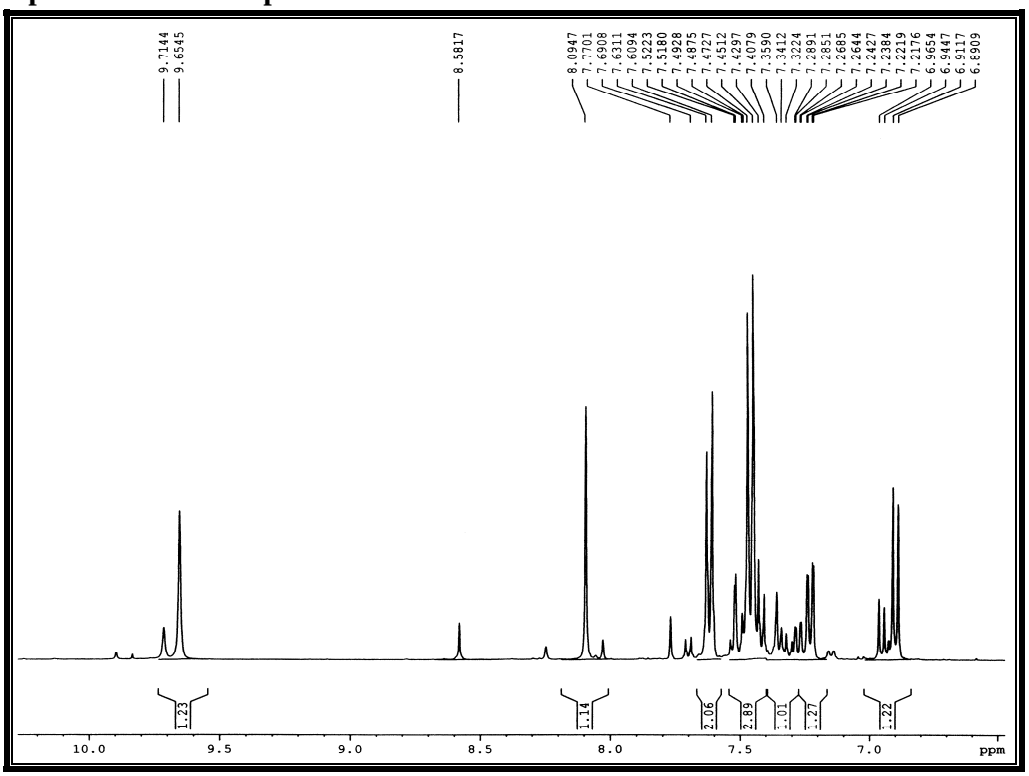
IR spectrum of TRM-15



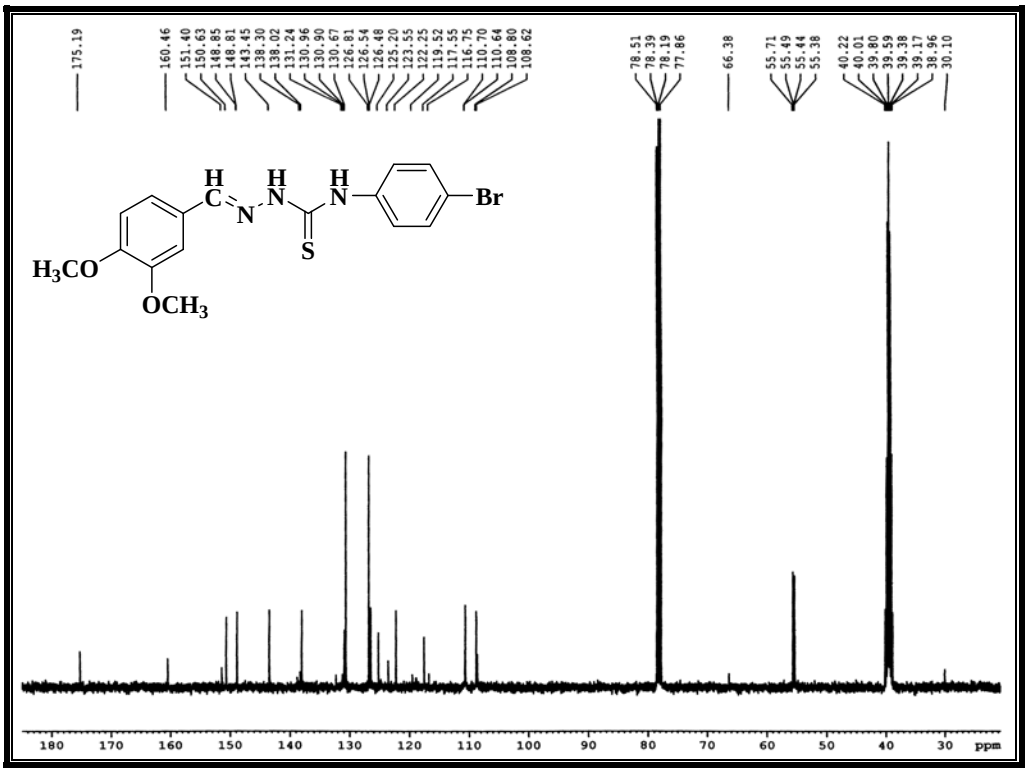
^{1}H NMR spectrum of TRM-15



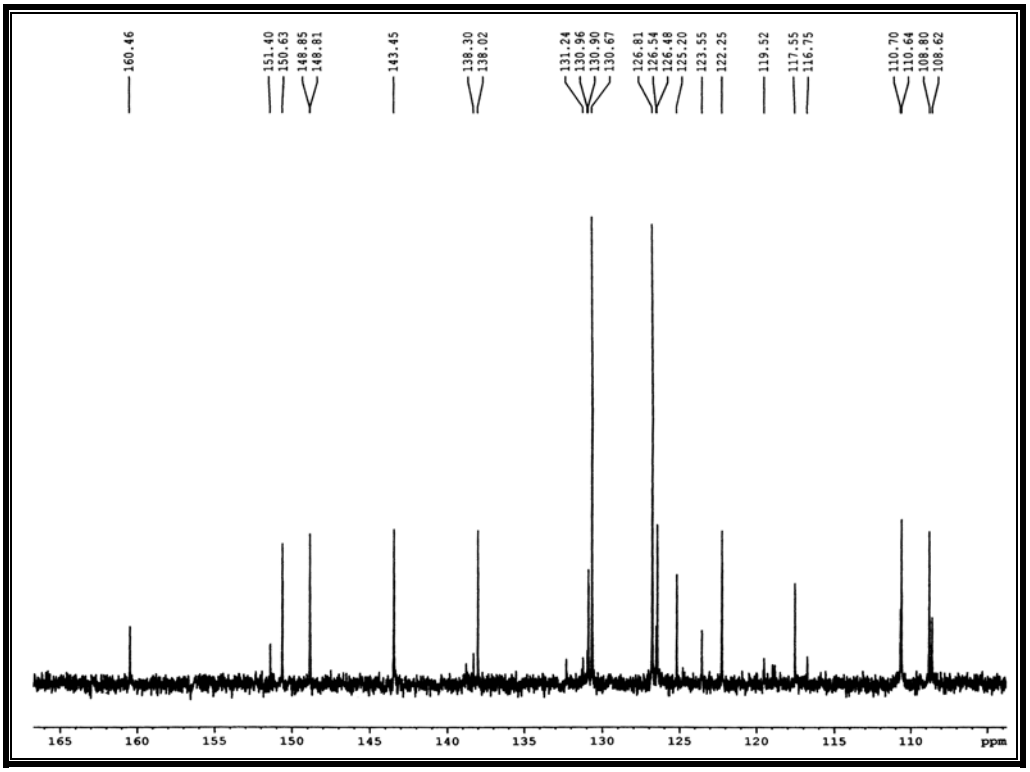
Expanded ^{1}H NMR spectrum of TRM-15



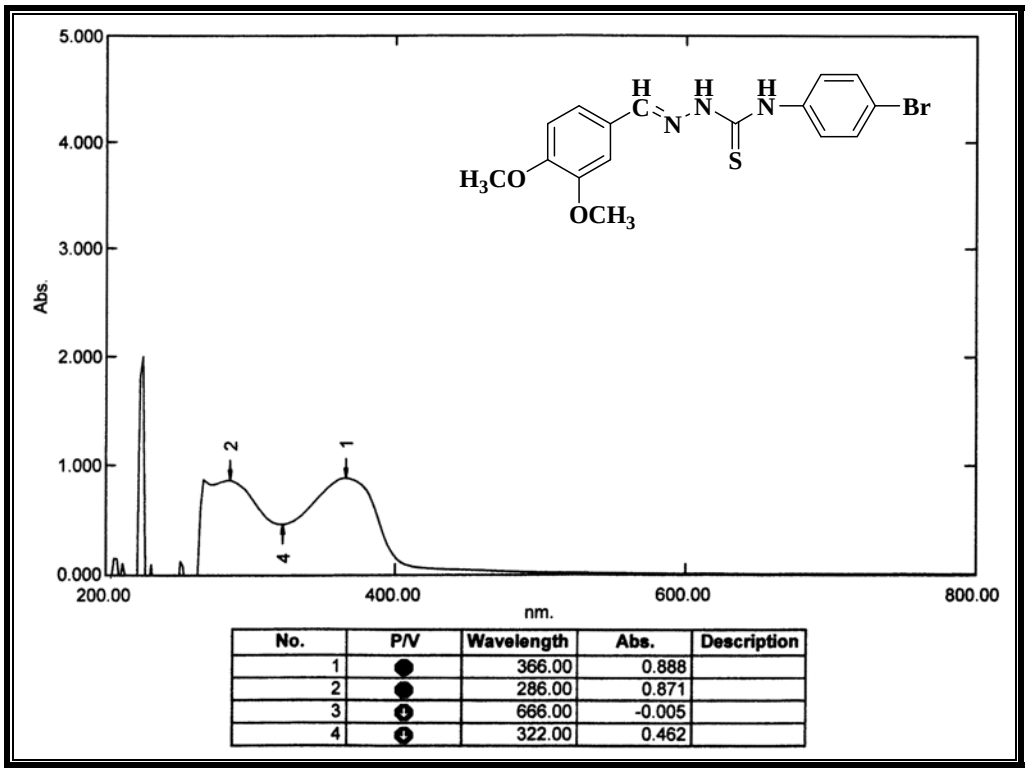
^{13}C NMR spectrum of TRM-15



Expanded ^{13}C NMR spectrum of TRM-15



UV-Visible spectrum of TRM-15



No.	P/V	Wavelength	Abs.	Description
1	●	366.00	0.888	
2	●	286.00	0.871	
3	⊖	666.00	-0.005	
4	⊖	322.00	0.462	

Results & Discussion

In the elemental analysis of the synthesized compound both calculated and found percentages of elements are matched so elemental analysis confirms the structure of the thiosemicarbazone. Mass spectral data confirm the structure of the ligand as indicated by the molecular ion peak (M-1) corresponding to their molecular weight.

Selected diagnostic bands of the IR spectra of the synthesized thiosemicarbazone showed useful information about the structure of the compound. In the IR spectra, some significant stretching bands due to -N-H, -N-N- and -C=S were observed at 3332 cm^{-1}, 1020 cm^{-1} and 1267 cm^{-1} respectively. The specific band for thiosemicarbazone (-CH=N-) was observed at 1600 cm^{-1}. The aromatic -C-H and -C=C bands due to at 3151-2998 cm^{-1} and 1509 cm^{-1} respectively.

In the ^{1}H NMR spectra, the signal due to (-CH=N-) proton, present in this compound, appeared at 8.09 ppm as a singlet. The, -C-NH, -N-NH and -O-CH_3 protons were observed at 9.65 ppm, 11.67 ppm and 3.88 ppm as a singlet, respectively. All the aromatic protons were observed in the expected regions. In the ^{13}C NMR spectra the signal due to (-CH=N-) carbon, appeared at 143.45 ppm and -C=S carbon, appeared at 175.19 ppm and all the aromatic carbons were observed in the expected regions. The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the synthesized compound.

Electronic spectroscopy is a very important tool for the structural identification of synthesized thiosemicarbazone. It is usually measured in the range 200-800 nm. This compound absorb in the region 250-350 nm and the bands are mainly due to at 286 nm $\pi \rightarrow \pi^*$ and 366 nm $n \rightarrow \pi^*$ transitions.

All spectral characterization and elemental analysis confirm the structure of 1-(3,4-dimethoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide(TRM-15).

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Synthesis and characterization of metal complexes

Section - B

2.1 Litreture survey of metal complexes of thiosemicarbazones

The transition metal complexes are far more biologically active than uncoordinated thiosemicarbazone and their enhanced biological activity has been an active area of investigation among medicinal researchers[1]. In general, thiosemicarbazones as chelating ligands with transition metal ions by binding through the thioketo sulphur and hydrazine nitrogen atoms and therefore this type of compounds can coordinate *in vivo* to metal ions. Because of such coordination, the thiosemicarbazones moiety undergoes a sterical reorientation that could favour its biological activity. The biological activity of thiosemicarbazones is also considered to involve the inhibition of ribonucleotide reductase, an obligatory enzyme in DNA synthesis. Ribonucleotide reductase, the enzyme that converts ribonucleotides to deoxy ribonucleotides, is a vital enzyme in DNA synthesis and a key target for the development of antineoplastic agents.

There is also growing consensus on the involvement of toxic oxygen species, such as superoxide and hydroxyl radicals, in many of the disease states for which thiosemicarbazones have been shown to be effective. Recent study has revealed the potential of using copper(II) bis(thiosemicarbazones) as superoxide dismutase (SOD)-like drug at the inter cellular sites[2].

The extreme insolubility of most thiosemicarbazones in water causes difficulty in the oral administration in clinical practice. The introduction of an unprotected carbohydrate moiety as a substituent in the thiosemicarbazones should increase its water solubility and at the same time, its cell membrane permeability. Khadem reported the synthesis of D-arabino-hexos-ulose disemicarbazone. Horton *et al* reported the synthesis of 3-deoxy-aldos-2-ulose-bis (thiosemicarbazones)[3]. Similarly when the ^{4}N substituted thiosemicarbazones moiety is attached to an amide carbon greater solubility in polar solvents is realized.

Thiosemicarbazones can coordinate to metal as neutral molecules or after deprotonation, as anionic ligands and can adopt a variety of different coordination modes. The possibility of their being able to transmit electronic effects between a reduce unit and a metal centre is suggested by the delocalization of the π bonds in the thiosemicarbazone chain[4]. Transition metal complexes with thiosemicarbazone exhibit a wide range of stereochemistry, biomimic activity and have potential application as sensors.

Recently radionuclides have attracted considerable attention in nuclear medicine because they include isotopes with both diagnostic and therapeutic potential[5]. They are becoming increasingly available to the medicinal community using generator systems and improvements in small cyclotron production. It is reported that Ga(III) complexes of 2-acetylpyridine thiosemicarbazones gained more attention because they offer a convenient source of γ-ray emitters for position emission tomography imaging in institutions that do not have a site cyclotron[6]. Recently Kepper *et al* developed gallium complexes which showed profound antiviral and antitumor activity with energy, which make them useful for medical diagnostic agent[7]. There appeared some reports on the synthesis and single crystal studies of thiosemicarbazones of aluminum.

Thiosemicarbazones exhibit significant antimycobacterial activity against both tubercle and leprosy bacilli *in vivo.* The antibacterial activity of thiosemicarbazones against mycobacterium tuberculosis *in vitro* was first reported by Domagk *et.al* and later confirmed *in vivo.* The most important one is thiacetazone (p-acetamido benzaldehyde) thiosemicarbazones. The drawbacks such as toxic effects including hemolytic anemia, edema, excessive skin eruptions and hepatic dysfunctions and development of resistance to the drugs are overcome by coupling thiacetazone with other antitubercular drugs, especially isoniazide. Dobek *et al* reported[8] the synthesis of certain thiosemicarbazones derived from 2-acetylpyridine, having substantial clinical significance for human beings.

Recently it is reported that thiosemicarbazones of 2-acetylpyridine possess antileprotic activity and ribonucleotide diphosphate reductase (RDR) activity. This series of compounds correlates well with the observed antileprotic properties in mycobacterial systems suitable for *in vitro* testing[9]. The strong metal chelating ability of tridentate thiosemicarbazones is thought to be responsible for their biological activity and any alteration that hinders this chelation leads to loss of activity. Recently there appeared a report on the biological effects of thiosemicarbazones on Friend erytholeukemia cells by an *in vitro* test[10].

The structural and biological studies of copper(II) complexes with thiosemicarbazones are reported by West *et al*[11]. Concerning the exact mechanism by which the Cu(II) complexes exert the anti tumor activity is not clear due to large number of potential sites of action within the cell and the difficulties associated with

monitoring and unequivocally assigning a reaction to a particular step. One of the proposed mechanisms is the interaction of the copper(II) drug with the thiol containing enzyme ribionucleoside diphosphate reductase, which is required for the synthesis of DNA precursors[12].

The nature of the substituent attached at ^{4}N can influence the biological activity, while the acid character of the ^{3}NH allows the ligand to be anionic and conjugation to be extended to include the thiosemicarbazones moiety. It has been proposed that this conjugated system enhances the antitumor activity. Extensive literatures on the antitumor properties of many heterocyclic carboxaldehyde thiosemicarbazones having uncommon coordination geometries are now available

Thiosemicarbazones and their copper complexes have been studied in recent years owing to their pharmacological interest. Thiosemicarbazones react as chelating ligands with transition metal ions by bonding through the thioketo sulphur and hydrazine nitrogen atoms. Therefore these types of compounds can coordinate *in* vivo to metal ion. Because of such coordination, the thiosemicarbazone moiety undergoes a sterical reorientation that could favor its biological activity.

Copper forms a variety of octahedral square planar square pyramidal, trigonal bipyramidal complexes with thiosemicarbazones. Electrochemical, structural and spectral investigations offer an insight in understanding various physico chemical properties such as stabilities, reaction pathways and structures and such information as are reported[13]. Biological activities of some N-N-S donor ligands have been screened and the results were appealing. Initial interest in such substituted derivatives of thiosemicarbazones derivatives arose from their marked antibacterial properties. It is reported that the nature of the substituent attached to the ^{4}N position of thiosemicarbazone can influence the biological activity while the acid character of ^{2}NH allows the ligand to be anionic and conjugation to be extended to include the thiosemicarbazone moiety[14]. It has been proposed that this conjugated system enhances the antitumour activity. Most studies to date have focused on the metal free ligands; it has been shown that they are inactive or partially active than the metal free chelates. The thiosemicarbazones have been found to be more active against influenza protozoa, smallpox, and certain kinds of tumor. They have been suggested as possible pesticides and fungicides. Higher activity of these compounds has frequently been thought to be due to their ability to chelate free metals[15]. Petering *et al* showed that

the active intermediate in the antitumour activity of 3-ethoxy - oxo butralehyde bis (thiosemicarbazone) was the copper(II) chelate. These findings have lead recently to an increased interest in the chemistry of copper chelate of thiosemicarbazones[16].

Thiosemicarbazones and their metal complexes have been very promising compounds among Schiff bases, due to their beneficial biological applications[17]. Domag *et al.*[18] had reported that thiosemicarbazones possess antitubercular activity and after that, many papers on the pharmacology of these compounds appeared, indicating that they have wide inhibitory activity against smallpox[19] and several kinds of tumours[20]. They can also be used as pesticides[21] and fungicides[22]. Presence of various donor atoms and ability to change dentacity depending on the reaction conditions and starting reagents make thiosemicarbazones of various aldehydes and ketones a special category among organic ligands[23].

2.2 CHAPTER-I

Synthesis and characterization of Cu(II), Ni(II) and Co(II) complexes of 1-substituted aryl/pyrazolyl/quinolinyl thiosemicarbazide

2.3 CHAPTER-II

Synthesis and characterization of Cu(II), Ni(II) and Co(II) complexes of 1-substituted arylidene-4-(pyridin-2-yl) thiosemicarbazide

2.4 CHAPTER-III

Synthesis and characterization of Cu(II), Ni(II) and Co(II) complexes of 1-substituted arylidene-4-(4-bromophenyl) thiosemicarbazide

CHAPTER-I

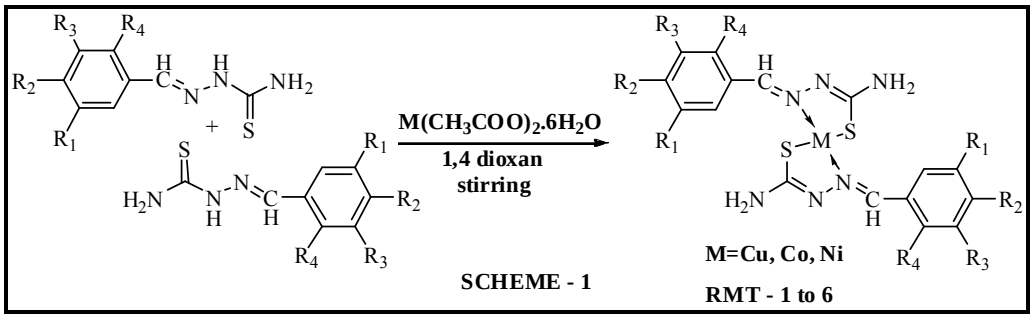
SYNTHESIS AND CHARACTERIZATION OF CU(II), NI(II) AND CO(II) COMPLEXES OF 1-SUBSTITUTED ARYL/PYRAZOLYL/ QUINOLINYL THIOSEMICARBAZIDE

2.2.1 EXPERIMENTAL SECTION

Synthesis of metal complexes

General procedure for the synthesis of copper(II), nickel(II) and cobalt(II) complexes of 1-substituted aryl thiosemicarbazide.

The corresponding metal acetate (0.01mol) was dissolved in minimum quantity of water and then was added to the hot solution of ligand (0.02 mol) in methanol (50-60 ml). The reaction mixture was heated on 80-90 °C for 1 hour with constant stirring and than the reaction mixture stirred for 3 days, until a colored solid mass separated out. The precipitate was filtered, washed with methanol and finally with diethyl ether and dried *in vacuum*.



SCHEME - 1

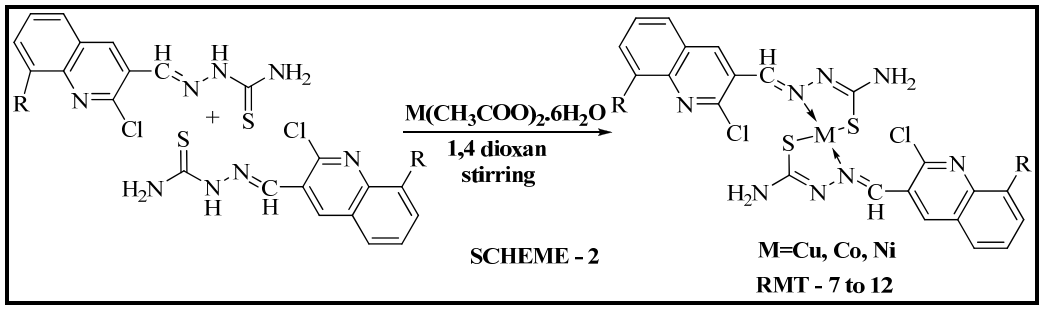
RMT - 1 to 6

TABLE - I

Comp. Code	M	R_1	R_2	R_3	R_4	Yield %	M. P. °C	Λ_m (Ω^{-1} cm^2 mol^{-1})	μ_{eff} B. M.
RMT-1	Cu(II)					76	192	3.52	1.80
RMT-2	Ni(II)	$-OCH_3$	-OH	-Br	-H	72	244	3.45	3.15
RMT-3	Co(II)					75	250	4.24	4.10
RMT-4	Cu(II)					62	234	4.67	2.11
RMT-5	Ni(II)	$-OCH_3$	$-OCH_3$	-H	$-NO_2$	70	280	3.81	3.38
RMT-6	Co(II)					68	278	4.06	4.78

General procedure for the synthesis of copper(II), nickel(II) and cobalt(II) complexes of 1-substituted quinolinyl thiosemicarbazide.

A quantity of 0.02 M 1-substituted quinolinyl thiosemicarbazide was dissolved in 50 ml 1,4 dioxan and a solution of the metal acetate (0.01 M) dissolved in minimum quantity of distilled water was added drop wise with the continues stirring, the mixture was stirred 80 °C for 1 hour. and continues stirred for 3 days at room temperature, The resulting mass were filtered and washed with distilled water and dried over P_2O_5 in a vacuum desiccator for 36 hours.



SCHEME - 2

TABLE - II

Comp. Code	M	R	Yield %	M. P. °C	Λ_m (Ω^{-1} cm^2 mol^{-1})	μ_{eff} B. M.
RMT-7	Cu(II)		58	308	4.31	2.16
RMT-8	Ni(II)	-H	68	262	3.88	3.22
RMT-9	Co(II)		71	354	4.10	4.56
RMT-10	Cu(II)		66	230	3.55	2.03
RMT-11	Ni(II)	$-CH_3$	63	256	4.13	3.71
RMT-12	Co(II)		75	272	4.24	4.25

General procedure for the synthesis of copper(II), nickel(II) and cobalt(II) complexes of 1-substituted pyrazolyl thiosemicarbazide.

To a solution of the Metal acetate (0.01 mol) in minimum quantity of distilled water was added to the hot methanolic solution of 1-substituted pyrazolyl thiosemicarbazide (0.02 mol) and heated at 80 °C with constant stirring for 1 hour. Than continues stirring for 3 days at room temperature after completion the reaction solid product was filtered, washed thoroughly with water, methanol and dried *in vacuum.*

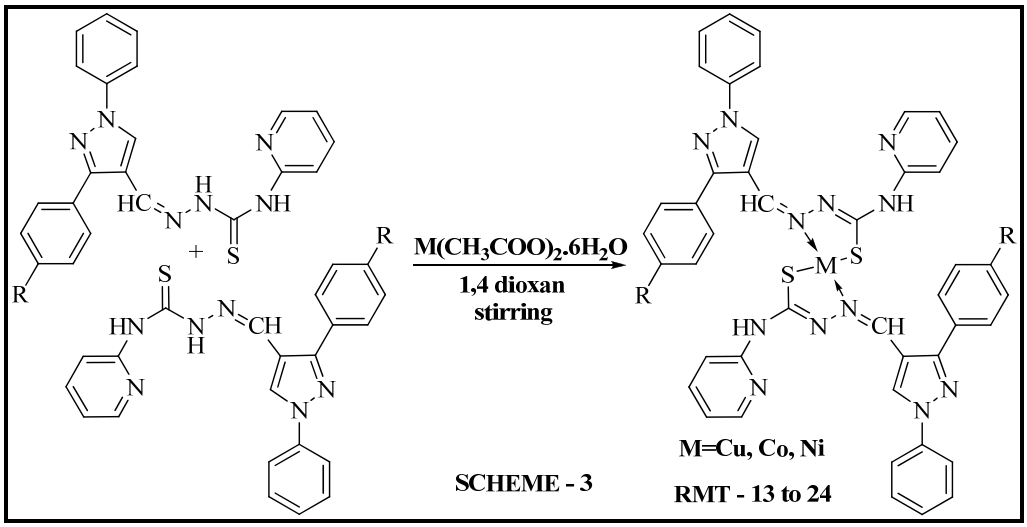


TABLE - III

Comp. Code	M	R	Yield %	M. P. °C	Λ_m (Ω^{-1} cm^2 mol^{-1})	μ_{eff} B. M.
RMT-13	Cu(II)		74	218	3.91	2.01
RMT-14	Ni(II)	-OCH_3	69	268	4.25	3.15
RMT-15	Co(II)		65	238	3.45	4.32
RMT-16	Cu(II)		78	230	4.72	1.91
RMT-17	Ni(II)	-H	70	254	4.59	3.10
RMT-18	Co(II)		67	228	4.97	4.24
RMT-19	Cu(II)		80	294	4.28	1.85
RMT-20	Ni(II)	-Cl	77	298	4.24	3.24
RMT-21	Co(II)		76	238	3.36	4.30
RMT-22	Cu(II)		66	210	4.88	1.95
RMT-23	Ni(II)	-NO_2	72	244	3.71	3.40
RMT-24	Co(II)		70	238	3.49	4.41

2.2.2 SPECTRAL DATA OF THE SYNTHESIZED METAL COMPLEXES

[1] Copper(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide(RMT-1).

Colour: Cream, **Anal. Calcd**. For $C_{18}H_{18}Br_2CuN_6O_4S_2$ (669.86 g/mol): C, 32.27%; H, 2.71%; N, 12.55%; S, 9.57%; Cu, 9.49%. **Found:** C, 32.40%; H, 2.58%; N, 12.46%; S, 9.51%; Cu, 9.62%; **ESI MS** (m/z): 671.1 (CuL_2)+; **IR (KBr, cm^{-1}):** *ν*(OH) 3471; *ν*(NH_2) 3246; *ν*(C=N) 1577; *ν*(N-N) 1045; *ν*(C=S) 1267; δ(C=S) 846; *ν*(Ar–C-H) 3136-3009; *ν*(Ar–C=C) 1460; *ν*(C-Br) 607; *ν*(Cu-N) 505; *ν*(Cu-S) 426; **^{1}H-NMR (DMSO-d$_6$):** δppm 3.81 (s, 3H, OMe); 6.65, (d, 2H, Ar-H); 7.40 (s, 2H, NH_2); 8.26 (s, 1H, HC=N); 9.66 (s, 1H, OH); **UV-Vis:(DMF)** (λ_{max}/ nm): 290, 348, 748; **TGA wt. loss in %(temp.):** 5.77 (100°C); 11.07 (200°C); 35.56 (300°C); 47.28 (400°C); 52.21 (500°C); 57.67 (600°C); 66.91 (700°C); 75.09 (800°C).

[2] Nickel(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide(RMT-2).

Colour: Gray, **Anal. Calcd**. For $C_{18}H_{18}Br_2N_6NiO_4S_2$ (665.0 g/mol): C, 32.51%; H, 2.73%; N, 12.64%; S, 9.64%; Ni, 8.83%. **Found:** C, 32.42%; H, 2.60%; N, 12.75%; S, 9.59%; Ni, 8.96%; **ESI MS** (m/z): 665.0 (NiL_2)+; **IR (KBr, cm^{-1}):** *ν*(OH) 3444; *ν*(NH_2) 3252; *ν*(C=N) 1577; *ν*(N-N) 1045; *ν*(C=S) 1286; δ(C=S) 873; *ν*(Ar–C-H) 3099-3014; *ν*(Ar–C=C) 1433; *ν*(C-Br) 610; *ν*(Ni-N) 538; *ν*(Ni-S) 416; **^{1}H-NMR (DMSO-d$_6$):** δppm 3.86 (s, 3H, OMe); 7.33, (d, 2H, Ar-H); 7.91 (s, 2H, NH_2); 8.02 (s, 1H, HC=N); 9.64 (s, br, 1H, OH); **UV-Vis:(DMF)** (λ_{max}/ nm): 266, 332, 740; **TGA wt. loss in %(temp.):** 0.00 (100°C); 4.83 (200°C); 37.65 (300°C); 56.54 (400°C); 71.89 (490°C).

[3] Cobalt(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide(RMT-3).

Colour: Pink, **Anal. Calcd**. For $C_{18}H_{18}Br_2CoN_6O_4S_2$ (665.24 g/mol): C, 32.50%; H, 2.73%; N, 12.63%; S, 9.64%; Co, 8.86%. **Found:** C, 32.62%; H, 2.65%; N, 12.51%; S, 9.73%; Co, 8.77%; **ESI MS** (m/z): 663.5 (CoL_2)+; **IR (KBr, cm^{-1}):** *ν*(OH) 3450; *ν*(NH_2) 3252; *ν*(C=N) 1581; *ν*(N-N) 1024; *ν*(C=S)

1257; δ(C=S) 829; *v*(Ar–C-H) 3117-3009; *v*(Ar–C=C) 1492; *v*(C-Br) 617; *v*(Co-N) 505; *v*(Co-S) 416; **^{1}H-NMR (DMSO-d_6):** δppm 3.39 (s, 3H, OMe); 7.39, (d, 2H, Ar-H); 7.91 (s, 2H, NH_2); 8.14 (s, 1H, HC=N); 9.64 (s, 1H, OH); **UV-Vis:(DMF)** (λ_{max}/ nm): 288, 332, 744; **TGA wt. loss in %(temp.):** 1.20 (100°C); 5.90 (200°C); 31.44 (300°C); 42.91 (400°C); 48.21 (490°C).

[4] Copper(II) complex of 1-(4,5-dimethoxy-2-nitrobenzylidene)thiosemicarbazide(RMT-4).

Colour: Yellow, **Anal. Calcd**. For $C_{20}H_{22}CuN_8O_8S_2$ (630.11 g/mol): C, 38.12%; H, 3.52%; N, 17.78%; S, 10.18%; Cu, 10.08%. **Found:** C, 38.01%; H, 3.60%; N, 17.91%; S, 10.06%; Cu, 9.99%; **ESI MS** (m/z): 631.3 (CuL_2)+; **IR (KBr, cm^{-1}):** *v*(NH_2) 3282; *v*(C=N) 1599; *v*(N-N) 1060; *v*(C=S) 1288; δ(C=S) 826; *v*(Ar–C-H) 3171-3010; *v*(Ar–C=C) 1514; *v*(C-NO_2) 1332; *v*(Cu-N) 526; *v*(Cu-S) 400.

[5] Nickel(II) complex of 1-(4,5-dimethoxy-2-nitrobenzylidene)thiosemicarbazide(RMT-5).

Colour: Orange, **Anal. Calcd**. For $C_{20}H_{22}N_8NiO_8S_2$ (625.26 g/mol): C, 38.42%; H, 3.55%; N, 17.92%; S, 10.26%; Ni, 9.39%. **Found:** C, 38.55%; H, 3.67%; N, 18.03%; S, 10.10%; Ni, 9.23%; **ESI MS** (m/z): 625.1 (NiL_2)+; **IR (KBr, cm^{-1}):** *v*(NH_2) 3219; *v*(C=N) 1589; *v*(N-N) 1037; *v*(C=S) 1259; δ(C=S) 824; *v*(Ar–C-H) 3178-3010; *v*(Ar–C=C) 1537; *v*(C-NO_2) 1344; *v*(Ni-N) 522; *v*(Ni-S) 406.

[6] Cobalt(II) complex of 1-(4,5-dimethoxy-2-nitrobenzylidene)thiosemicarbazide(RMT-6).

Colour: Yellow, **Anal. Calcd**. For $C_{20}H_{22}CoN_8O_8S_2$ (625.5 g/mol): C, 38.40%; H, 3.55%; N, 17.91%; S, 10.25%; Co, 9.42%. **Found:** C, 38.51%; H, 3.46%; N, 17.98%; S, 10.11%; Co, 9.50%; **ESI MS** (m/z): 617.2 (CoL_2)+; **IR (KBr, cm^{-1}):** *v*(NH_2) 3221; *v*(C=N) 1597; *v*(N-N) 1041; *v*(C=S) 1282; δ(C=S) 829; *v*(Ar–C-H) 3088-3007; *v*(Ar–C=C) 1514; *v*(C-NO_2) 1338; *v*(Co-N) 518; *v*(Co-S) 414.

[7] Copper(II) complex of 1-((2-chloroquinolin-3-yl)methylene)thiosemicarbazide(RMT-7).

Colour: Brown, **Anal. Calcd**. For $C_{22}H_{16}Cl_2CuN_8S_2$ (591.0 g/mol): C, 44.71%; H, 2.73%; N, 18.96%; S, 10.85%; Cu, 10.75%. **Found:** C, 44.64%; H, 2.87%; N, 18.80%; S, 10.97%; Cu, 10.68%; **ESI MS** (m/z): 595.4 (CuL_2)+; **IR (KBr, cm^{-1}):** $\nu(NH_2)$ 3252; ν(C=N) 1566; ν(N-N) 1099; ν(C=S) 1251; δ(C=S) 835; ν(Ar–C-H) 3142-2928; ν(Ar–C=C) 1491; ν(C-Cl) 752; ν(Cu-N) 503; ν(Cu-S) 401.

[8] Nickel(II) complex of 1-((2-chloroquinolin-3-yl)methylene)thiosemicarbazide(RMT-8).

Colour: Redish, **Anal. Calcd**. For $C_{22}H_{16}Cl_2N_8NiS_2$ (586.15 g/mol): C, 45.08%; H, 2.75%; N, 19.12%; S, 10.94%; Ni, 10.01%. **Found:** C, 44.15%; H, 2.69%; N, 19.01%; S, 11.08%; Ni, 9.91%; **ESI MS** (m/z): 583.3 (NiL_2)+; **IR (KBr, cm^{-1}):** $\nu(NH_2)$ 3284; ν(C=N) 1566; ν(N-N) 1018; ν(C=S) 1172; δ(C=S) 833; ν(Ar–C-H) 3157-2991; ν(Ar–C=C) 1491; ν(C-Cl) 707; ν(Ni-N) 513; ν(Ni-S) 416.

[9] Cobalt(II) complex of 1-((2-chloroquinolin-3-yl)methylene)thiosemicarbazide(RMT-9).

Colour: Yellowish, **Anal. Calcd**. For $C_{22}H_{16}Cl_2CoN_8S_2$ (586.39 g/mol): C, 45.06%; H, 2.75%; N, 19.11%; S, 10.94%; Co, 10.05%. **Found:** C, 45.20%; H, 2.89%; N, 19.02%; S, 9.91%; Co, 10.13%; **ESI MS** (m/z): 589.1 (CoL_2)+; **IR (KBr, cm^{-1}):** $\nu(NH_2)$ 3246; ν(C=N) 1568; ν(N-N) 1097; ν(C=S) 1166; δ(C=S) 846; ν(Ar–C-H) 3155-2987; ν(Ar–C=C) 1490; ν(C-Cl) 769; ν(Co-N) 488; ν(Co-S) 408.

[10] Copper(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide(RMT-10).

Colour: Brown, **Anal. Calcd**. For $C_{24}H_{20}Cl_2CuN_8S_2$ (619.05 g/mol): C, 46.56%; H, 3.26%; N, 18.10%; S, 10.36%; Cu, 10.27%. **Found:** C, 46.41%; H, 3.35%; N, 18.03%; S, 10.46%; Cu, 10.15%; **ESI MS** (m/z): 616.5 (CuL_2)+; **IR (KBr, cm^{-1}):** $\nu(NH_2)$ 3292; ν(C=N) 1593; ν(N-N) 1089; ν(C=S) 1209; δ(C=S)

834; *ν*(Ar–C-H) 3147-2953; *ν*(Ar–C=C) 1479; *ν*(C-Cl) 754; *ν*(Cu-N) 518; *ν*(Cu-S) 410; **^{1}H-NMR (DMSO-d$_6$):** δppm 2.64, (s, 3H, CH_3); 7.56, (d, 1H, Ar-H); 7.75, (s, 1H, Ar-H); 8.00, (s, 1H, Ar-H); 8.17, (s, 1H, Ar-H); 8.51 (s, 2H, NH_2); 9.08 (s, 1H, HC=N); **UV-Vis:(DMF)** (λ_{max}/ nm): 266, 290, 332, 348, 748; **TGA wt. loss in %(temp.):** 3.93 (100°C); 7.20 (200°C); 18.46 (300°C); 27.20 (400°C); 33.88 (500°C); 61.68 (600°C); 80.97 (700°C); 78.31 (800°C); 79.54 (900°C).

[11] Nickel(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide(RMT-11).

Colour: Cream, **Anal. Calcd**. For $C_{24}H_{20}Cl_2N_8NiS_2$ (614.2 g/mol): C, 46.93%; H, 3.28%; N, 18.24%; S, 10.44%; Ni, 9.56%. **Found:** C, 46.99%; H, 3.37%; N, 18.11%; S, 10.40%; Ni, 9.43%; **ESI MS** (m/z): 615.2 (NiL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH_2) 3213; *ν*(C=N) 1593; *ν*(N-N) 1084; *ν*(C=S) 1209; δ(C=S) 844; *ν*(Ar–C-H) 3151-2976; *ν*(Ar–C=C) 1475; *ν*(C-Cl) 767; *ν*(Ni-N) 489; *ν*(Ni-S) 416; **^{1}H-NMR (DMSO-d$_6$):** δppm 2.56, (s, 3H, CH_3); 7.62, (d, 1H, Ar-H); 7.80, (s, 1H, Ar-H); 8.02, (s, 1H, Ar-H); 8.26, (s, 1H, Ar-H); 8.56 (s, 2H, NH_2); 9.13 (s, 1H, HC=N); **UV-Vis:(DMF)** (λ_{max}/ nm): 268, 340, 684; **TGA wt. loss in %(temp.):** 2.48 (100°C); 4.73 (200°C); 25.81 (300°C); 33.46 (400°C); 39.44 (500°C); 71.12 (600°C); 76.47 (700°C); 76.15 (800°C); 77.15 (900°C).

[12] Cobalt(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide(RMT-12).

Colour: Brown, **Anal. Calcd**. For $C_{24}H_{20}Cl_2CoN_8S_2$ (614.44 g/mol): C, 46.91%; H, 3.28%; N, 18.24%; S, 10.44%; Co, 9.59%. **Found:** C, 46.78%; H, 3.38%; N, 18.40%; S, 10.53%; Co, 9.47%; **ESI MS** (m/z): 615.2 (CoL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH_2) 3244; *ν*(C=N) 1589; *ν*(N-N) 1085; *ν*(C=S) 1211; δ(C=S) 846; *ν*(Ar–C-H) 3138-2964; *ν*(Ar–C=C) 1475; *ν*(C-Cl) 763; *ν*(Co-N) 486; *ν*(Co-S) 435; **^{1}H-NMR (DMSO-d$_6$):** δppm 2.56, (s, 3H, CH_3); 7.61, (d, 1H, Ar-H); 7.79, (s, 1H, Ar-H); 8.01, (s, 1H, Ar-H); 8.25, (s, 1H, Ar-H); 8.55 (s, 2H, NH_2); 9.16 (s, 1H, HC=N); **UV-Vis:(DMF)** (λ_{max}/ nm): 250, 268, 748; **TGA wt. loss in %(temp.):** 2.65 (100°C); 7.61 (200°C); 22.50 (300°C); 32.80 (400°C); 37.96 (500°C); 60.71 (600°C); 84.79 (700°C); 84.23 (800°C); 84.47 (900°C).

[13] Copper(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide(RMT-13).

Colour: Brown, **Anal. Calcd**. For $C_{36}H_{32}CuN_{10}O_2S_2$ (764.38 g/mol): C, 56.57%; H, 4.22%; N, 18.32%; S, 8.39%; Cu, 8.31%. **Found:** C, 56.68%; H, 4.11%; N, 18.21%; S, 8.54%; Cu, 8.43%; **ESI MS** (m/z): 763.2 (CuL_2)+; **IR (KBr, cm^{-1}):** *v*(NH_2) 3178; *v*(C=N) 1593; *v*(N-N) 1047; *v*(C=S) 1246; δ(C=S) 831; *v*(Ar–C-H) 3051-2937; *v*(Ar–C=C) 1500; *v*(Cu-N) 501; *v*(Cu-S) 424; **^{1}H-NMR (DMSO-d_6):** δppm 3.81, (s, 3H, OMe); 7.00, (d, 1H, Ar-H); 7.10, (s, 2H, Ar-H); 7.28, (s, 1H, Ar-H); 7.49, (s, 2H, Ar-H); 7.56, (d, 1H, Ar-H); 7.63, (s, 1H, Ar-H); 7.82, (d, 1H, Ar-H); 7.88, (d, 2H, NH_2); 8.10, (s, 1H, Ar-H); 9.34 (s, 1H, HC=N); **UV-Vis:(DMF)** (λ_{max}/ nm): 286, 364, 742; **TGA wt. loss in %(temp.):** 1.24 (100°C); 2.48 (200°C); 10.72 (300°C); 45.27 (400°C); 53.61 (500°C); 60.98 (600°C); 66.85 (700°C); 71.03 (800°C); 77.00 (900°C).

[14] Nickel(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide(RMT-14).

Colour: Green, **Anal. Calcd**. For $C_{36}H_{32}N_{10}NiO_2S_2$ (759.53 g/mol): C, 56.93%; H, 4.25%; N, 18.44%; S, 8.44%; Ni, 7.73%. **Found:** C, 57.02%; H, 4.16%; N, 18.51%; S, 8.59%; Ni, 7.80%; **ESI MS** (m/z): 759.2 (NiL_2)+; **IR (KBr, cm^{-1}):** *v*(NH_2) 3286; *v*(C=N) 1587; *v*(N-N) 1047; *v*(C=S) 1246; δ(C=S) 831; *v*(Ar–C-H) 3157-2937; *v*(Ar–C=C) 1518; *v*(Ni-N) 528; *v*(Ni-S) 430; **^{1}H-NMR (DMSO-d_6):** δppm 3.85, (s, 3H, OMe); 7.11, (d, 2H, Ar-H); 7.34, (tri, 2H, Ar-H); 7.50, (tri, 2H, Ar-H); 7.60, (d, 1H, Ar-H); 7.87, (d, 1H, Ar-H); 7.96, (d, 2H, Ar-H); 8.13, (s, 2H, NH_2); 9.39 (s, 1H, HC=N); **UV-Vis:(DMF)** (λ_{max}/ nm): 288, 334, 742; **TGA wt. loss in %(temp.):** 1.00 (100°C); 1.82 (200°C); 11.58 (300°C); 48.66 (400°C); 57.01 (500°C); 61.92 (600°C); 67.90 (700°C); 72.58 (800°C); 77.82 (900°C).

[15] Cobalt(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide(RMT-15).

Colour: Brown, **Anal. Calcd**. For $C_{36}H_{32}CoN_{10}O_2S_2$ (759.77 g/mol): C, 56.91%; H, 4.25%; N, 18.44%; S, 8.44%; Co, 7.76%. **Found:** C, 56.80%; H, 4.34%; N, 18.36%; S, 8.51%; Co, 7.66%; **ESI MS** (m/z): 759.0 (CoL_2)+; **IR**

(KBr, cm^{-1}): $\nu(NH_2)$ 3277; ν(C=N) 1589; ν(N-N) 1053; ν(C=S) 1249; δ(C=S) 837; ν(Ar–C-H) 3180-2933; ν(Ar–C=C) 1496; ν(Co-N) 524; ν(Co-S) 426; **^{1}H-NMR (DMSO-d_6):** δppm 3.88, (s, 3H, OMe); 6.53, (m, 2H, Ar-H); 7.50, (m, 8H, Ar-H); 8.11, (s, 2H, NH_2); 9.62 (s, 1H, HC=N); **UV-Vis:(DMF)** (λ_{max}/ nm): 212, 268, 746; **TGA wt. loss in %(temp.):** 4.64 (100°C); 5.81 (200°C); 18.03 (300°C); 49.23 (400°C); 55.54 (500°C); 61.20 (600°C); 68.46 (700°C); 75.94 (800°C); 82.89 (900°C).

[16] Copper(II) complex of 1-((1,3-diphenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide(RMT-16).

Colour: Gray, **Anal. Calcd**. For $C_{34}H_{28}CuN_{10}S_2$ (704.33 g/mol): C, 57.98%; H, 4.01%; N, 19.89%; S, 9.11%; Cu, 9.02%. **Found:** C, 57.90%; H, 3.96%; N, 19.97%; S, 9.20%; Cu, 8.91%; **ESI MS** (m/z): 705.2 (CuL_2)+; **IR (KBr, cm^{-1}):** $\nu(NH_2)$ 3242; ν(C=N) 1583; ν(N-N) 1051; ν(C=S) 1211; δ(C=S) 856; ν(Ar–C-H) 3045; ν(Ar–C=C) 1496; ν(Cu-N) 499; ν(Cu-S) 422.

[17] Nickel(II) complex of 1-((1,3-diphenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide(RMT-17).

Colour: Green, **Anal. Calcd**. For $C_{34}H_{28}N_{10}NiS_2$ (699.48 g/mol): C, 58.38%; H, 4.03%; N, 20.02%; S, 9.17%; Ni, 8.39%. **Found:** C, 58.25%; H, 4.11%; N, 19.94%; S, 9.22%; Ni, 8.30%; **ESI MS** (m/z): 693.0 (NiL_2)+; **IR (KBr, cm^{-1}):** $\nu(NH_2)$ 3252; ν(C=N) 1585; ν(N-N) 1049; ν(C=S) 1211; δ(C=S) 860; ν(Ar–C-H) 3140-3049; ν(Ar–C=C) 1504; ν(Ni-N) 495; ν(Ni-S) 430.

[18] Cobalt(II) complex of 1-((1,3-diphenyl-1*H*-pyrazol-4-yl)methylene)thiosemicarbazide(RMT-18).

Colour: Redish, **Anal. Calcd**. For $C_{34}H_{28}CoN_{10}S_2$ (699.72 g/mol): C, 58.36%; H, 4.03%; N, 20.02%; S, 9.17%; Co, 8.42%. **Found:** C, 58.50%; H, 3.92%; N, 19.87%; S, 9.30%; Co, 8.53%; **ESI MS** (m/z): 699.2 (CoL_2)+; **IR (KBr, cm^{-1}):** $\nu(NH_2)$ 3292; ν(C=N) 1581; ν(N-N) 1053; ν(C=S) 1213; δ(C=S) 854; ν(Ar–C-H) 3053; ν(Ar–C=C) 1502; ν(Co-N) 503; ν(Co-S) 422.

[19] Copper(II) complex of 1-((3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide(RMT-19).

Colour: Green, **Anal. Calcd**. For $C_{34}H_{26}Cl_2CuN_{10}S_2$ (773.22 g/mol): C, 52.81%; H, 3.39%; N, 18.11%; S, 8.29%; Cu, 8.22%. **Found:** C, 52.96%; H, 3.28%; N, 18.06%; S, 8.41%; Cu, 7.34%; **ESI MS** (m/z): 773.0 (CuL_2)+; **IR (KBr, cm^{-1}):** *v*(NH_2) 3190; *v*(C=N) 1599; *v*(N-N) 1095; *v*(C=S) 1288; δ(C=S) 831; *v*(Ar–C-H) 3144-3016; *v*(Ar–C=C) 1506; *v*(C-Cl) 754; *v*(Cu-N) 524; *v*(Cu-S) 426.

[20] Nickel(II) complex of 1-((3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide(RMT-20).

Colour: Green, **Anal. Calcd**. For $C_{34}H_{26}Cl_2N_{10}NiS_2$ (768.37 g/mol): C, 53.15%; H, 3.41%; N, 18.23%; S, 8.35%; Ni, 7.64%. **Found:** C, 53.03%; H, 3.37%; N, 18.33%; S, 8.45%; Ni, 7.75%; **ESI MS** (m/z): 764.3 (NiL_2)+; **IR (KBr, cm^{-1}):** *v*(NH_2) 3186; *v*(C=N) 1595; *v*(N-N) 1093; *v*(C=S) 1292; δ(C=S) 831; *v*(Ar–C-H) 3157-3016; *v*(Ar–C=C) 1504; *v*(C-Cl) 752; *v*(Ni-N) 503; *v*(Ni-S) 422.

[21] Cobalt(II) complex of 1-((3-(4-chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide(RMT-21).

Colour: Brown, **Anal. Calcd**. For $C_{34}H_{26}Cl_2CoN_{10}S_2$ (768.61 g/mol): C, 53.13%; H, 3.41%; N, 18.22%; S, 8.34%; Co, 7.67%. **Found:** C, 53.26%; H, 3.34%; N, 18.10%; S, 8.47%; Co, 7.55%; **ESI MS** (m/z): 768.4 (CoL_2)+; **IR (KBr, cm^{-1}):** *v*(NH_2) 3248; *v*(C=N) 1595; *v*(N-N) 1093; *v*(C=S) 1280; δ(C=S) 815; *v*(Ar–C-H) 3155-2924; *v*(Ar–C=C) 1502; *v*(C-Cl) 734; *v*(Co-N) 526; *v*(Co-S) 408.

[22] Copper(II) complex of 1-((3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide(RMT-22).

Colour: Yellowish, **Anal. Calcd**. For $C_{34}H_{26}CuN_{12}O_4S_2$ (794.32 g/mol): C, 51.41%; H, 3.30%; N, 21.16%; S, 8.07%; Cu, 8.00%. **Found:** C, 51.28%; H, 3.37%; N, 21.05%; S, 8.13%; Cu, 8.08%; **ESI MS** (m/z): 792.2 (CuL_2)+; **IR (KBr, cm^{-1}):** *v*(NH_2) 3182; *v*(C=N) 1597; *v*(N-N) 1062; *v*(C=S) 1292; δ(C=S)

860; *v*(Ar–C-H) 3134-3018; *v*(Ar–C=C) 1510; *v*(C-NO_2) 1342; *v*(Cu-N) 530; *v*(Cu-S) 410.

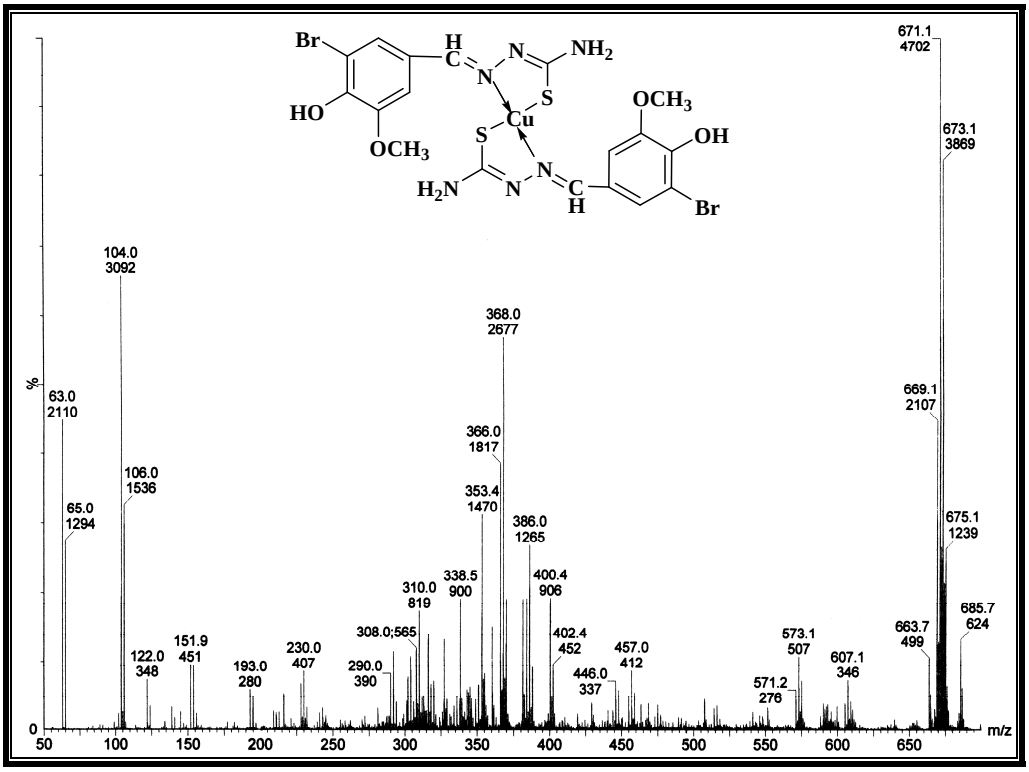
[23] Nickel(II) complex of 1-((3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide(RMT-23).

Colour: Greenish, **Anal. Calcd**. For $C_{34}H_{26}N_{12}NiO_4S_2$ (789.47 g/mol): C, 51.73%; H, 3.32%; N, 21.29%; S, 8.12%; Ni, 7.43%. **Found:** C, 51.82%; H, 3.41%; N, 21.18%; S, 8.25%; Ni, 7.51%; **ESI MS** (m/z): 791.0 (NiL_2)+; **IR (KBr, cm^{-1}):** *v*(NH_2) 3176; *v*(C=N) 1597; *v*(N-N) 1062; *v*(C=S) 1292; δ(C=S) 860; *v*(Ar–C-H) 3136-3016; *v*(Ar–C=C) 1508; *v*(C-NO_2) 1342; *v*(Ni-N) 501; *v*(Ni-S) 426.

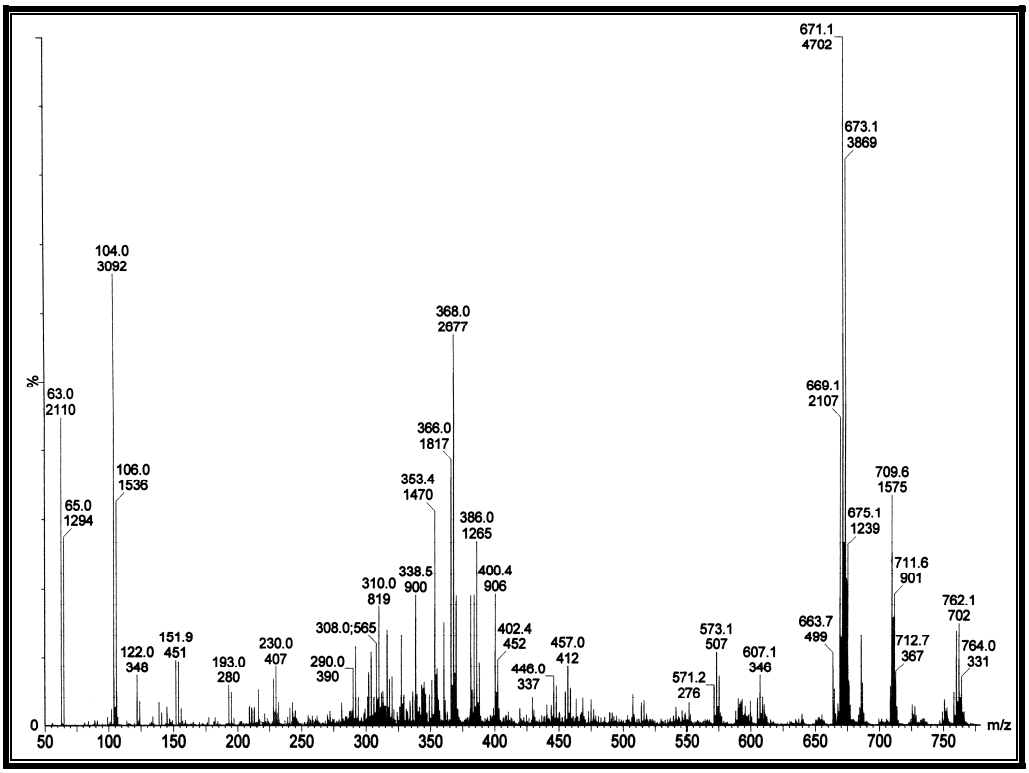
[24] Cobalt(II) complex of 1-((3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide(RMT-24).

Colour: Greenish, **Anal. Calcd**. For $C_{34}H_{26}CoN_{12}O_4S_2$ (789.71 g/mol): C, 51.71%; H, 3.32%; N, 21.28%; S, 8.12%; Co, 7.46%. **Found:** C, 51.60%; H, 3.39%; N, 21.37%; S, 8.04%; Co, 7.58%; **ESI MS** (m/z): 782.2 (CoL_2)+; **IR (KBr, cm^{-1}):** *v*(NH_2) 3178; *v*(C=N) 1597; *v*(N-N) 1064; *v*(C=S) 1294; δ(C=S) 860; *v*(Ar–C-H) 3140-3007; *v*(Ar–C=C) 1508; *v*(C-NO_2) 1342; *v*(Co-N) 528; *v*(Co-S) 422.

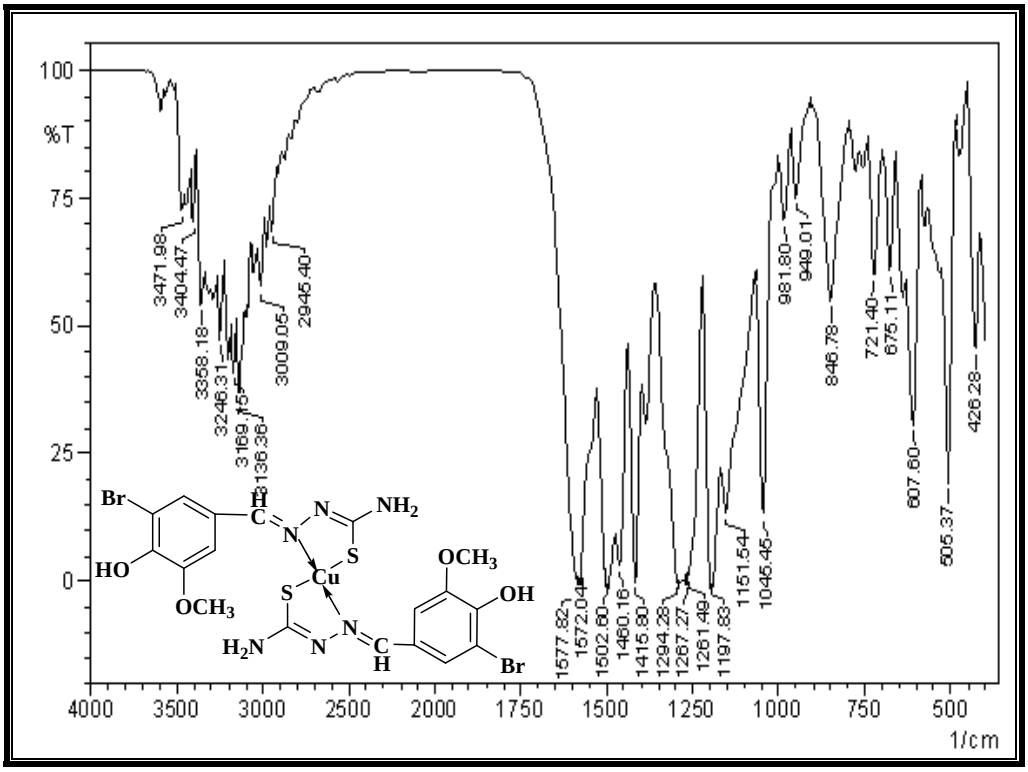
ESI Mass spectrum of RMT- 1



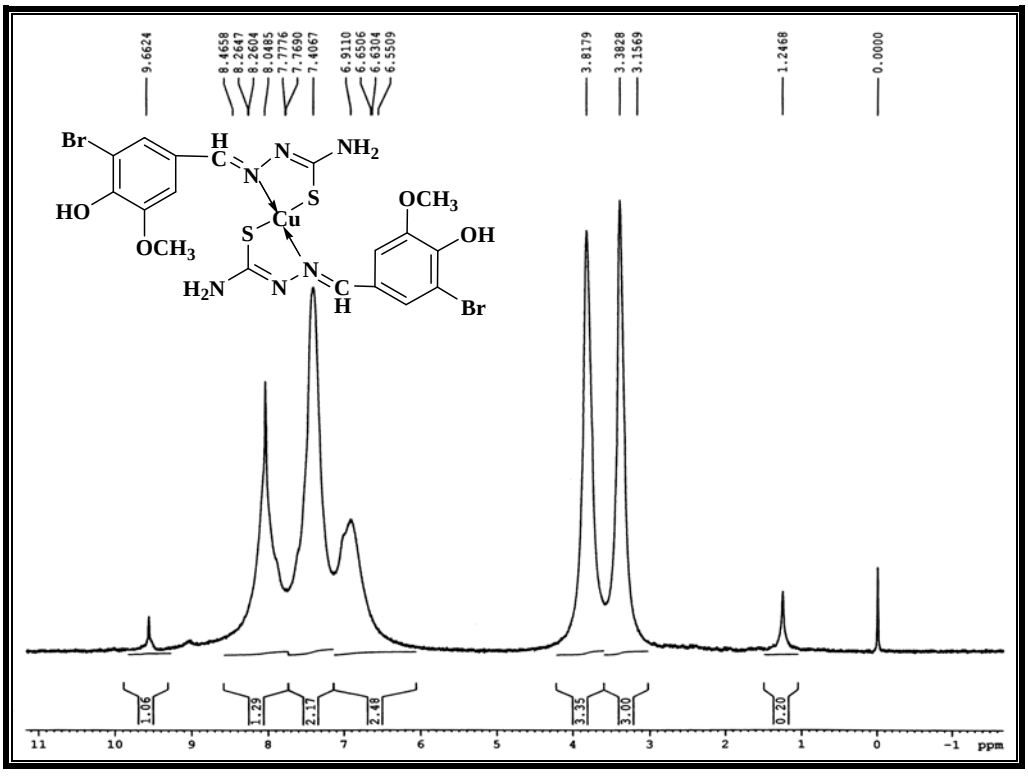
Expanded ESI Mass spectrum of RMT- 1



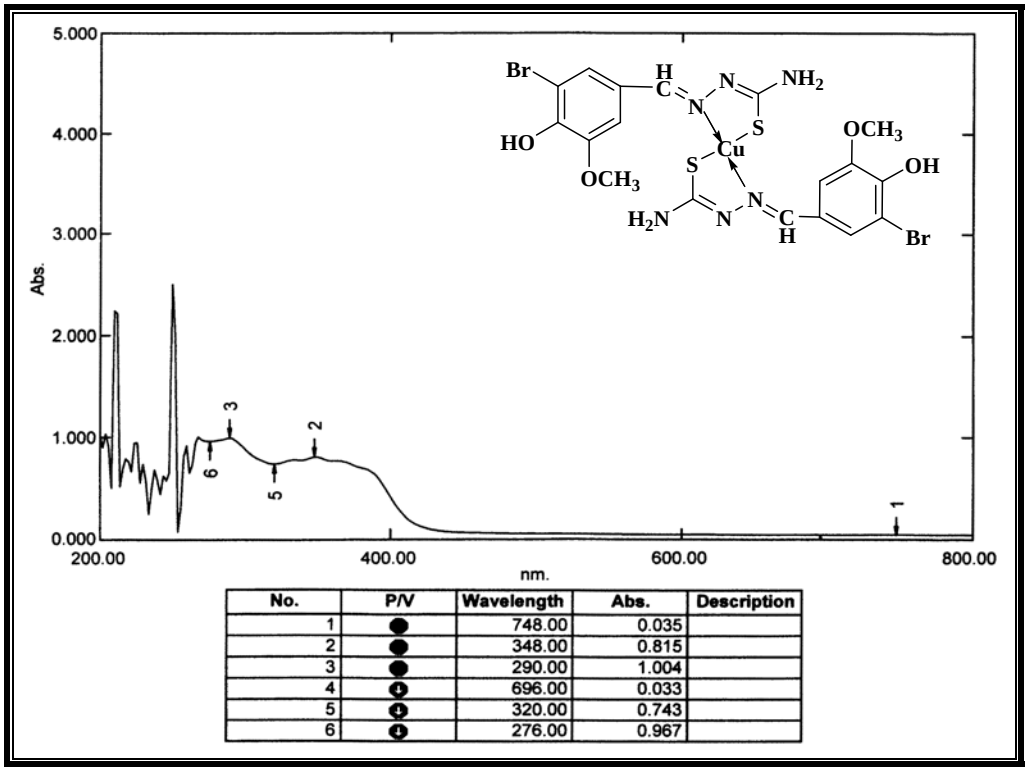
IR spectrum of RMT- 1



^{1}H NMR spectrum of RMT- 1

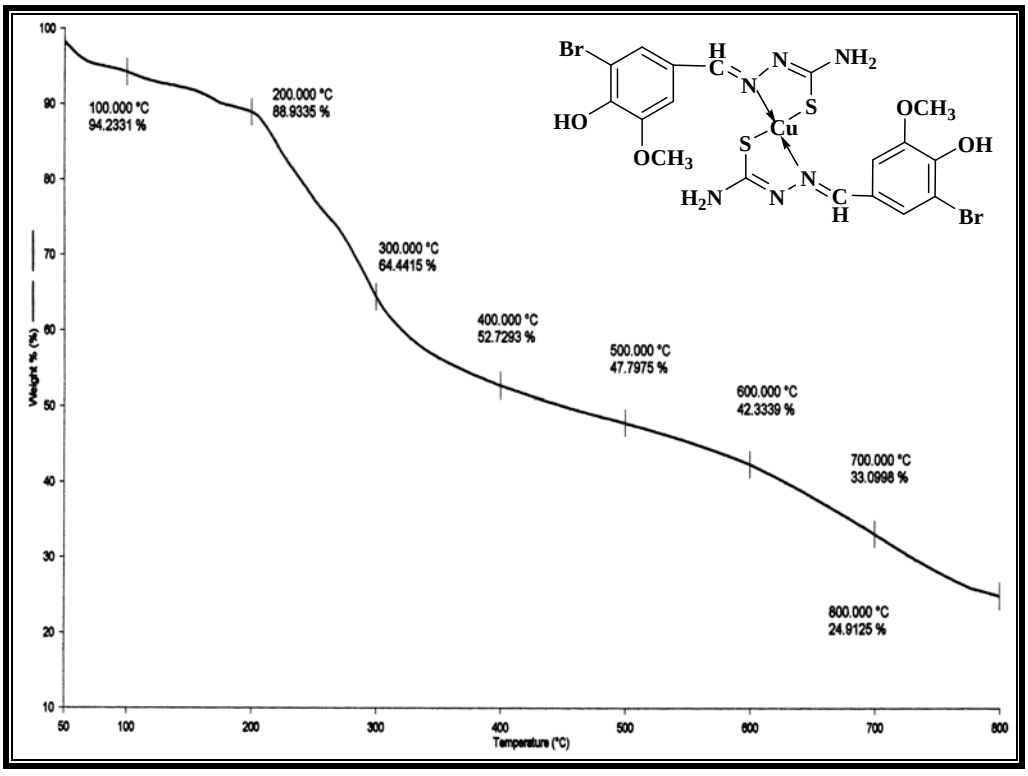


UV-Visible spectrum of RMT- 1



No.	P/V	Wavelength	Abs.	Description
1	●	748.00	0.035	
2	●	348.00	0.815	
3	●	290.00	1.004	
4	◆	696.00	0.033	
5	◆	320.00	0.743	
6	◆	276.00	0.967	

TGA spectrum of RMT- 1



Results & Discussion

The most important bands in the infrared spectra of the Copper(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Copper(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide exhibited a broad band at 3471 cm^{-1} that are attributed to substituted -OH group and -OH of crystal water molecules, while the bands observed at 3246 cm^{-1}, 1045 cm^{-1} and 1267 cm^{-1} of $-NH_2$, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1577 cm^{-1} and aromatic -C-H and -C=C bands due to at 3136-3009 cm^{-1} and 1460 cm^{-1} respectively. The specific bands (Cu-N) and (Cu-S) observed at 505 cm^{-1} and 426 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Copper(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other $-NH_2$ protons signals observed as singlets at 7.40 ppm. The signals of the (-HC=N) proton which appear as singlet at 8.26 ppm in the complex.

The signal as compare to ligand show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine nitrogen to the metal centre. The signals of -OH and -OCH_3 protons observed as singlet at 9.66 ppm and 3.81 ppm respectively. The signals of the aromatic protons of the Cu(II) complex appeared at δ 6.65-7.91 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ interaligand transition. There are two detected absorption bands at around 290 nm and 348 nm assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ interaligand transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 650-800 nm with maximum absorbance at 748 nm is assigned to a merges of $^2T_{2g} \leftarrow ^2E_g$ transition in square planer geometry.

The TGA curves of the Copper(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Cu(L_2)\,(H_2O)_n] \cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Cu(L_2)\,(H_2O)_n] + nH_2O$$

$$[Cu(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Cu(L_2)] + (H_2O)_n$$

$$[Cu(L_2)] \xrightarrow{180\text{-}300\ ^0C} [CuL] + L$$

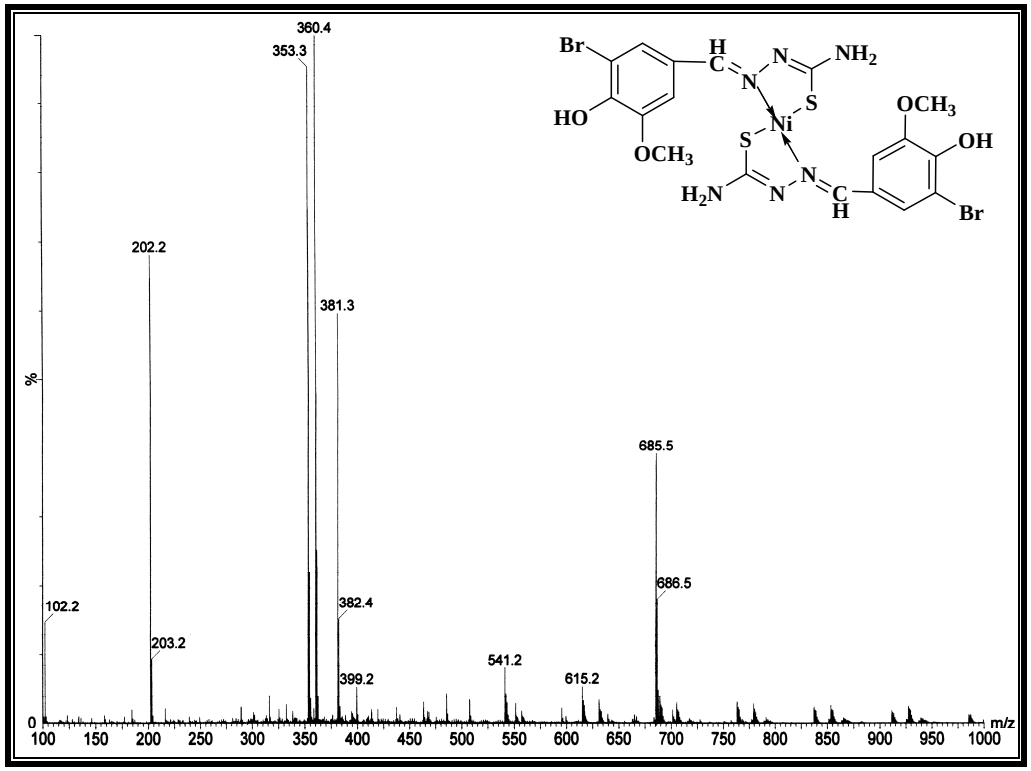
$$[CuL] \xrightarrow{300\text{-}600\ ^0C} CuO + L$$

(Where n = 0, 1 or 2).

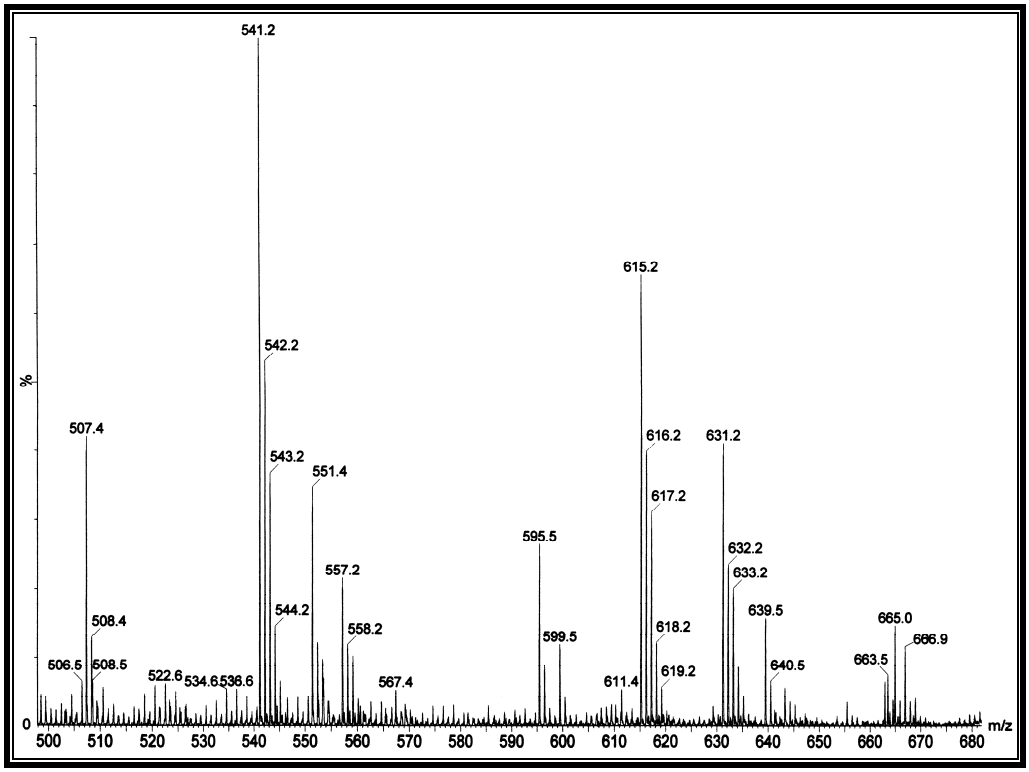
The room temperature magnetic moments for the copper(II) complex 1.74 BM correspond to the values normally observed for square-planar copper(II) compound. The room temperature value for μ_{eff} (1.80) (where μ_{eff} is the effective magnetic moment) is very close to the spin-only value of 1.73 B.M. for d^9.

All spectral characterization and thermal analysis confirms the structure of Copper(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene) thiosemicarbazide(RMT-1). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the square planer type geometries of the present complex.

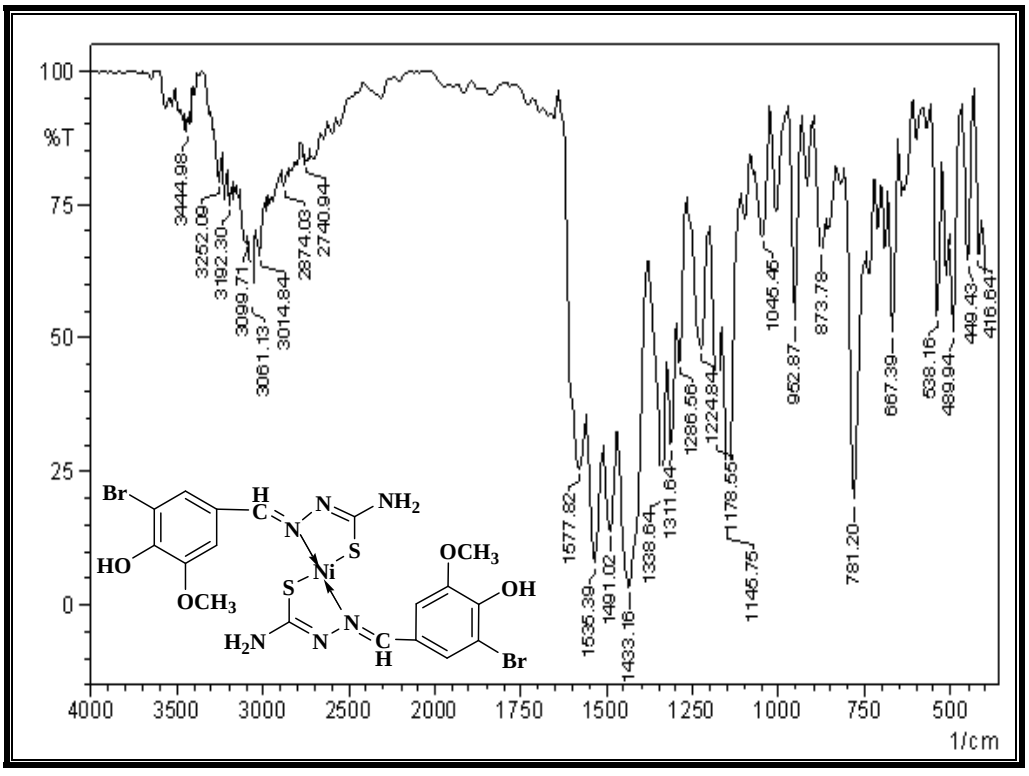
ESI Mass spectrum of RMT- 2



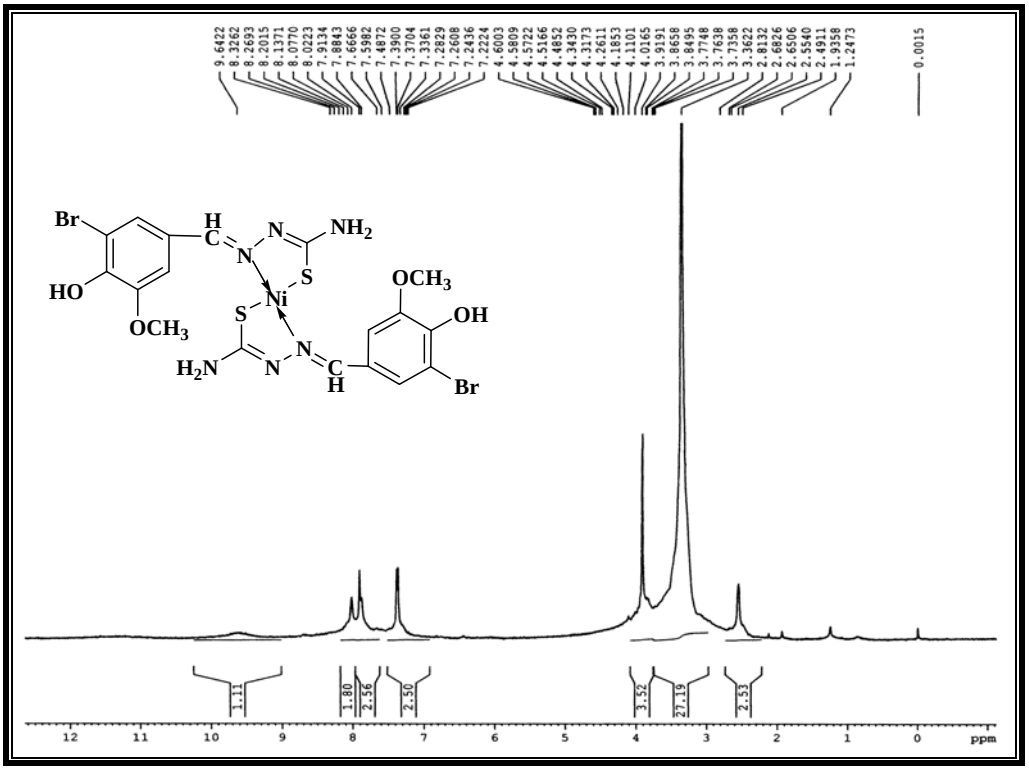
Expanded ESI Mass spectrum of RMT- 2



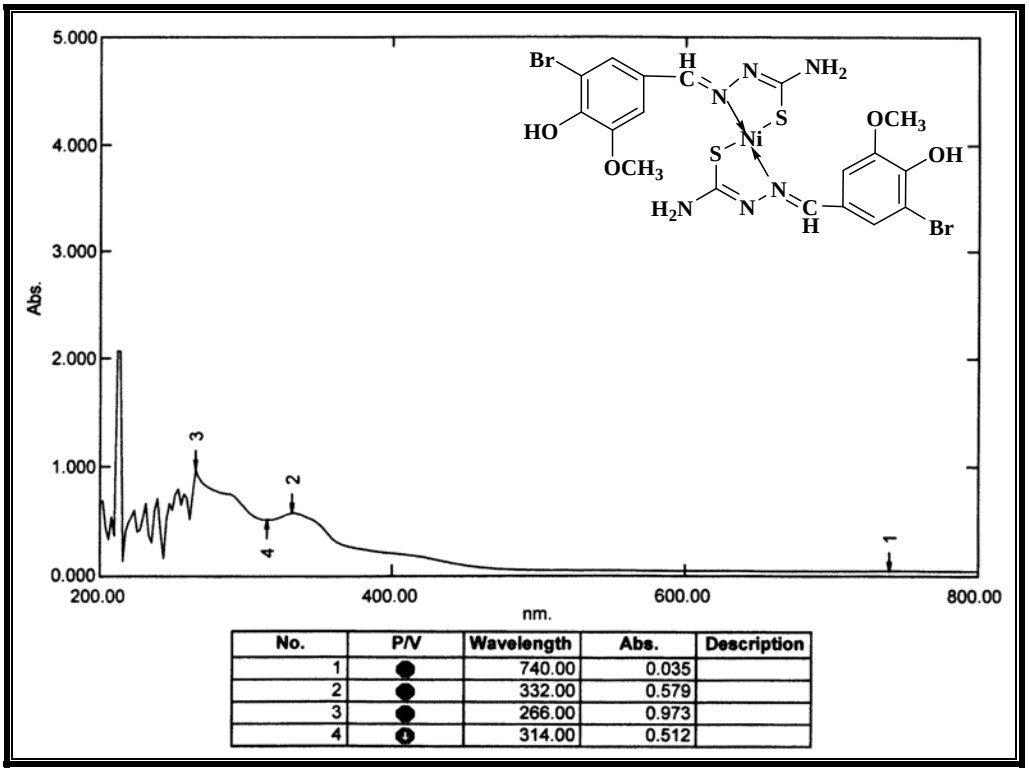
IR spectrum of RMT- 2



^{1}H NMR spectrum of RMT- 2

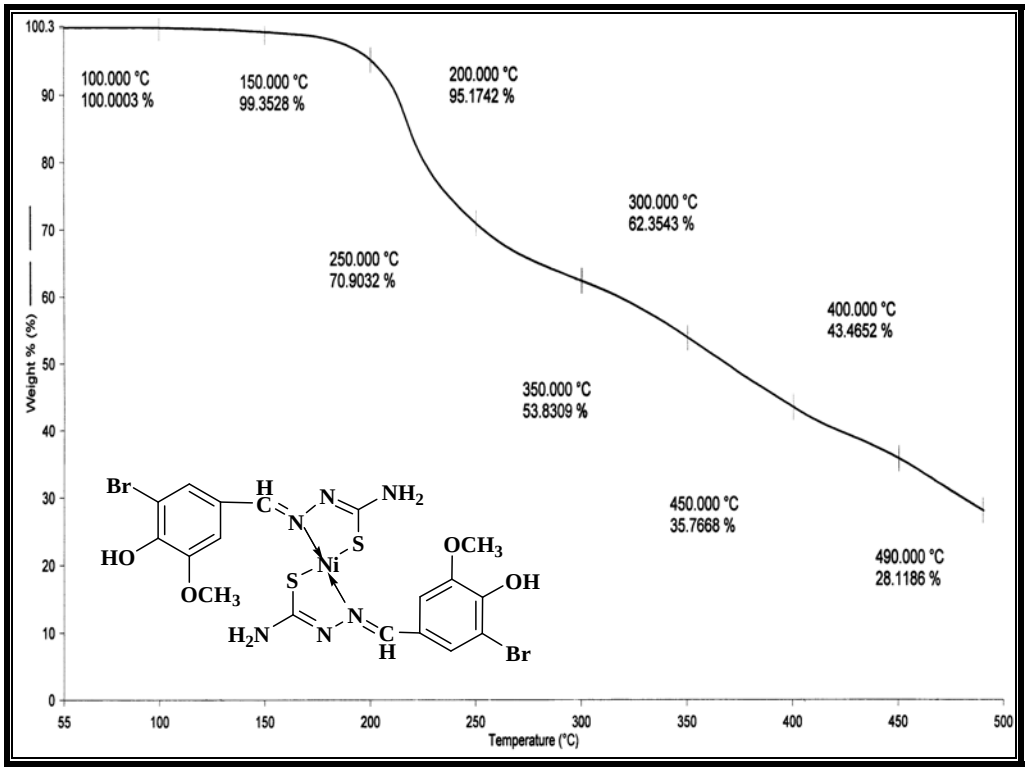


UV-Visible spectrum of RMT- 2



No.	P/V	Wavelength	Abs.	Description
1		740.00	0.035	
2		332.00	0.579	
3		266.00	0.973	
4		314.00	0.512	

TGA spectrum of RMT- 2



Results & Discussion

The most important bands in the infrared spectra of the Nickel(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating

that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Nickel(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide exhibited a broad band at 3444 cm^{-1} that are attributed to substituted -OH group and -OH of crystal water molecules, while the bands observed at 3252 cm^{-1}, 1045 cm^{-1} and 1286 cm^{-1} of $-NH_2$, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1577 cm^{-1} and aromatic -C-H and -C=C bands due to at 3099-3014 cm^{-1} and 1433 cm^{-1} respectively. The specific bands (Ni-N) and (Ni-S) observed at 538 cm^{-1} and 416 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Nickel(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other $-NH_2$ protons signals observed as singlets at 7.91 ppm. The signals of the (-HC=N) protons which appear as singlets at 8.02 ppm in the complex. The signal as compare to ligands show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine nitrogen to the metal centre. The signals of -OH and $-OCH_3$ protons observed as singlet at 9.64 ppm and 3.86 ppm respectively. The signals of the aromatic protons of the Ni(II) complex appeared at δ 6.65-7.91 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi\rightarrow\pi^*$ and/or $n\rightarrow\pi^*$ interaligand transition. There are two detected absorption bands at around 266 nm assigned to $\pi\rightarrow\pi^*$ interaligand transition and 332 nm assigned to $^3T_{1g}(P)\leftarrow{}^3A_{2g}(F)$ transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 740 nm is assigned to a merges of $^3T_{1g}(F)\leftarrow{}^3A_{2g}(F)$ transition in tetrahedral geometry.

The TGA curves of the Nickel(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Ni(L_2)\,(H_2O)_n] \cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Ni(L_2)\,(H_2O)_n] + nH_2O$$

$$[Ni(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Ni(L_2)] + (H_2O)_n$$

$$[Ni(L_2)] \xrightarrow{180\text{-}300\ ^0C} [NiL] + L$$

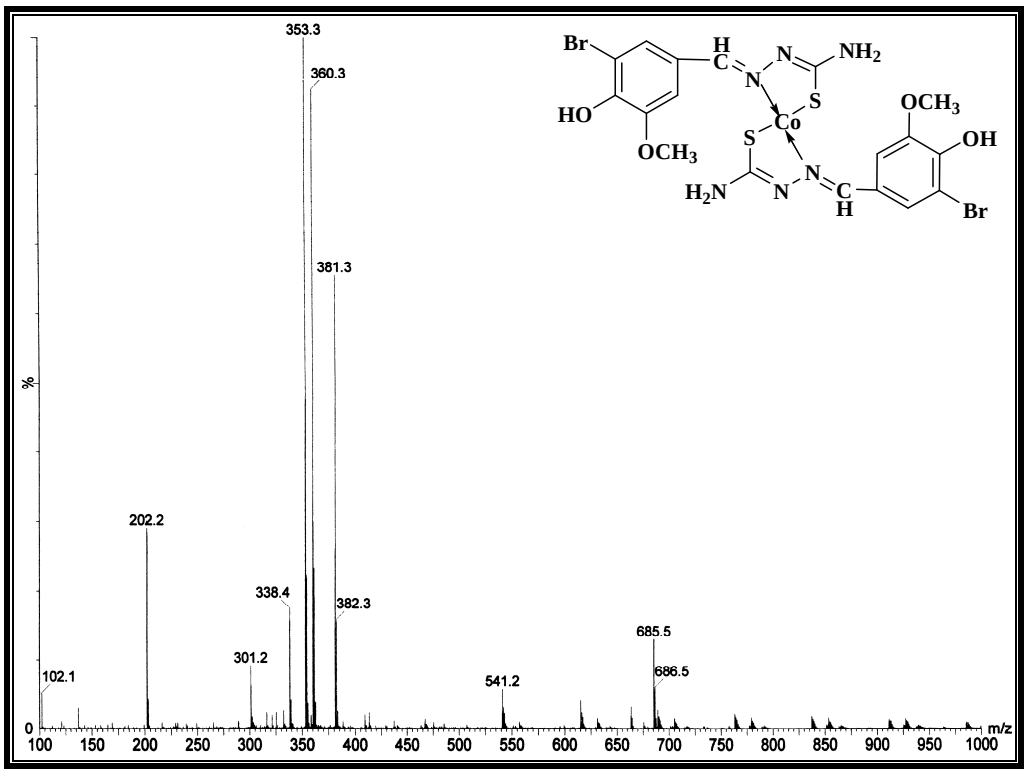
$$[NiL] \xrightarrow{300\text{-}600\ ^0C} NiO + L$$

(Where n = 0, 1 or 2).

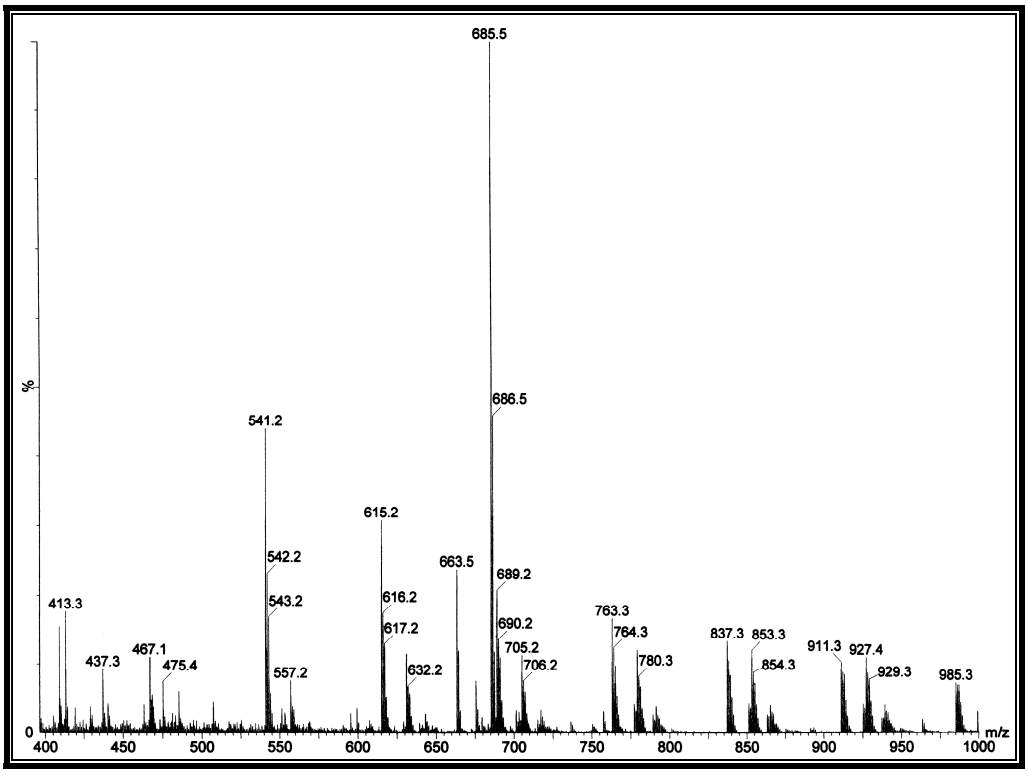
The magnetic moment of the nickel complex was found to be 3.15 B.M. which falls in the range generally observed for the four-coordinated Ni(II) complex. The magnetic data of the Ni(II) complex agree with a d^8 metal ion in an tetrahedral configuration.

All spectral characterization and thermal analysis confirms the structure of Nickel(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene) thiosemicarbazide(RMT-2). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the tetrahedral type geometries of the present complex.

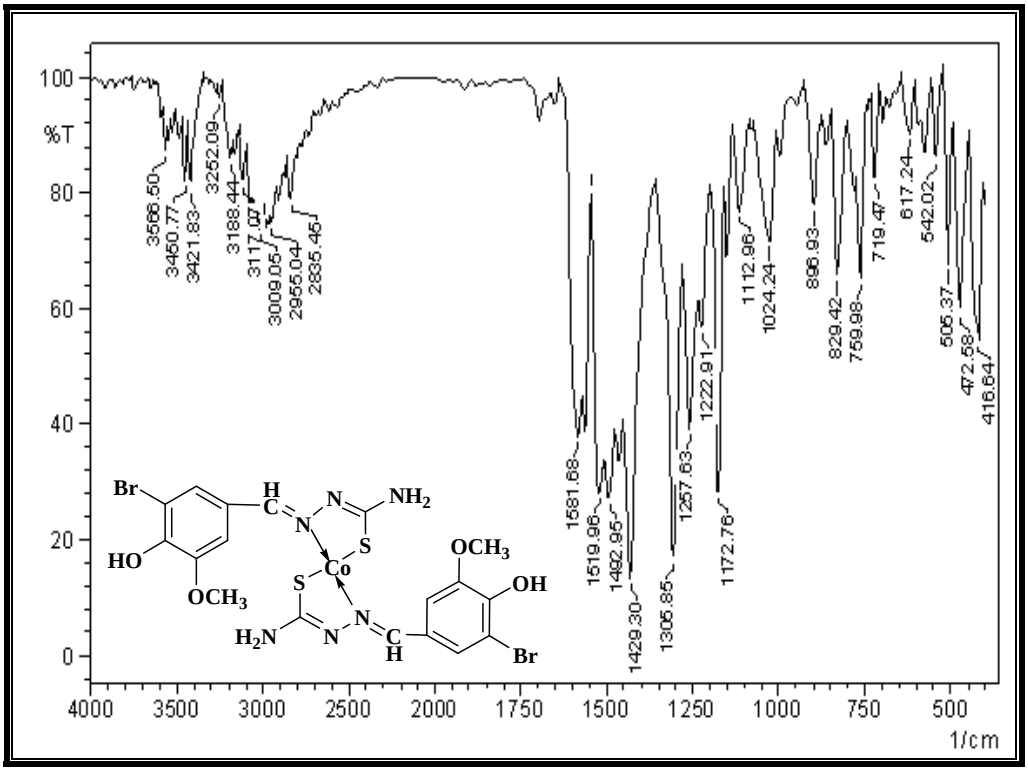
ESI Mass spectrum of RMT- 3



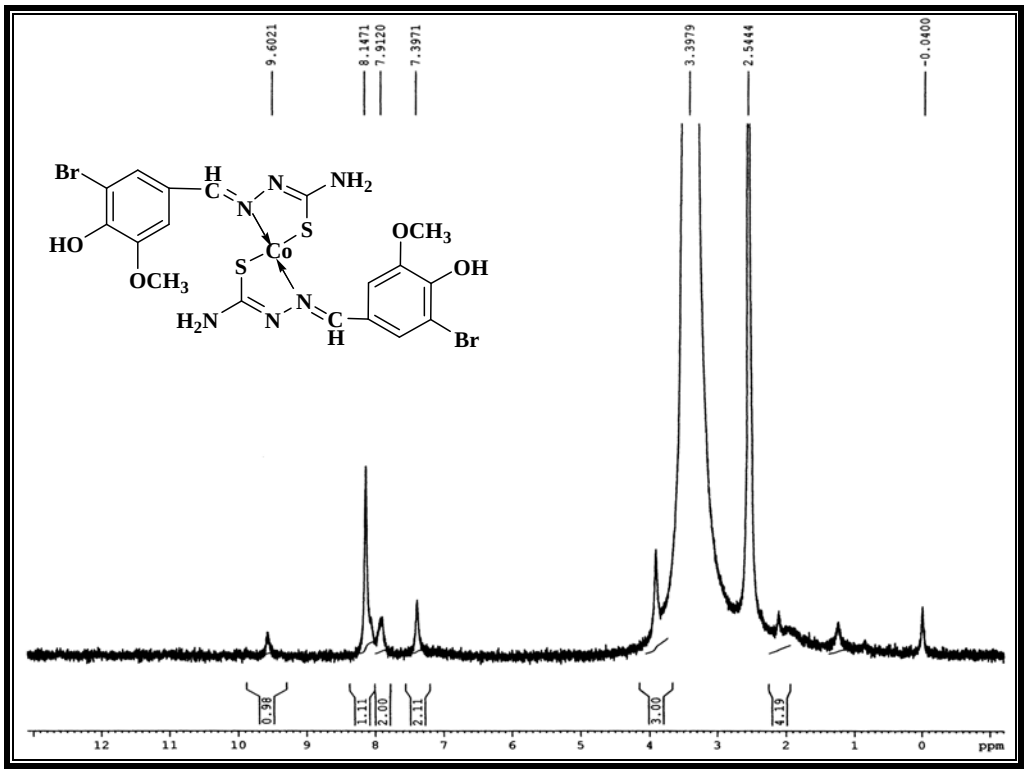
Expanded ESI Mass spectrum of RMT- 3



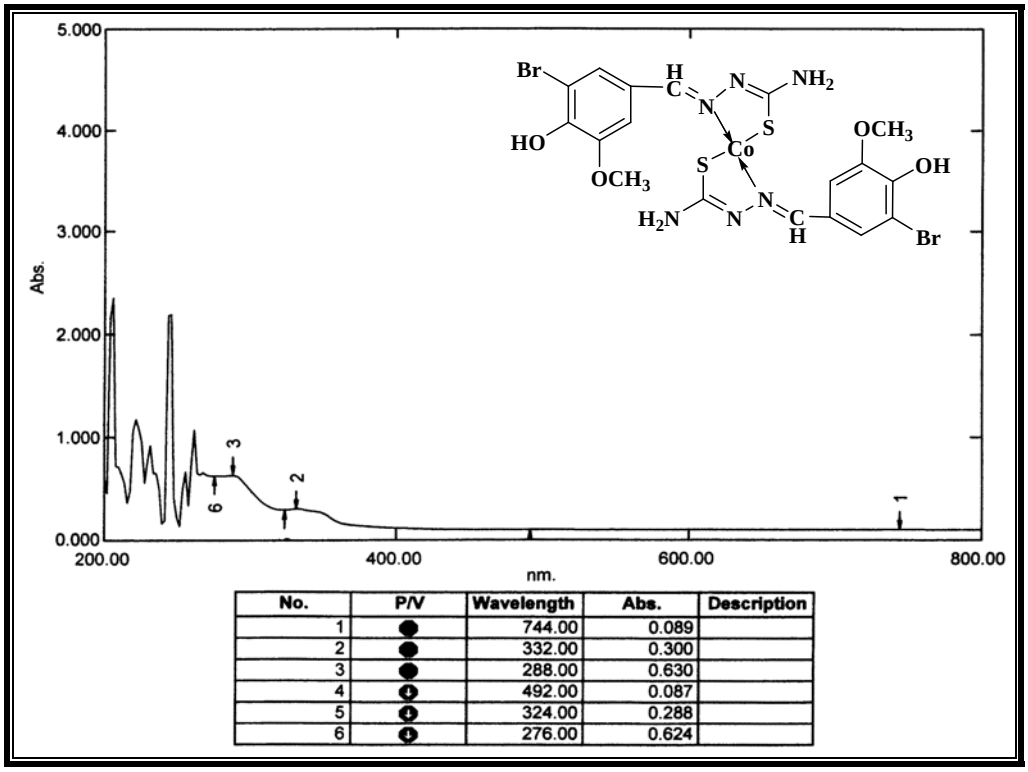
IR spectrum of RMT- 3



^{1}H NMR spectrum of RMT- 3



UV-Visible spectrum of RMT- 3



No.	P/V	Wavelength	Abs.	Description
1	●	744.00	0.089	
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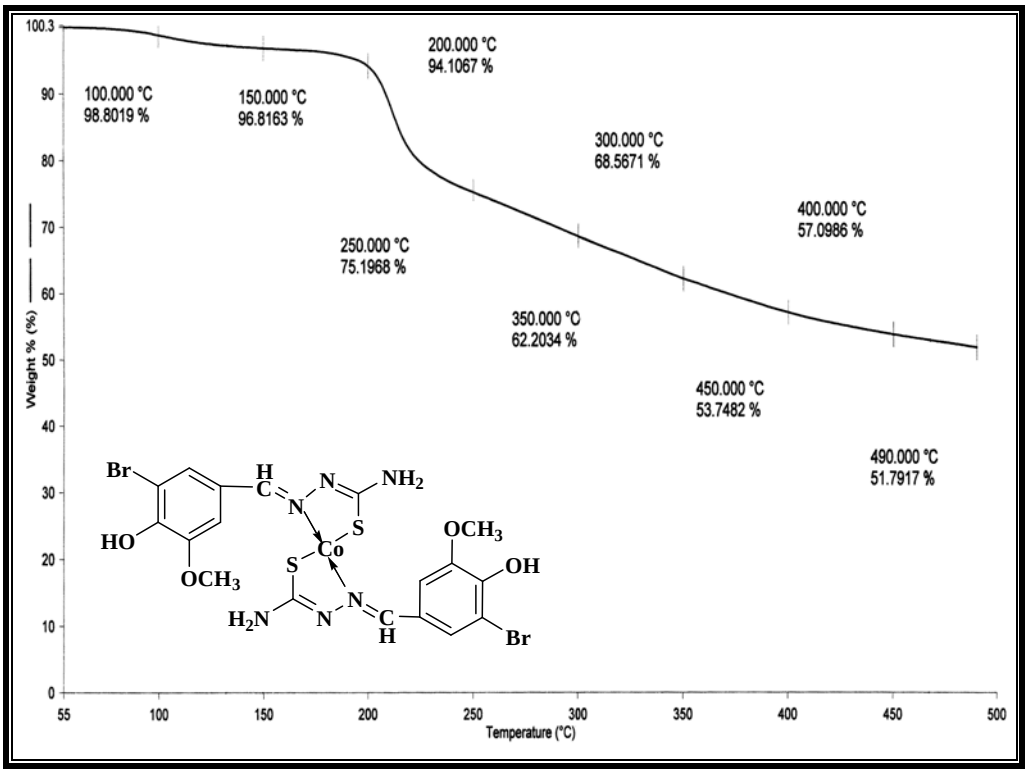
4	◆	492.00	0.087	
5	◆	324.00	0.288	
6	◆	276.00	0.624	

TGA spectrum of RMT- 3



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In the ^{1}H-NMR spectra of the Cobalt(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other $-NH_2$ protons signals observed as singlets at 7.91 ppm. The signals of the (-HC=N) protons which appear as singlets at 8.14 ppm in the complex.

The signal as compare to ligands show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine nitrogen to the metal centre. The signals of -OH and -OCH_3 protons observed as singlet at 9.64 ppm and 3.39 ppm respectively. The signals of the aromatic protons of the Co(II) complex appeared at δ 6.65-7.91 ppm, and the resonance lines found correspond to the calculated multiplicity.

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The TGA curves of the Cobalt(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Co(L_2)\,(H_2O)_n] \cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Co(L_2)\,(H_2O)_n] + nH_2O$$

$$[Co(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Co(L_2)] + (H_2O)_n$$

$$[Co(L_2)] \xrightarrow{180\text{-}300\ ^0C} [CoL] + L$$

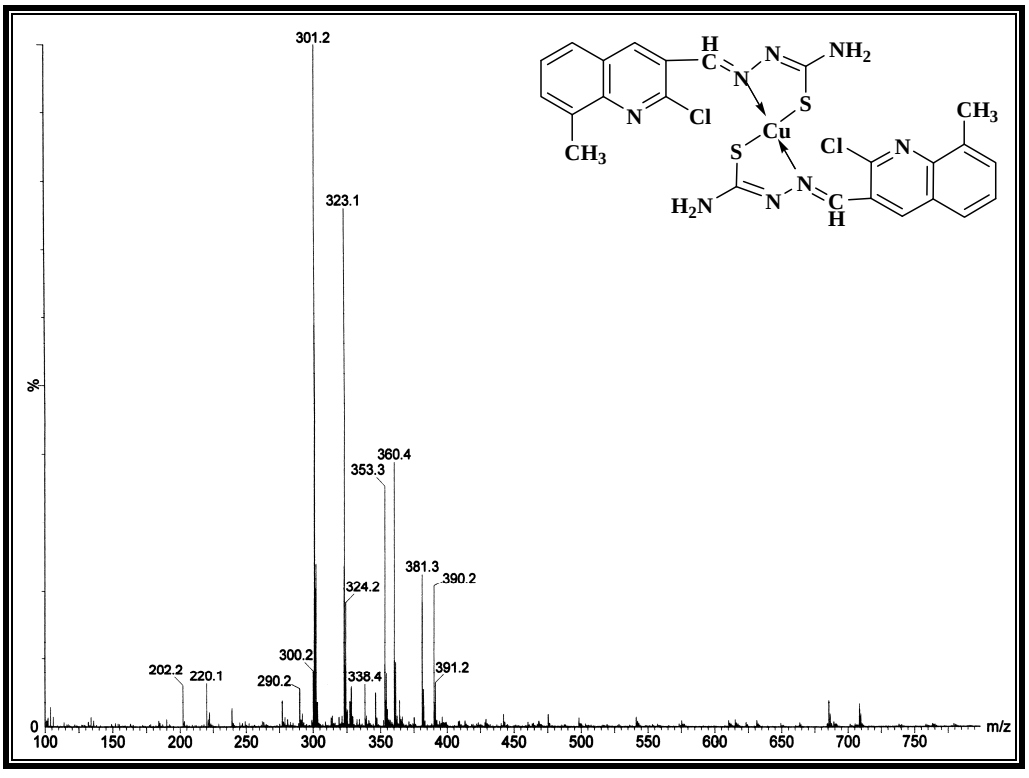
$$[CoL] \xrightarrow{300\text{-}600\ ^0C} CoO + L$$

(Where n = 0, 1 or 2).

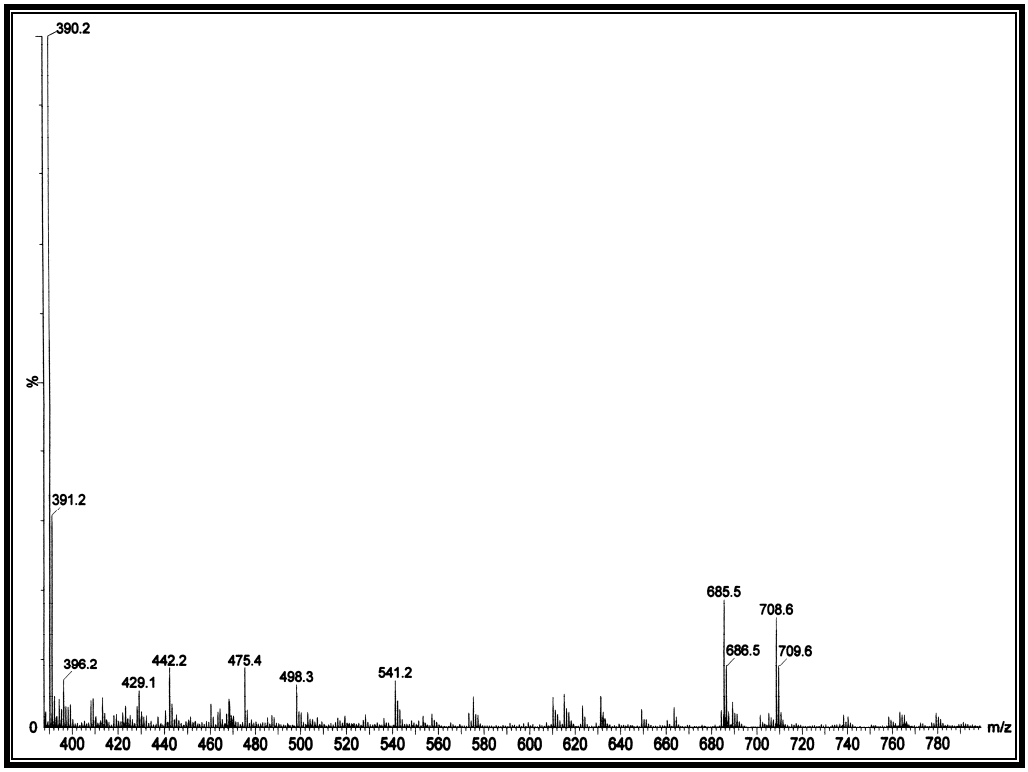
Magnetic moment measurements for the complexes were made at room temperature. The cobalt(II) complex show magnetic moment 4.10 BM, a value in accordance with a high spin configuration showing the presence of tetrahedral environment around the cobalt(II) ion in the complex. The experimental values are higher than spin only value due to orbital angular momentum contribution in d^7 system.

All spectral characterization and thermal analysis confirms the structure of Cobalt(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene) thiosemicarbazide(RMT-3). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the tetrahedral type geometries of the present complex.

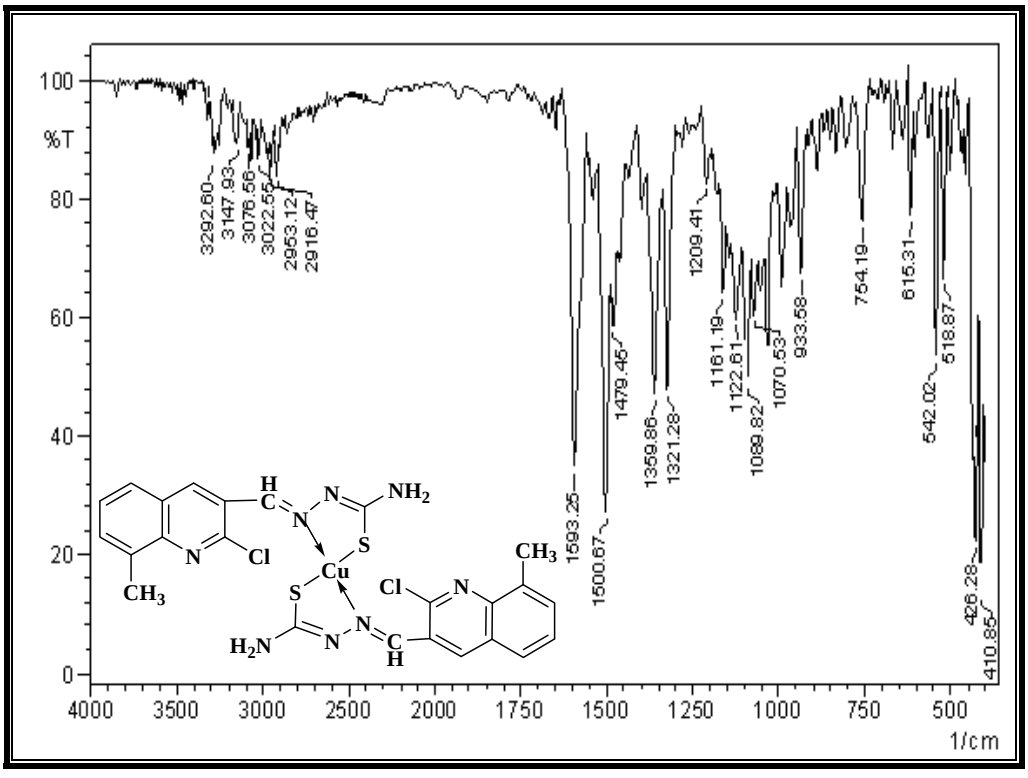
ESI Mass spectrum of RMT- 10



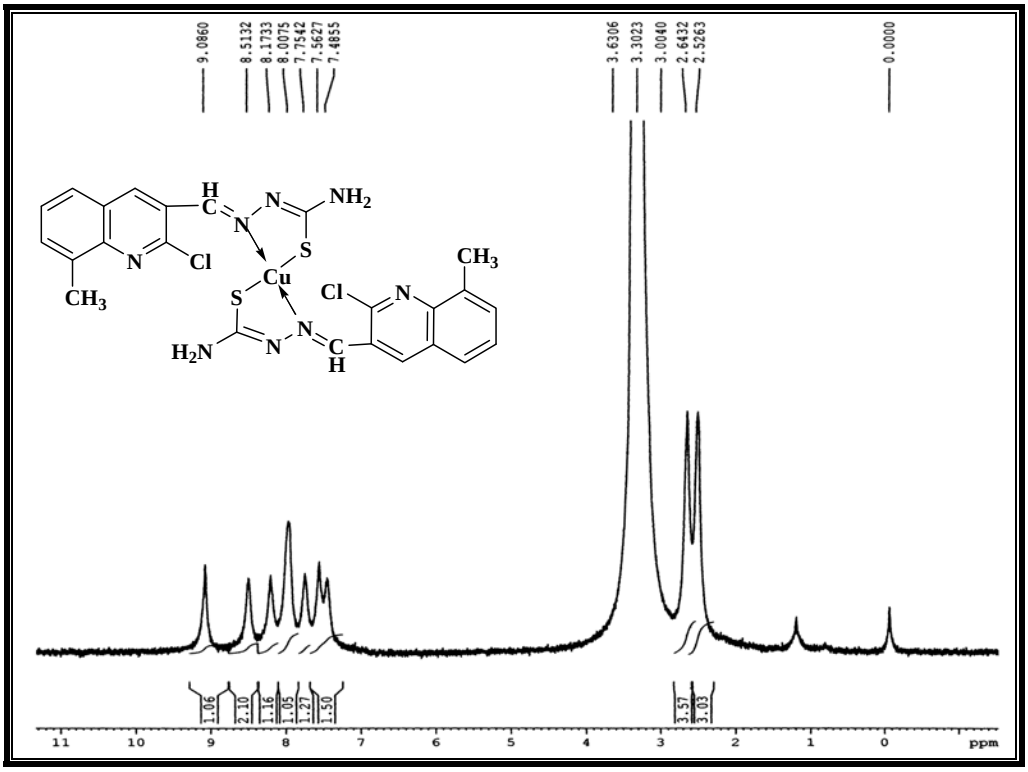
Expanded ESI Mass spectrum of RMT- 10



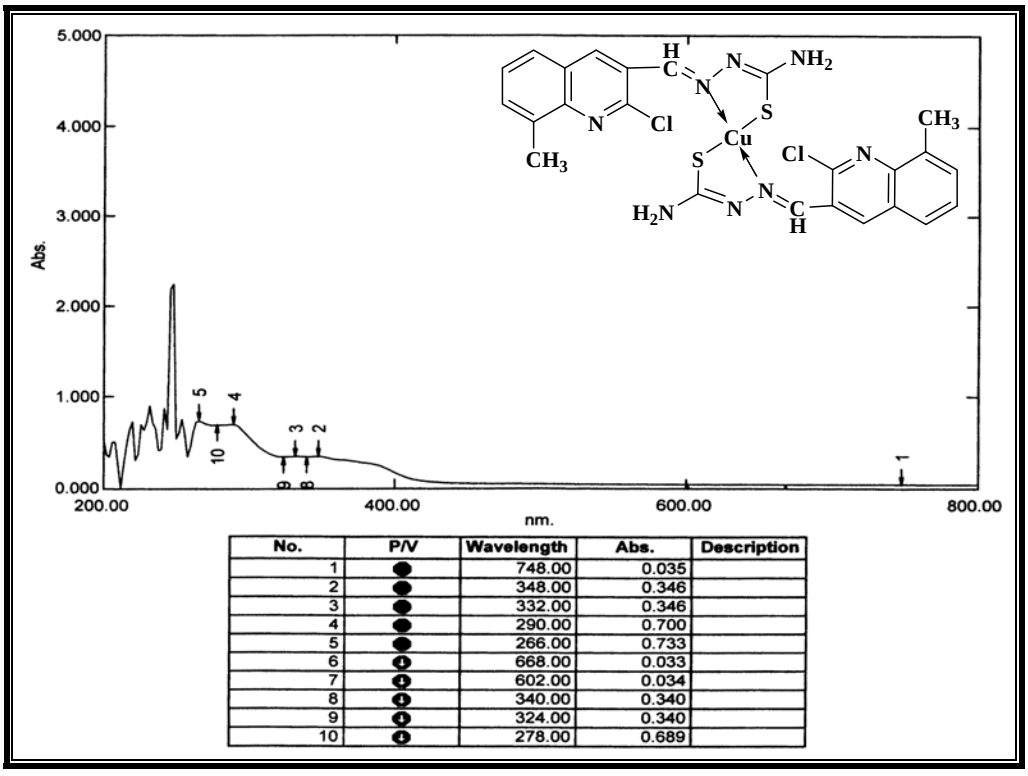
IR spectrum of RMT- 10



^{1}H NMR spectrum of RMT- 10



UV-Visible spectrum of RMT- 10



No.	P/V	Wavelength	Abs.	Description
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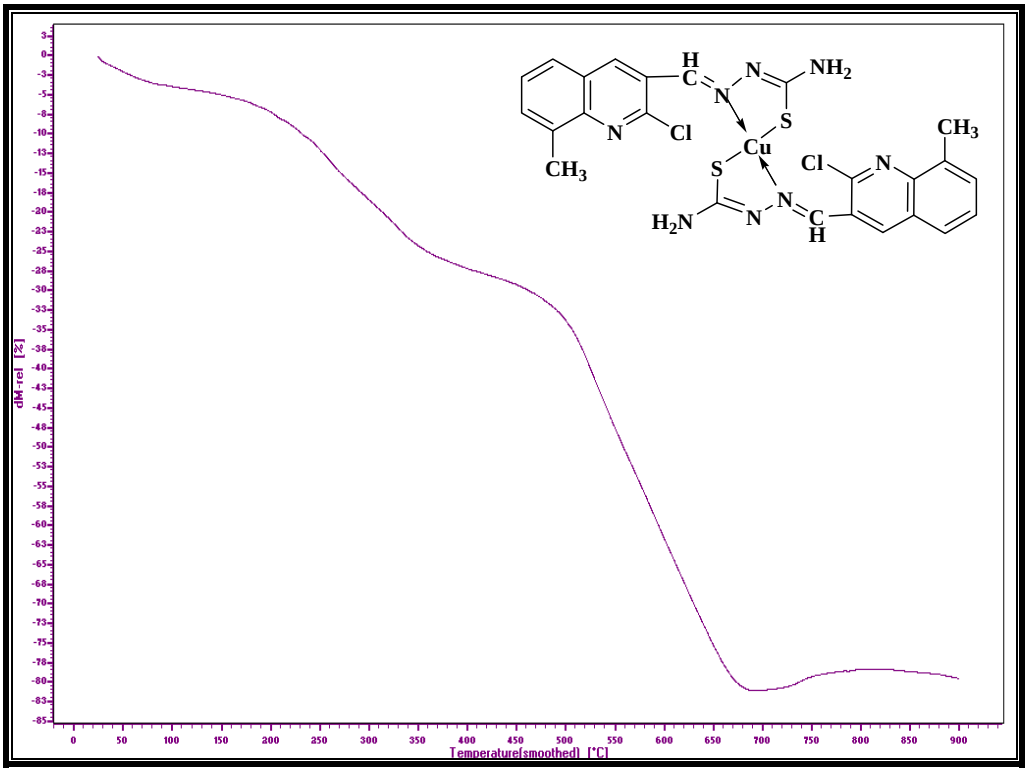
4	●	290.00	0.700	
5	●	266.00	0.733	
6	▼	668.00	0.033	
7	▼	602.00	0.034	
8	▼	340.00	0.340	
9	▼	324.00	0.340	
10	▼	278.00	0.689	

TGA spectrum of RMT- 10



Results & Discussion

The most important bands in the infrared spectra of the Copper(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating

that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Copper(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide exhibited a bands observed at 3292 cm^{-1}, 1089 cm^{-1} and 1209 cm^{-1} of $-NH_2$, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1593 cm^{-1} and aromatic -C-H and -C=C bands due to at 3147-2953 cm^{-1} and 1479 cm^{-1} respectively. The specific bands (Cu-N) and (Cu-S) observed at 518 cm^{-1} and 410 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Copper(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other $-NH_2$ protons signals observed as singlets at 8.51 ppm. The signals of the (-HC=N) proton which appear as singlet at 9.08 ppm in the complex. The signal as compare to ligand show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine nitrogen to the metal centre. The signal of $-CH_3$ protons observed as singlet at 2.64 ppm. The signals of the aromatic protons of the Cu(II) complex appeared at δ 7.56-8.17 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi\rightarrow\pi^*$ and/or $n\rightarrow\pi^*$ interaligand transition. There are two detected absorption bands at around 290 nm and 348 nm assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ interaligand transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 748 nm is assigned to a merges of $^2T_{2g}\leftarrow{}^2E_g$ transition in square planer geometry.

The TGA curves of the Copper(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly

indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Cu(L_2)\,(H_2O)_n] \cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Cu(L_2)\,(H_2O)_n] + nH_2O$$

$$[Cu(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Cu(L_2)] + (H_2O)_n$$

$$[Cu(L_2)] \xrightarrow{180\text{-}300\ ^0C} [CuL] + L$$

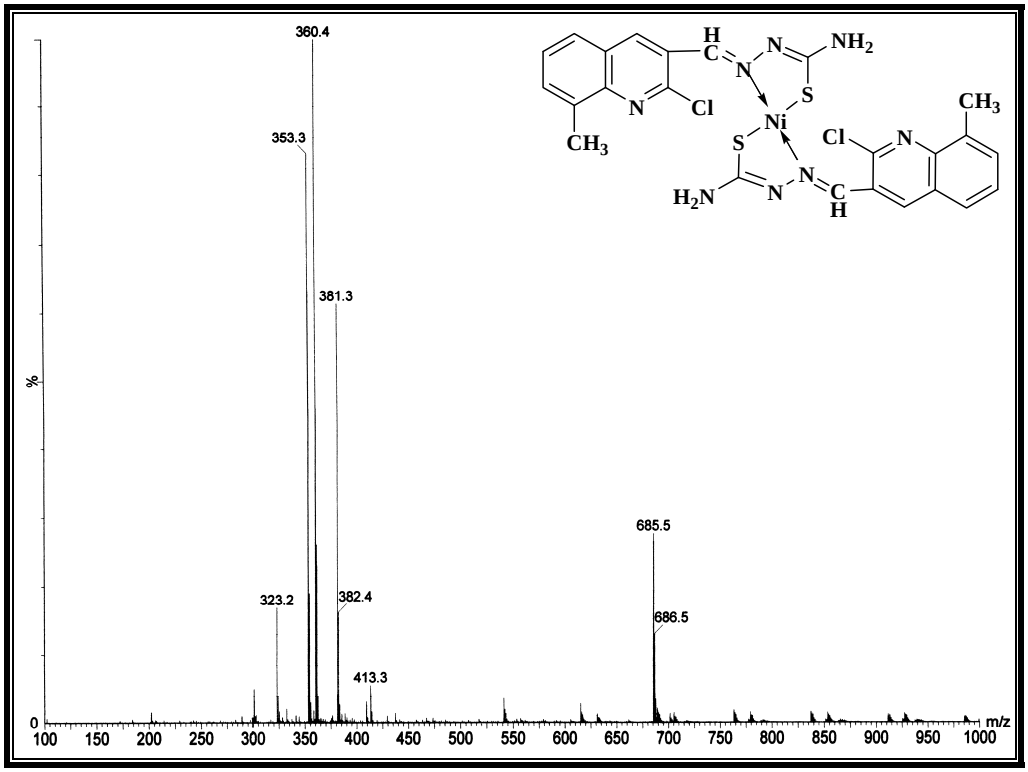
$$[CuL] \xrightarrow{300\text{-}600\ ^0C} CuO + L$$

(Where n = 0, 1 or 2).

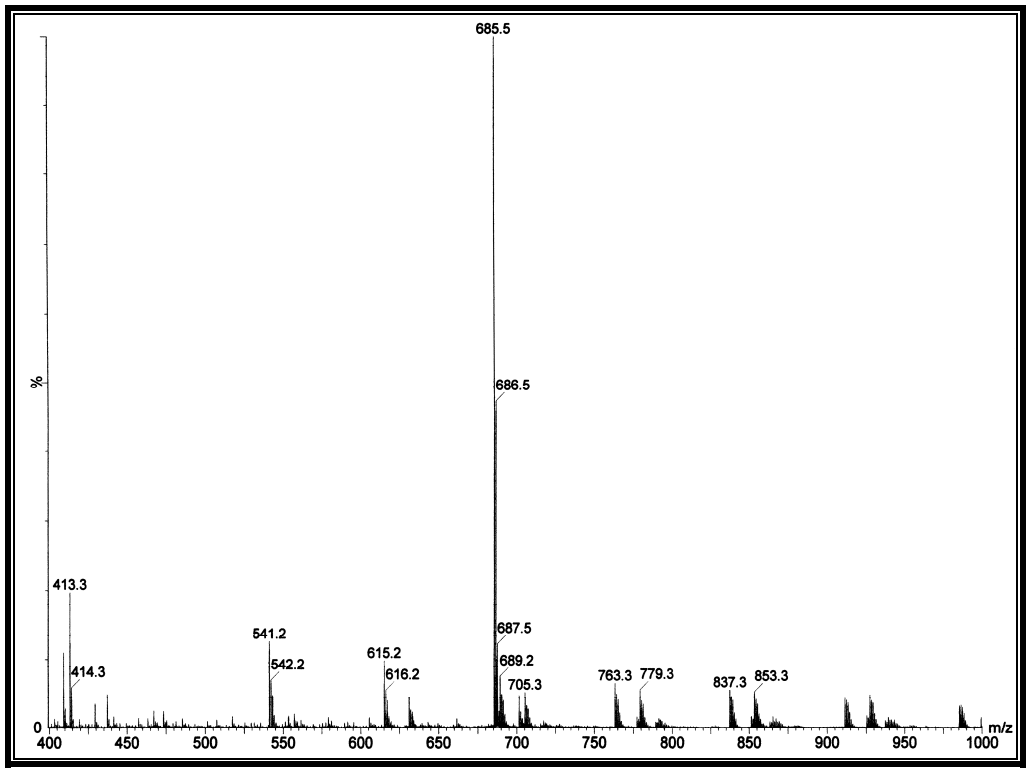
The room temperature magnetic moments for the copper(II) complex 1.74 BM correspond to the values normally observed for square-planar copper(II) compound. The room temperature value for μ_{eff} (2.03) (where μ_{eff} is the effective magnetic moment) is very close to the spin-only value of 1.73 B.M. for d^9.

All spectral characterization and thermal analysis confirms the structure of Copper(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene) thiosemicarbazide(RMT-10). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the square planer type geometries of the present complex.

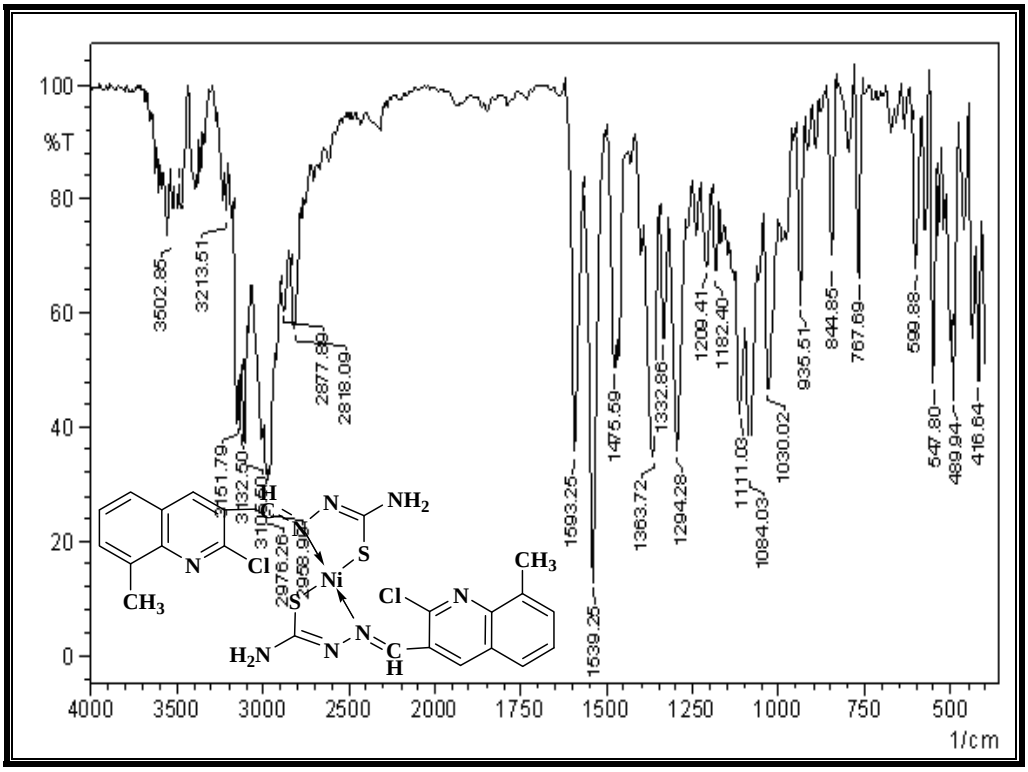
ESI Mass spectrum of RMT- 11



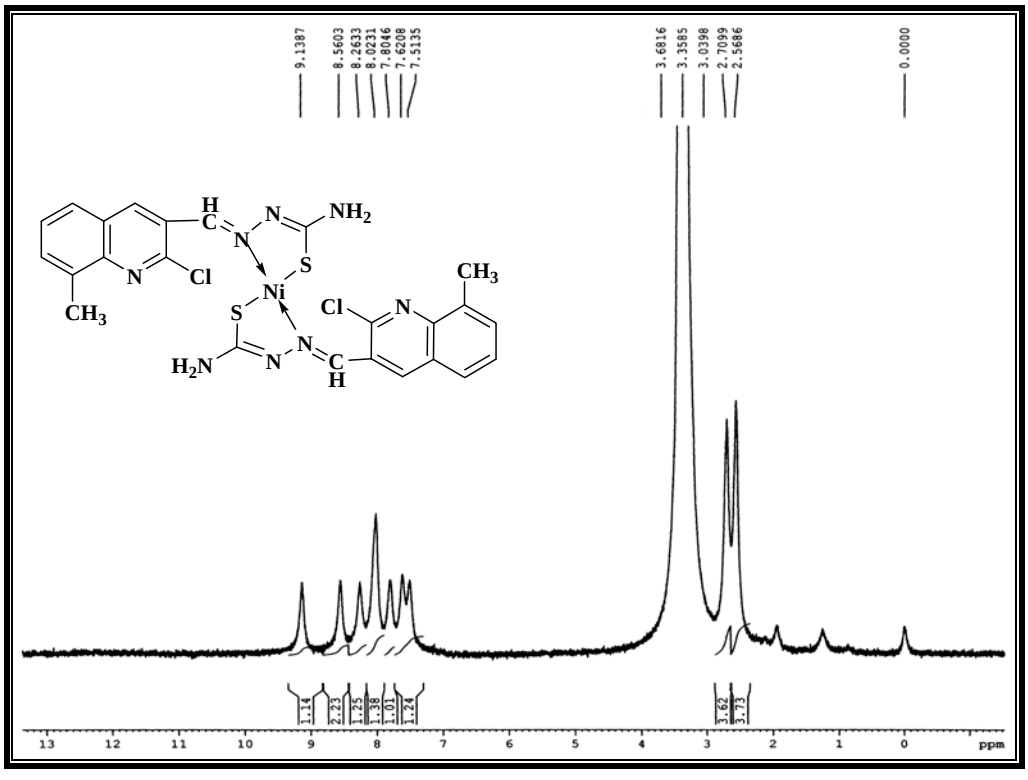
Expanded ESI Mass spectrum of RMT- 11



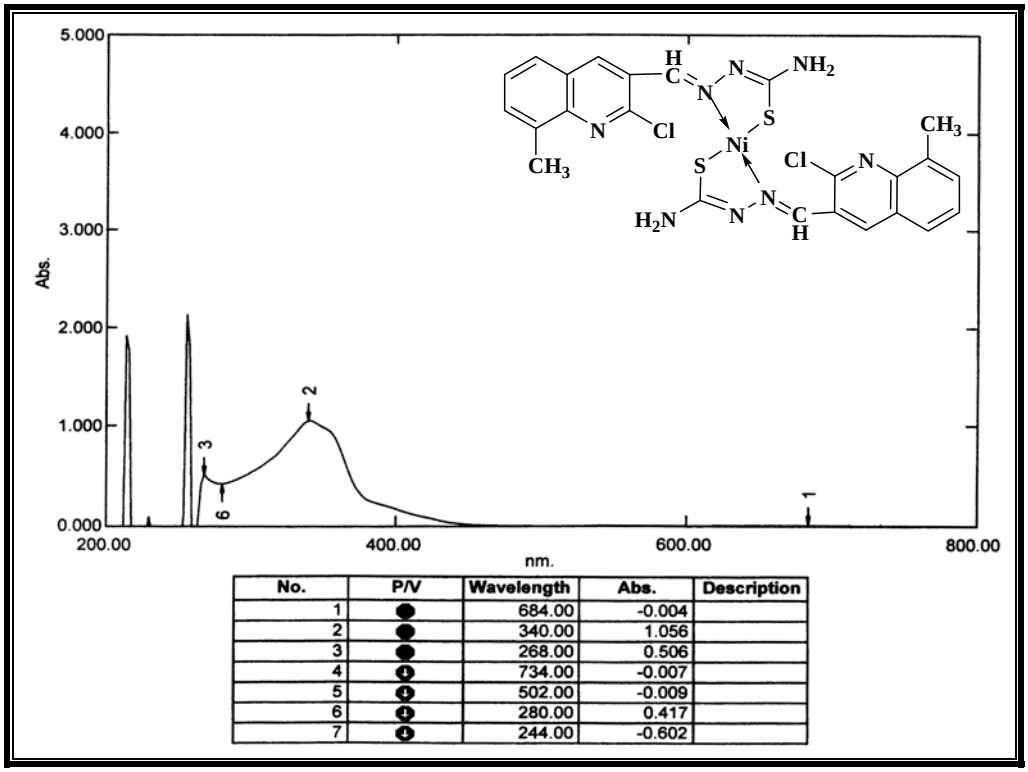
IR spectrum of RMT- 11



^{1}H NMR spectrum of RMT- 11

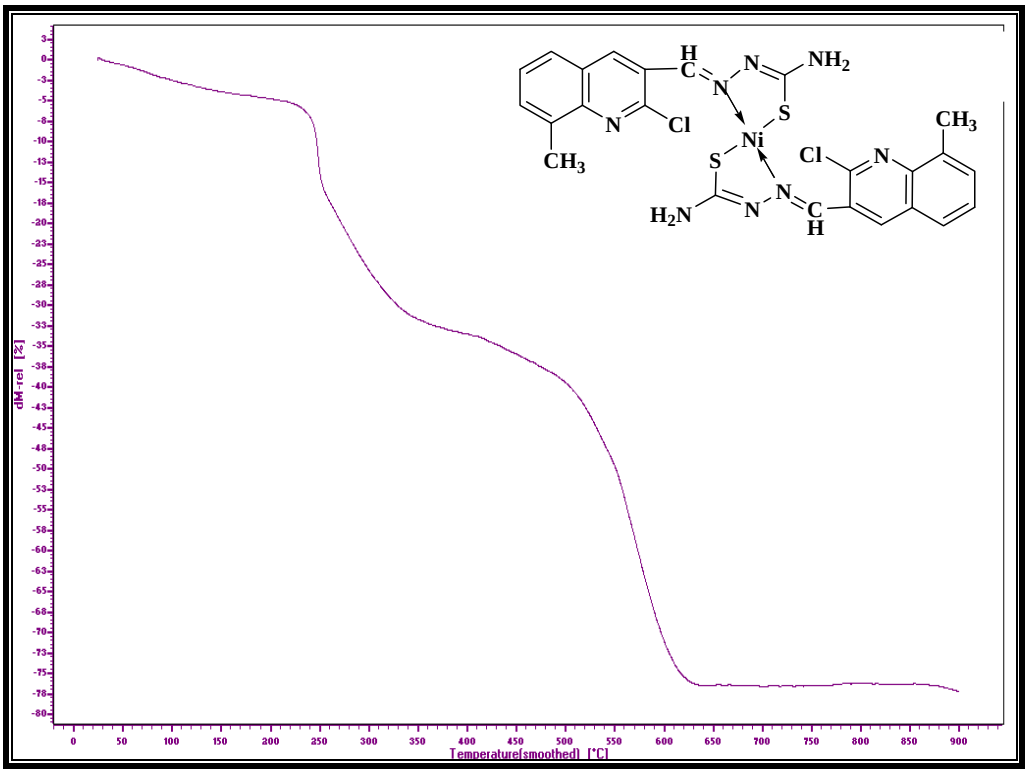


UV-Visible spectrum of RMT- 11



No.	P/V	Wavelength	Abs.	Description
1	●	684.00	-0.004	
2	●	340.00	1.056	
3	●	268.00	0.506	
4	▼	734.00	-0.007	
5	▼	502.00	-0.009	
6	▼	280.00	0.417	
7	▼	244.00	-0.602	

TGA spectrum of RMT- 11



Results & Discussion

The most important bands in the infrared spectra of the Nickel(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Nickel(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide exhibited a bands observed at 3213 cm^{-1}, 1084 cm^{-1} and 1209 cm^{-1} of -NH_2, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1593 cm^{-1} and aromatic -C-H and -C=C bands due to at 3151-2976 cm^{-1} and 1475 cm^{-1} respectively. The specific bands (Ni-N) and (Ni-S) observed at 489 cm^{-1} and 416 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Nickel(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other -NH_2 protons signals observed as singlets at 8.56 ppm. The signals of the (-HC=N) protons which appear as singlets at 9.13 ppm in the complex. The signal as compare to ligands show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine nitrogen to the

metal centre. The signal of -CH_3 protons observed as singlet at 2.56 ppm. The signals of the aromatic protons of the Ni(II) complex appeared at δ 7.62-8.26 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ interaligand transition. There are two detected absorption bands at around 268 nm assigned to $\pi \rightarrow \pi^*$ interaligand transition and 340 nm assigned to $^3T_{1g}(P) \leftarrow {}^3A_{2g}(F)$ transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 684 nm is assigned to a merges of $^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)$ transition in tetrahedral geometry.

The TGA curves of the Nickel(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Ni(L_2)\,(H_2O)_n] \cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Ni(L_2)\,(H_2O)_n] + nH_2O$$

$$[Ni(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Ni(L_2)] + (H_2O)_n$$

$$[Ni(L_2)] \xrightarrow{180\text{-}300\ ^0C} [NiL] + L$$

$$[NiL] \xrightarrow{300\text{-}600\ ^0C} NiO + L$$

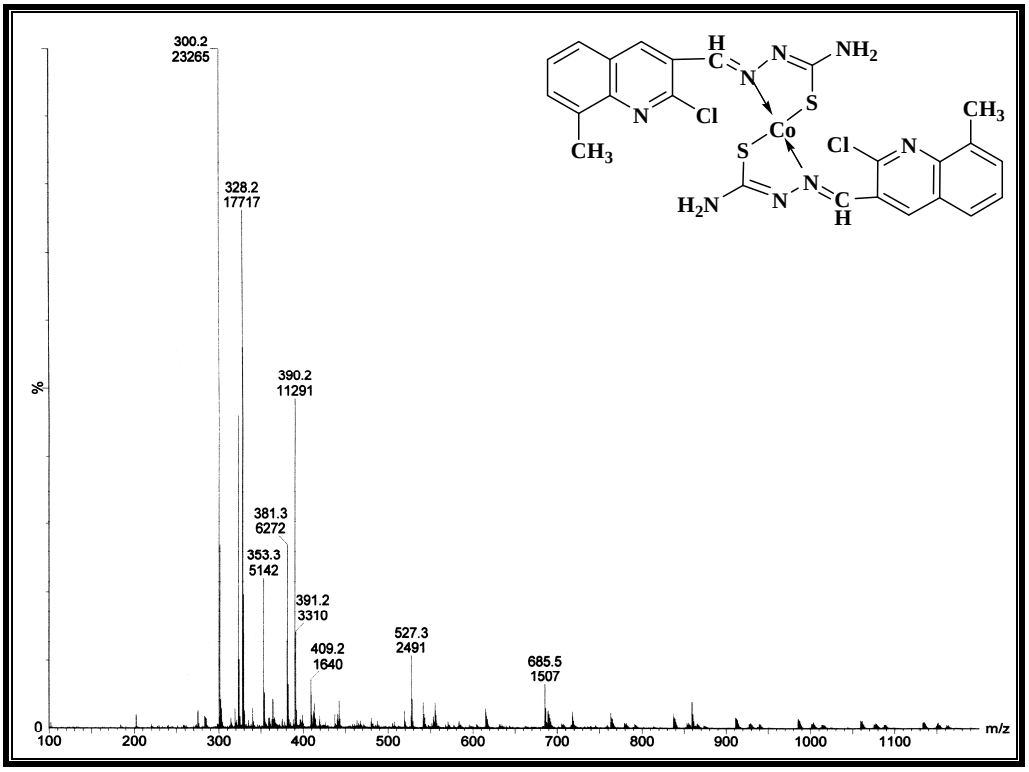
(Where n = 0, 1 or 2).

The magnetic moment of the nickel complex was found to be 3.71 B.M. which falls in the range generally observed for the four-coordinated Ni(II) complex. The

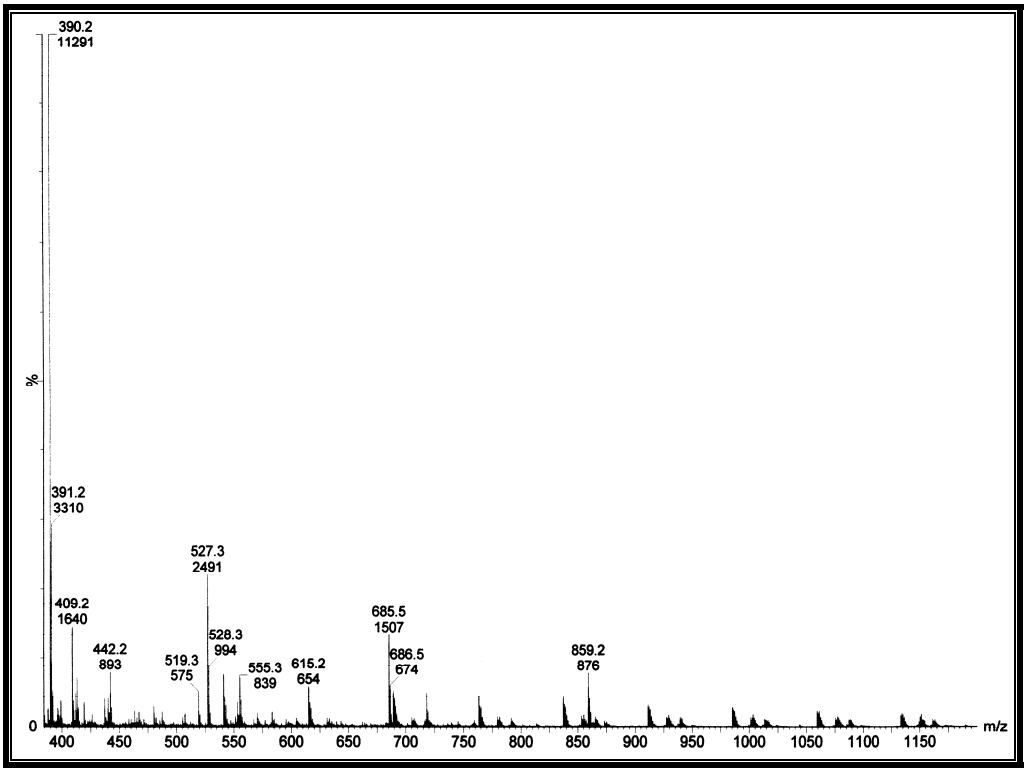
magnetic data of the Ni(II) complex agree with a d^8 metal ion in an tetrahedral configuration.

All spectral characterization and thermal analysis confirms the structure of Nickel(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene) thiosemicarbazide(RMT-11). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the tetrahedral type geometries of the present complex.

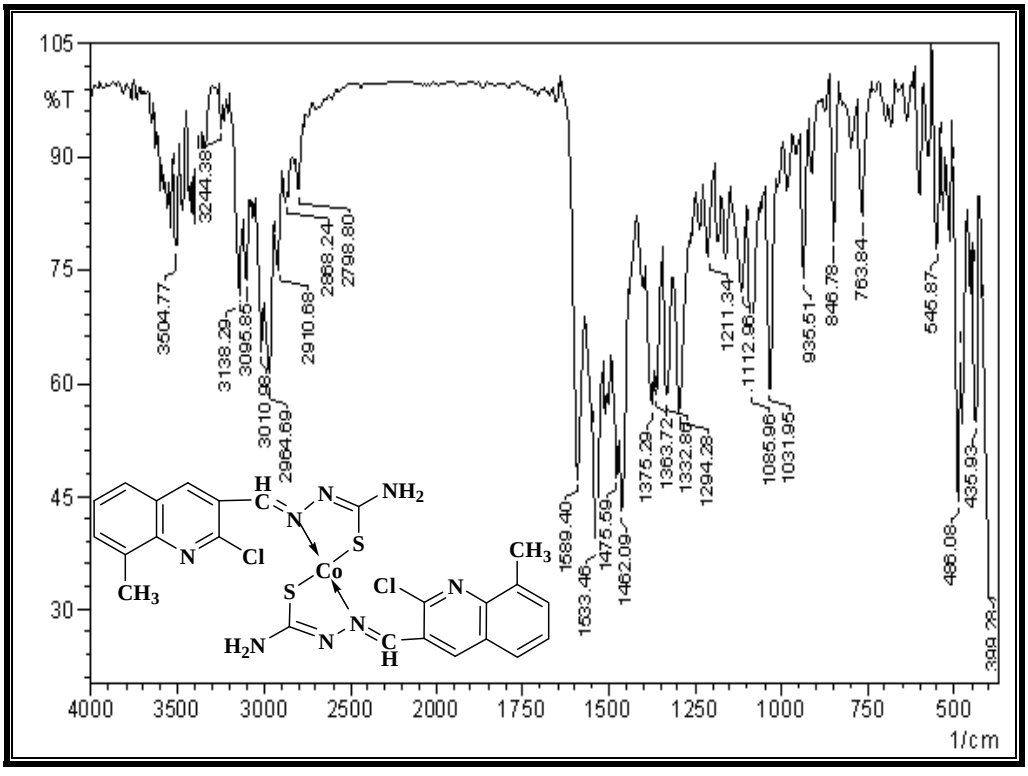
ESI Mass spectrum of RMT- 12



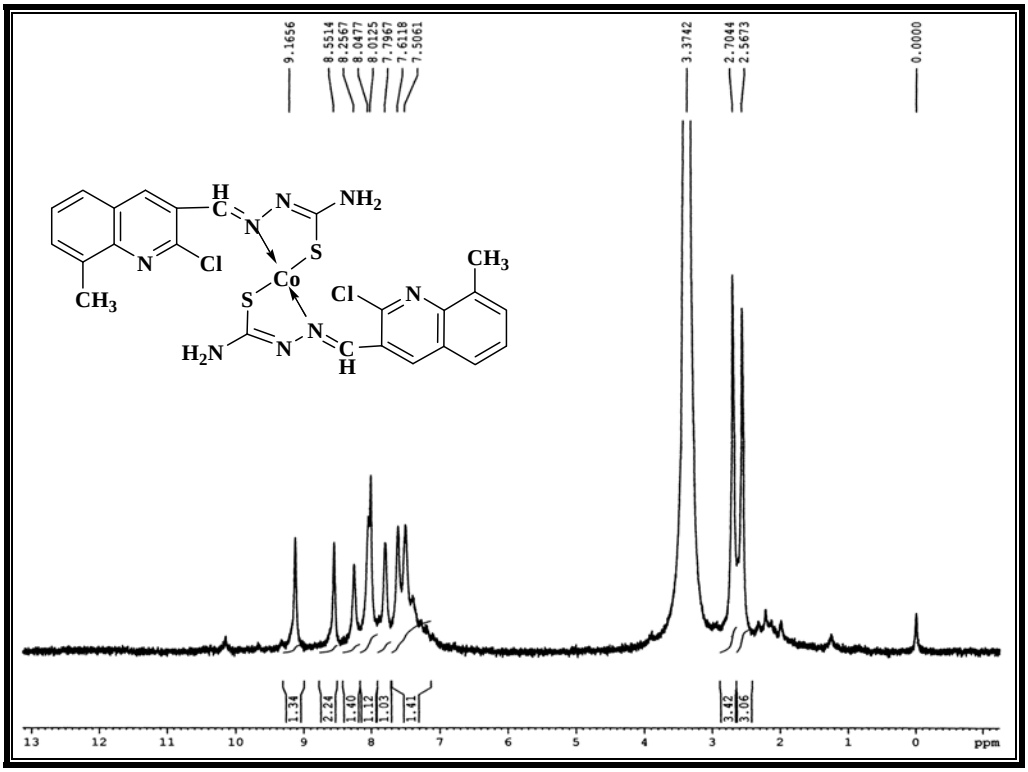
Expanded ESI Mass spectrum of RMT- 12



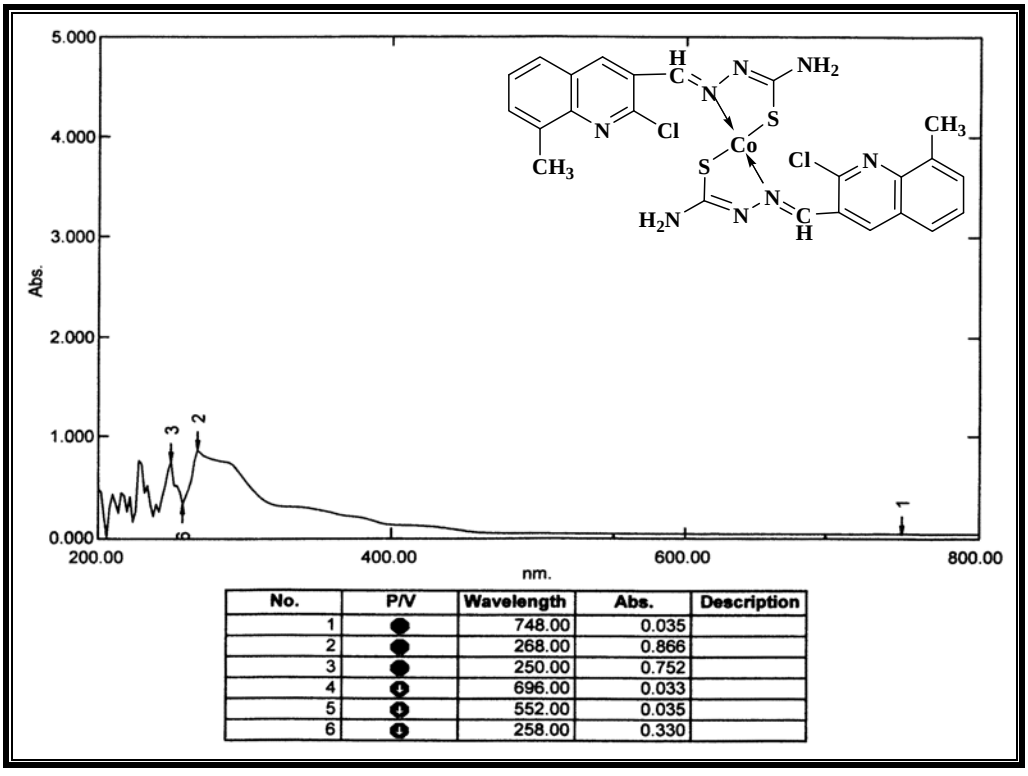
IR spectrum of RMT- 12



^{1}H NMR spectrum of RMT- 12

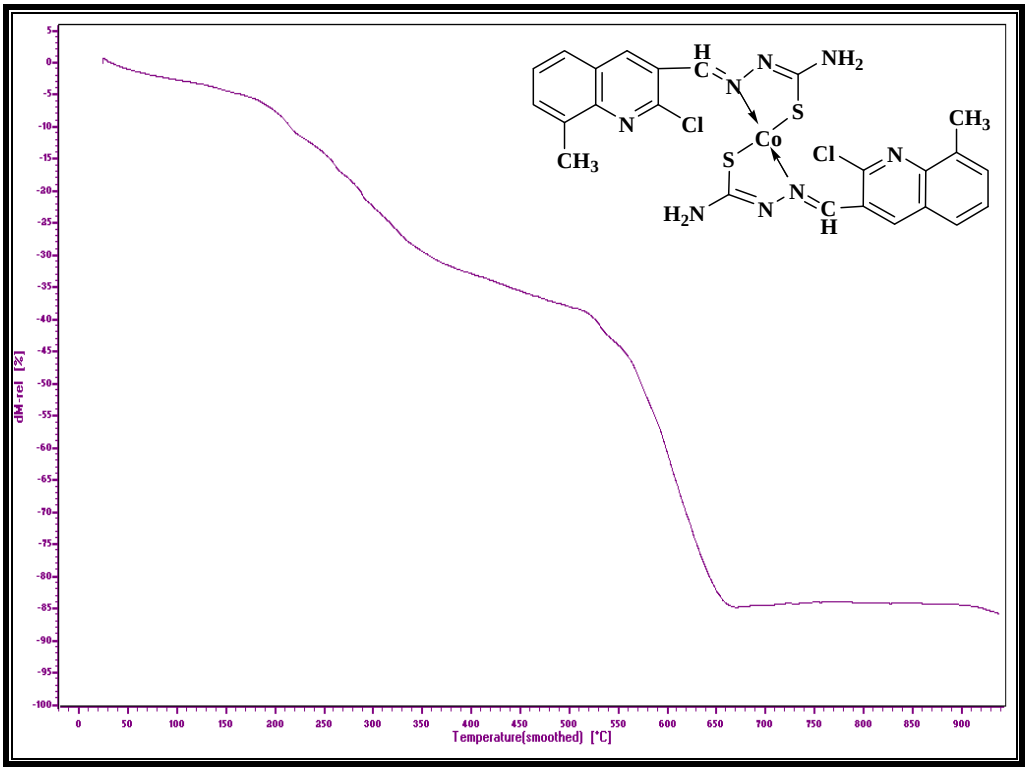


UV-Visible spectrum of RMT- 12



No.	P/V	Wavelength	Abs.	Description
1	●	748.00	0.035	
2	●	268.00	0.866	
3	●	250.00	0.752	
4	◆	696.00	0.033	
5	◆	552.00	0.035	
6	◆	258.00	0.330	

TGA spectrum of RMT- 12



Results & Discussion

The most important bands in the infrared spectra of the Cobalt(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating

that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Cobalt(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide exhibited a bands observed at 3244 cm^{-1}, 1085 cm^{-1} and 1211 cm^{-1} of $-NH_2$, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1589 cm^{-1} and aromatic -C-H and -C=C bands due to at 3138-2964 cm^{-1} and 1475 cm^{-1} respectively. The specific bands (Co-N) and (Co-S) observed at 486 cm^{-1} and 435 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Cobalt(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other $-NH_2$ protons signals observed as singlets at 8.55 ppm. The signals of the (-HC=N) protons which appear as singlets at 9.16 ppm in the complex. The signal as compare to ligands show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine nitrogen to the metal centre. The signal of $-CH_3$ protons observed as singlet at 2.56 ppm. The signals of the aromatic protons of the Co(II) complex appeared at δ 7.61-8.25 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi\rightarrow\pi^*$ and/or $n\rightarrow\pi^*$ interaligand transition. There are two detected absorption bands at around 250 nm and 268 nm assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ interaligand transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 748 nm is assigned to a merges of $^4T_{2g}(F)\leftarrow{}^4T_{1g}(F)$ transition in tetrahedral geometry.

The TGA curves of the Cobalt(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly

indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Co(L_2)\,(H_2O)_n]\cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Co(L_2)\,(H_2O)_n] + nH_2O$$

$$[Co(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Co(L_2)] + (H_2O)_n$$

$$[Co(L_2)] \xrightarrow{180\text{-}300\ ^0C} [CoL] + L$$

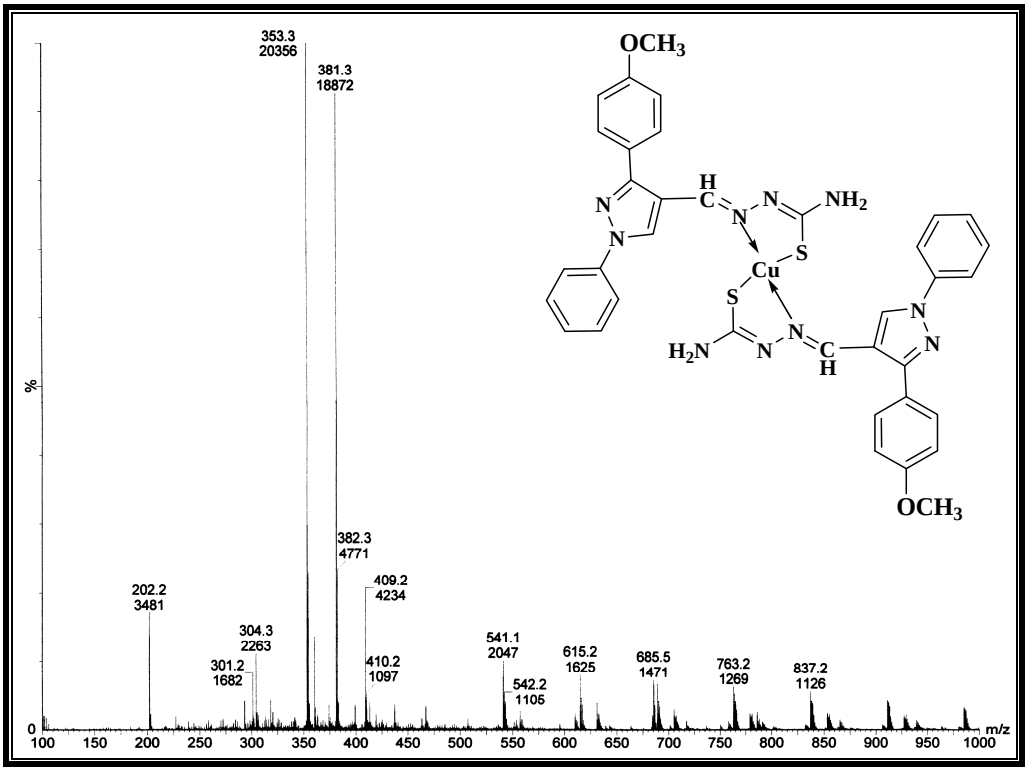
$$[CoL] \xrightarrow{300\text{-}600\ ^0C} CoO + L$$

(Where n = 0, 1 or 2).

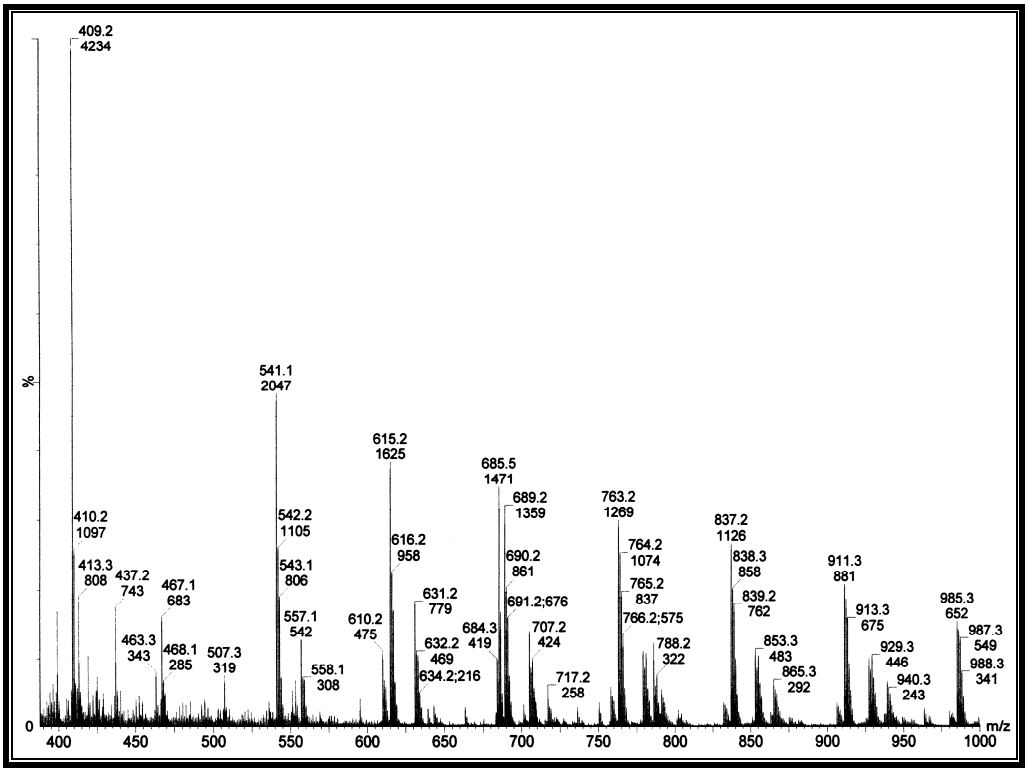
Magnetic moment measurements for the complexes were made at room temperature. The cobalt(II) complex show magnetic moment 4.25 BM, a value in accordance with a high spin configuration showing the presence of tetrahedral environment around the cobalt(II) ion in the complex. The experimental values are higher than spin only value due to orbital angular momentum contribution in d^7 system.

All spectral characterization and thermal analysis confirms the structure of Cobalt(II) complex of 1-((2-chloro-8-methylquinolin-3-yl)methylene) thiosemicarbazide(RMT-12). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the tetrahedral type geometries of the present complex.

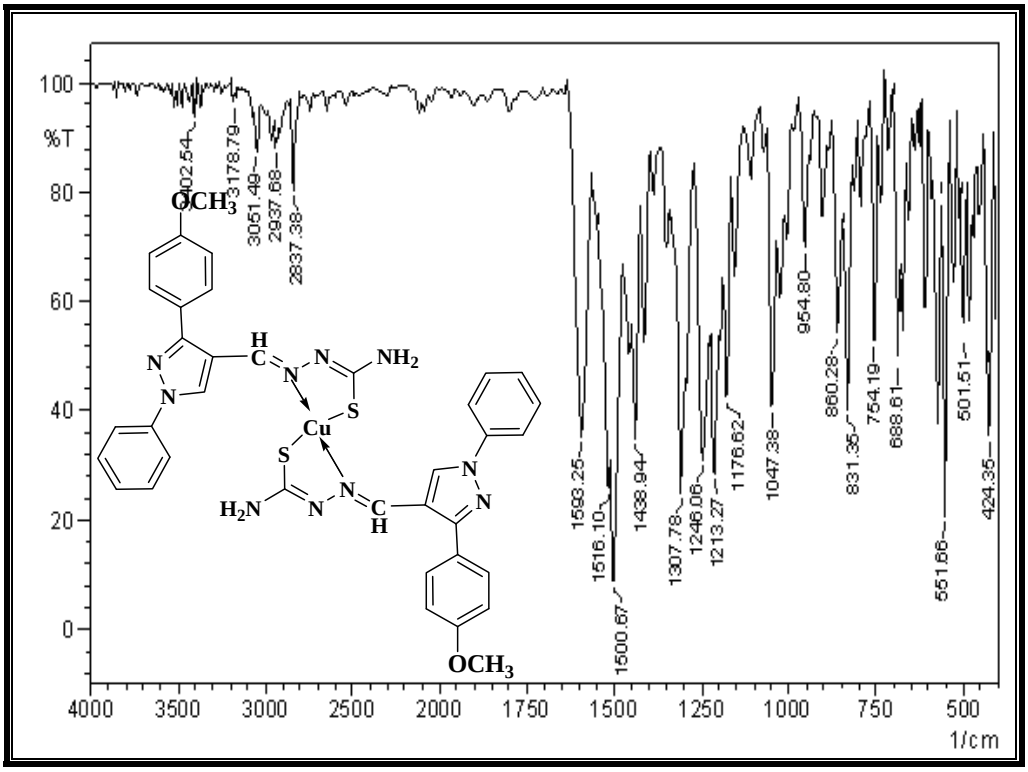
ESI Mass spectrum of RMT- 13



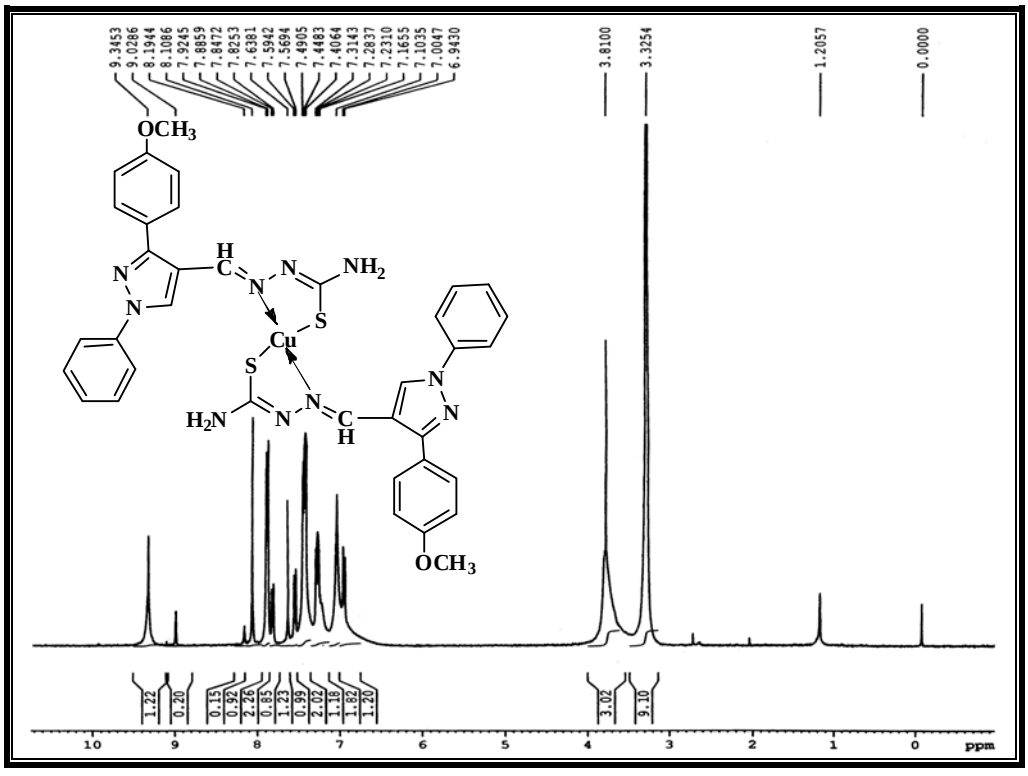
Expanded ESI Mass spectrum of RMT- 13



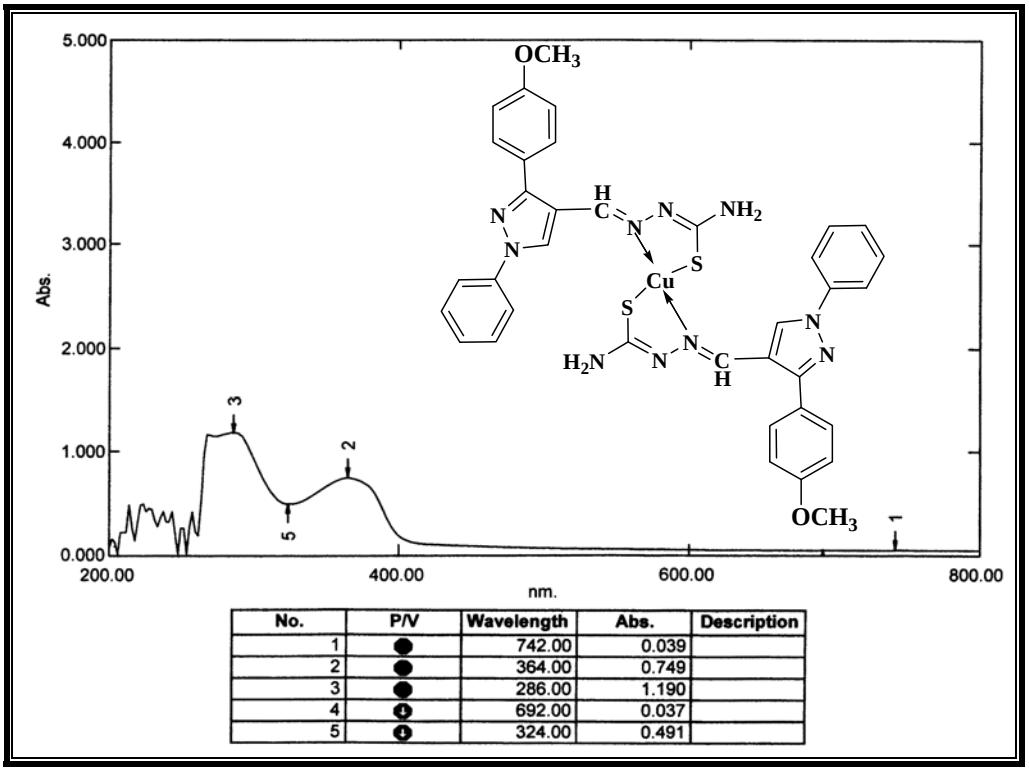
IR spectrum of RMT- 13



^{1}H NMR spectrum of RMT- 13

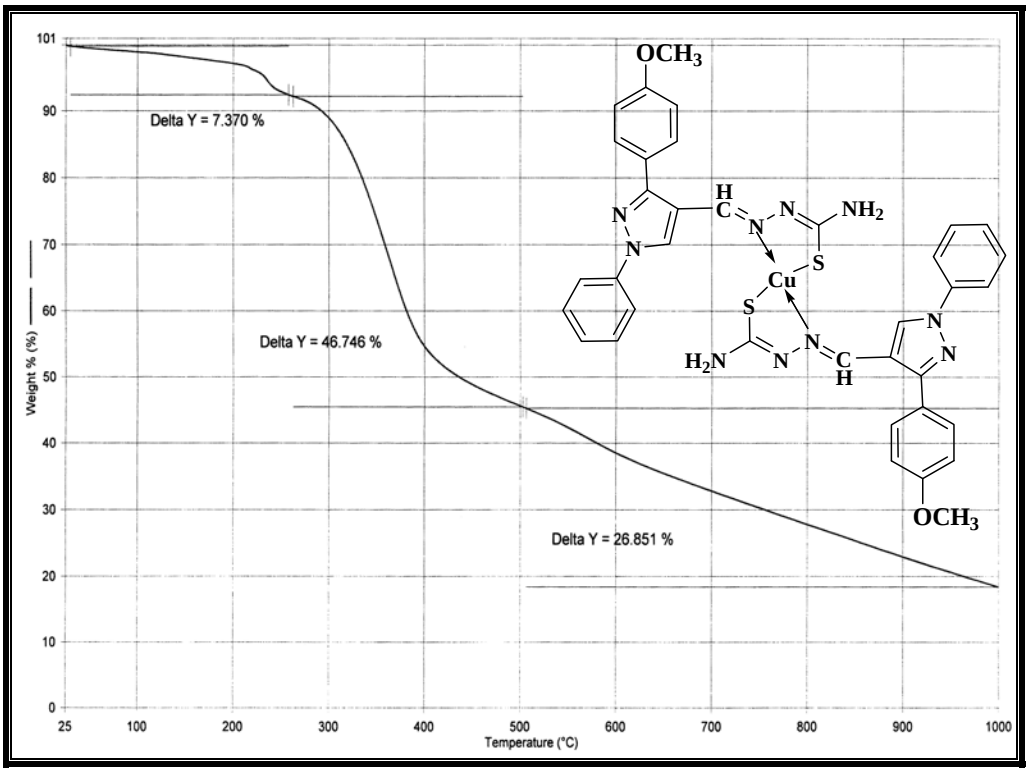


UV-Visible spectrum of RMT- 13



No.	P/V	Wavelength	Abs.	Description
1	●	742.00	0.039	
2	●	364.00	0.749	
3	●	286.00	1.190	
4	◆	692.00	0.037	
5	◆	324.00	0.491	

TGA spectrum of RMT- 13



Results & Discussion

The most important bands in the infrared spectra of the Copper(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Copper(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide exhibited a bands observed at 3178 cm^{-1}, 1047 cm^{-1} and 1246 cm^{-1} of -NH_2, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1593 cm^{-1} and aromatic -C-H and -C=C bands due to at 3051-2937 cm^{-1} and 1500 cm^{-1} respectively. The specific bands (Cu-N) and (Cu-S) observed at 501 cm^{-1} and 424 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Copper(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other -NH_2 protons signals observed as singlets at 7.88 ppm. The signals of the (-HC=N) proton which appear as singlet at 9.34 ppm in the complex. The signal as compare to ligand show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine

nitrogen to the metal centre. The signal of -OCH_3 protons observed as singlet at 3.81 ppm. The signals of the aromatic protons of the Cu(II) complex appeared at δ 7.00-7.82 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi\rightarrow\pi^*$ and/or $n\rightarrow\pi^*$ interaligand transition. There are two detected absorption bands at around 286 nm and 364 nm assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ interaligand transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 742 nm is assigned to a merges of $^2T_{2g}\leftarrow{}^2E_g$ transition in square planer geometry.

The TGA curves of the Copper(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Cu(L_2)\,(H_2O)_n]\cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Cu(L_2)\,(H_2O)_n] + nH_2O$$

$$[Cu(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Cu(L_2)] + (H_2O)_n$$

$$[Cu(L_2)] \xrightarrow{180\text{-}300\ ^0C} [CuL] + L$$

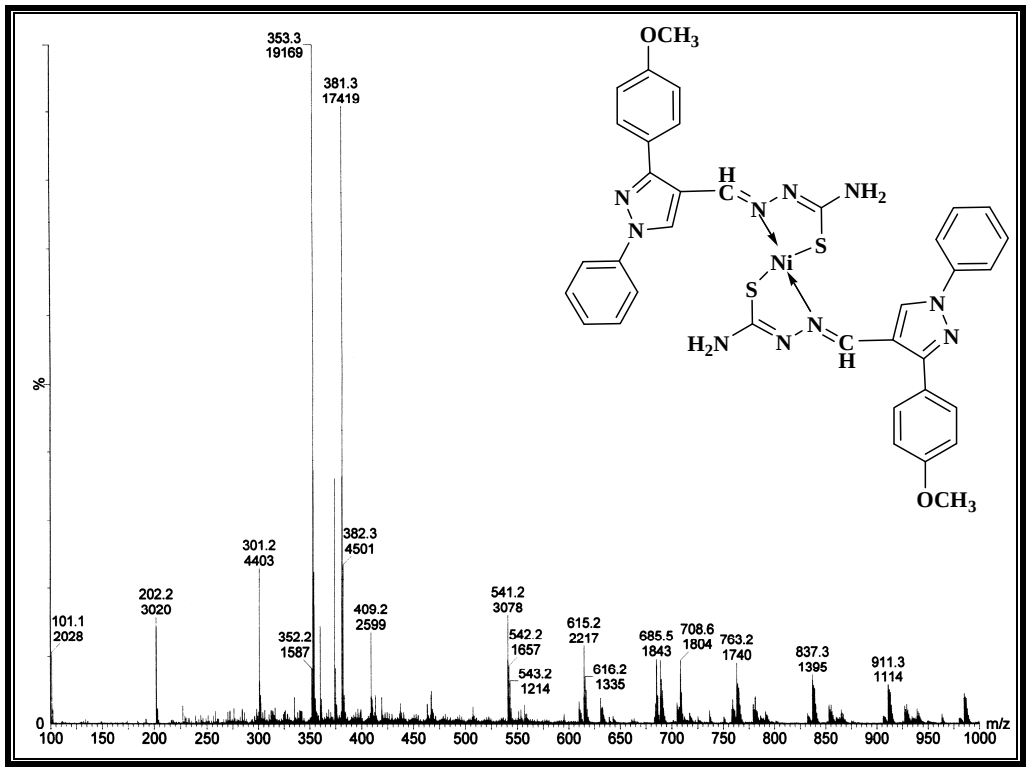
$$[CuL] \xrightarrow{300\text{-}600\ ^0C} CuO + L$$

(Where n = 0, 1 or 2).

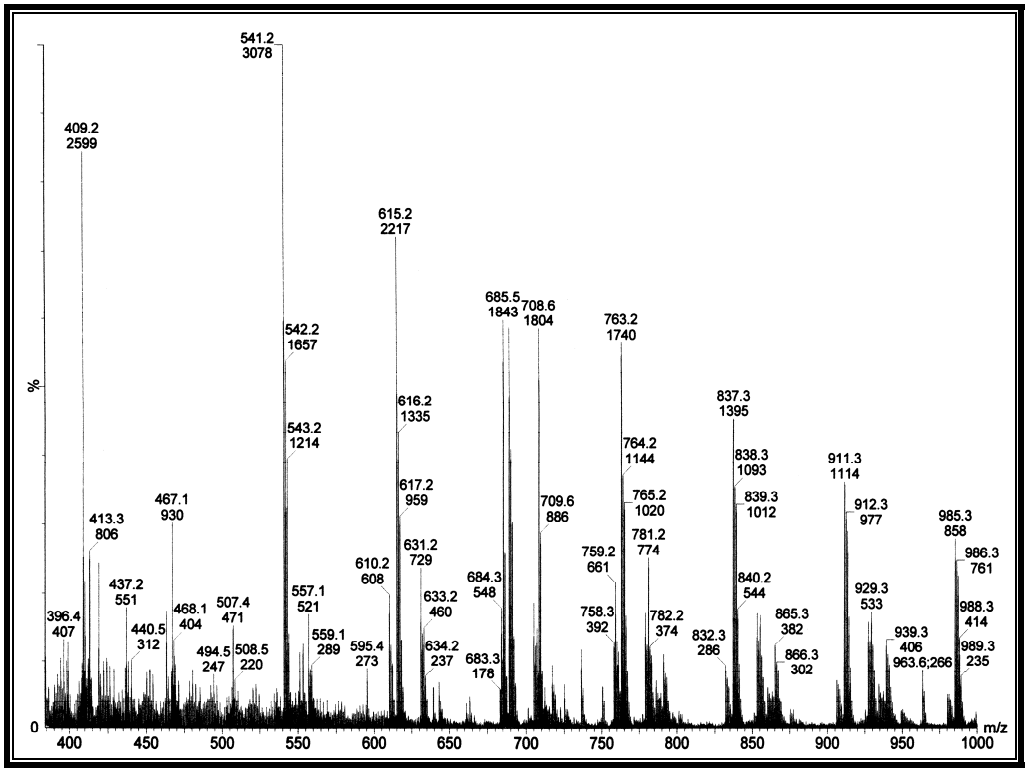
The room temperature magnetic moments for the copper(II) complex 1.74 BM correspond to the values normally observed for square-planar copper(II) compound. The room temperature value for μ_{eff} (2.01) (where μ_{eff} is the effective magnetic moment) is very close to the spin-only value of 1.73 B.M. for d^9.

All spectral characterization and thermal analysis confirms the structure of Copper(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide(RMT-13). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the square planer type geometries of the present complex.

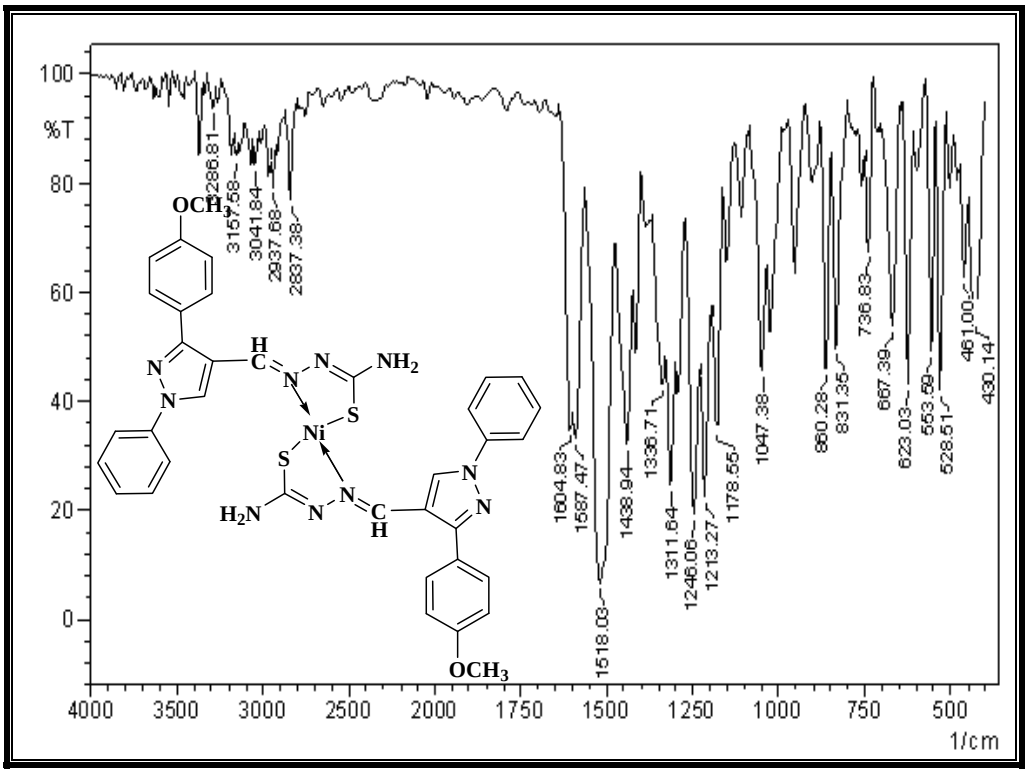
ESI Mass spectrum of RMT- 14



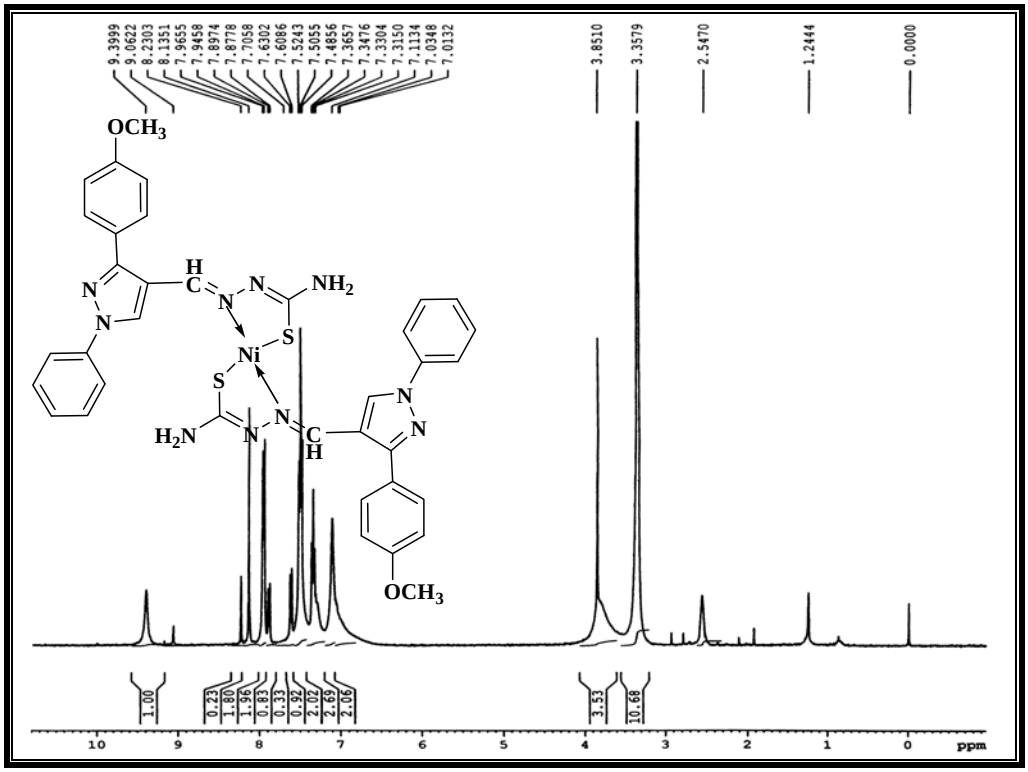
Expanded ESI Mass spectrum of RMT- 14



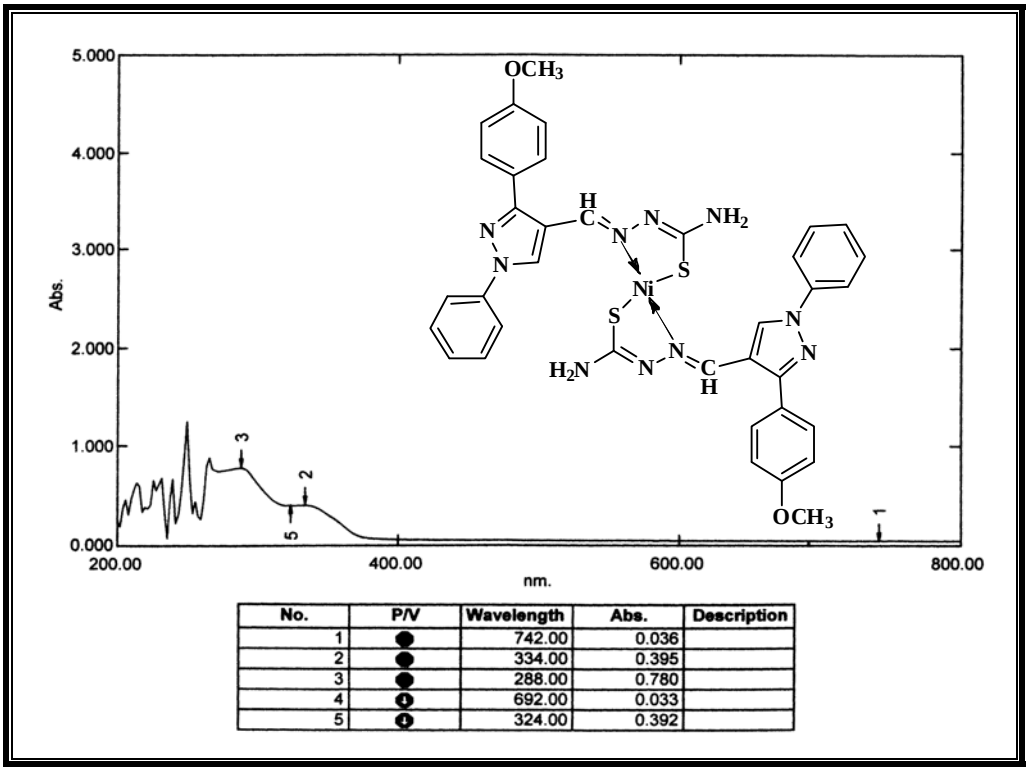
IR spectrum of RMT- 14



^{1}H NMR spectrum of RMT- 14



UV-Visible spectrum of RMT- 14



No.	P/V	Wavelength	Abs.	Description
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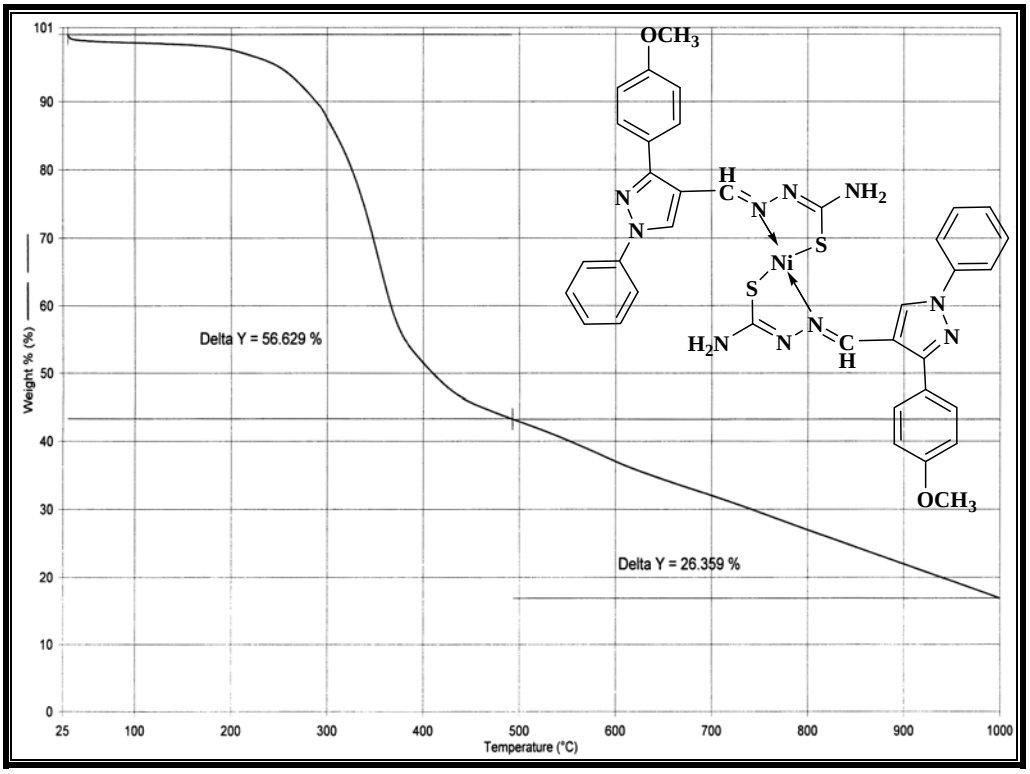
2	●	334.00	0.395	
3	●	288.00	0.780	
4	▼	692.00	0.033	
5	▼	324.00	0.392	

TGA spectrum of RMT- 14



Results & Discussion

The most important bands in the infrared spectra of the Nickel(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating

that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Nickel(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide exhibited a bands observed at 3286 cm^{-1}, 1047 cm^{-1} and 1246 cm^{-1} of -NH_2, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1587 cm^{-1} and aromatic -C-H and -C=C bands due to at 3157-2937 cm^{-1} and 1518 cm^{-1} respectively. The specific bands (Ni-N) and (Ni-S) observed at 528 cm^{-1} and 430 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Nickel(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other -NH_2 protons signals observed as singlets at 8.13 ppm. The signals of the (-HC=N) protons which appear as singlets at 9.39 ppm in the complex. The signal as compare to ligands show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine nitrogen to the metal centre. The signal of -OCH_3 protons observed as singlet at 3.85 ppm. The signals of the aromatic protons of the Ni(II) complex appeared at δ 7.11-7.96 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi\rightarrow\pi^*$ and/or $n\rightarrow\pi^*$ interaligand transition. There are two detected absorption bands at around 288 nm assigned to $\pi\rightarrow\pi^*$ interaligand transition and 334 nm assigned to $^3T_{1g}(P)\leftarrow{}^3A_{2g}(F)$ transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 742 nm is assigned to a merges of $^3T_{1g}(F)\leftarrow{}^3A_{2g}(F)$ transition in tetrahedral geometry.

The TGA curves of the Nickel(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from

thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Ni(L_2)\,(H_2O)_n] \cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Ni(L_2)\,(H_2O)_n] + nH_2O$$

$$[Ni(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Ni(L_2)] + (H_2O)_n$$

$$[Ni(L_2)] \xrightarrow{180\text{-}300\ ^0C} [NiL] + L$$

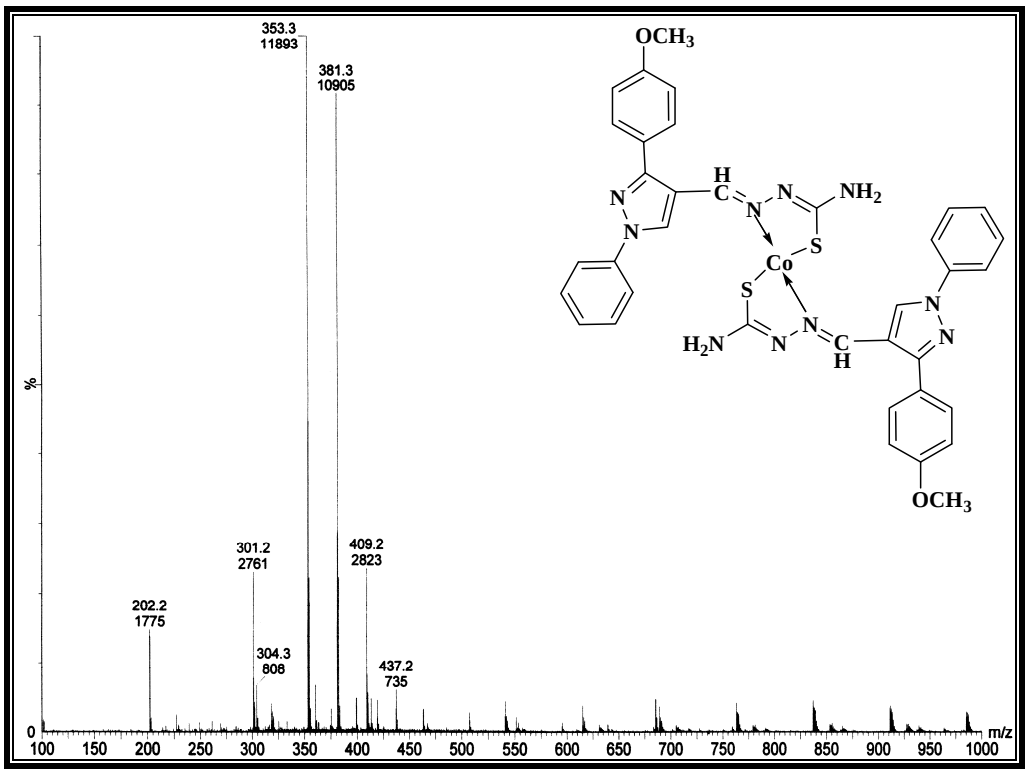
$$[NiL] \xrightarrow{300\text{-}600\ ^0C} NiO + L$$

(Where n = 0, 1 or 2).

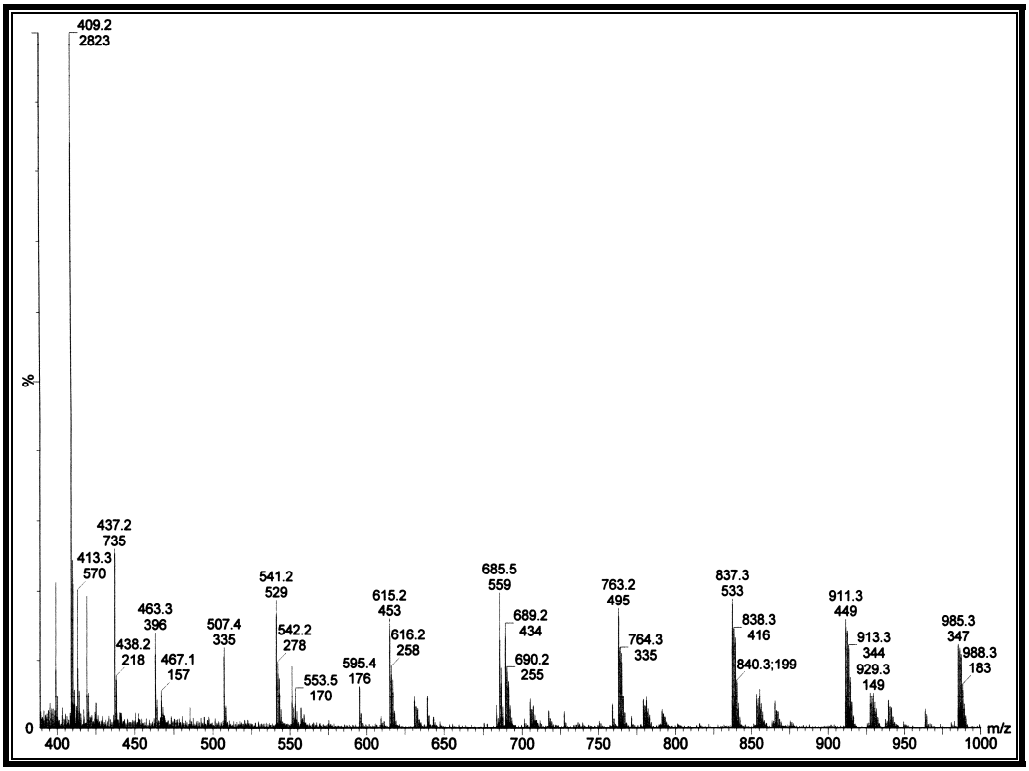
The magnetic moment of the nickel complex was found to be 3.15 B.M. which falls in the range generally observed for the four-coordinated Ni(II) complex. The magnetic data of the Ni(II) complex agree with a d^8 metal ion in an tetrahedral configuration.

All spectral characterization and thermal analysis confirms the structure of Nickel(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide(RMT-14). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the tetrahedral type geometries of the present complex.

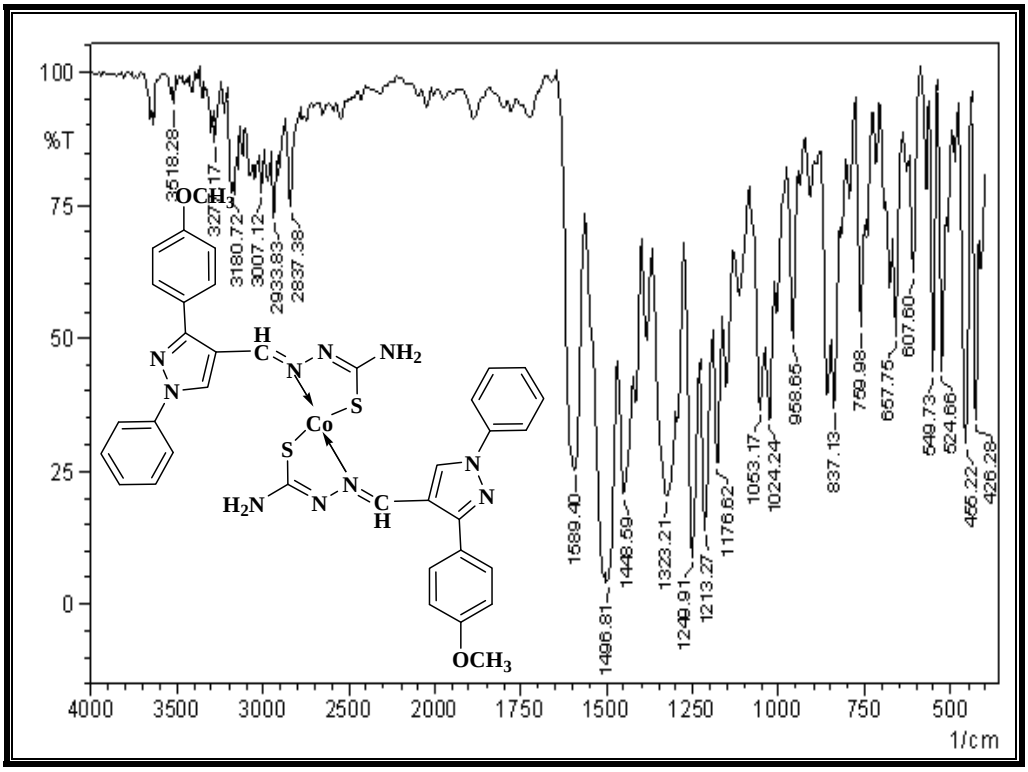
ESI Mass spectrum of RMT- 15



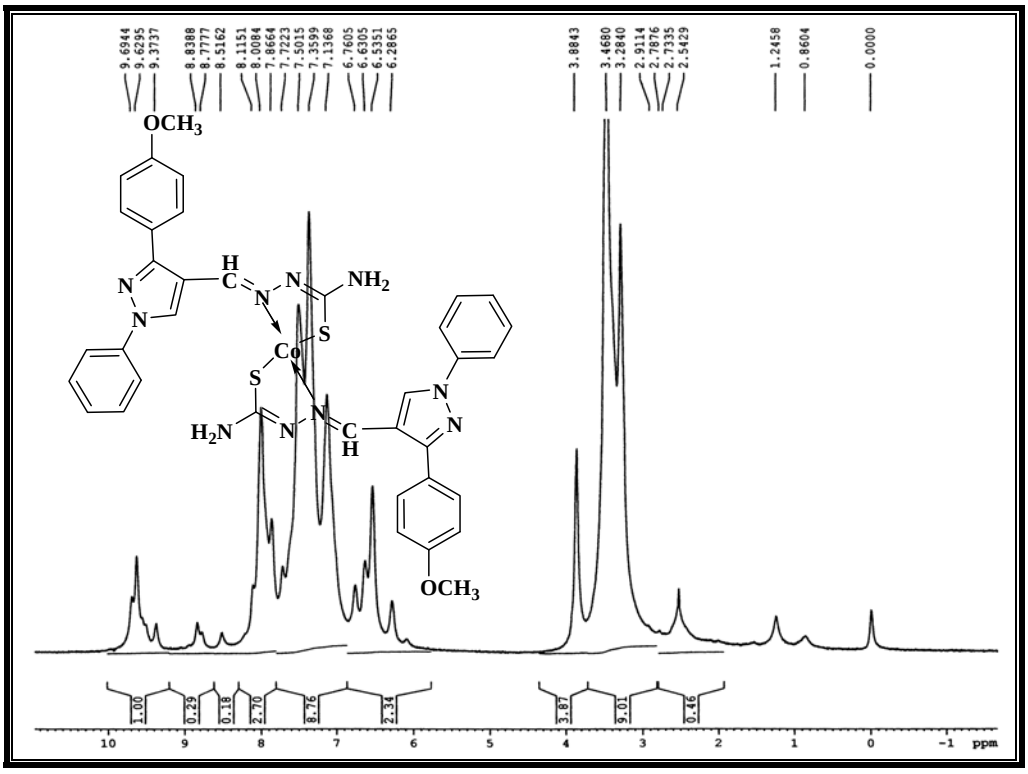
Expanded ESI Mass spectrum of RMT- 15



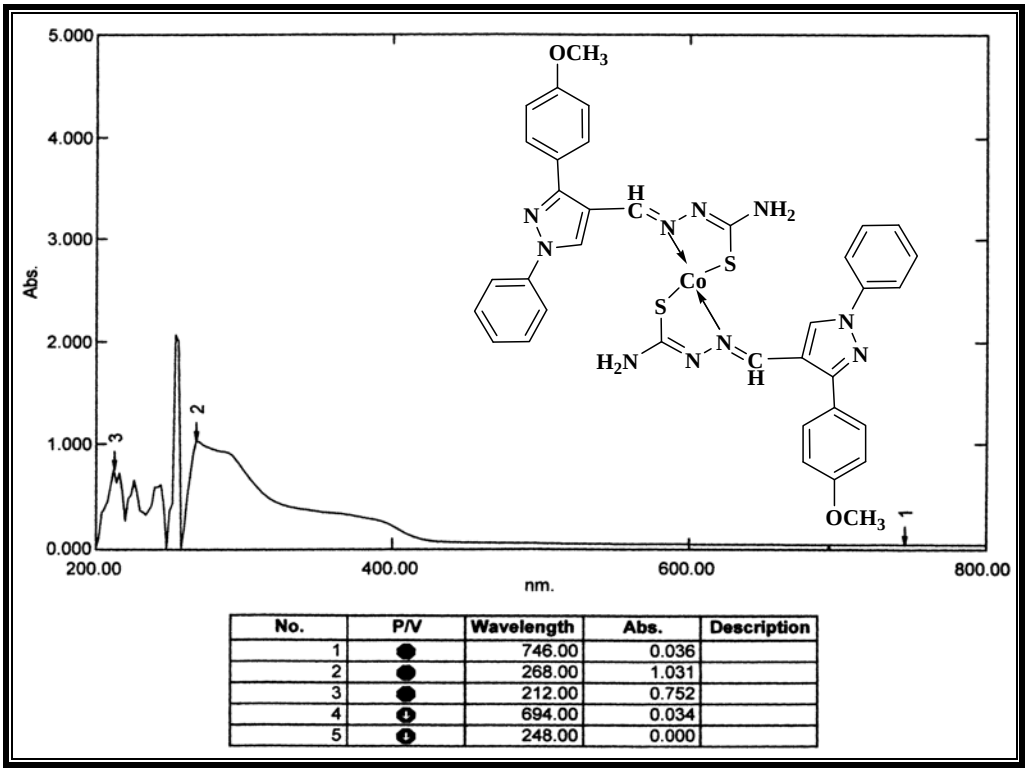
IR spectrum of RMT- 15



^{1}H NMR spectrum of RMT- 15

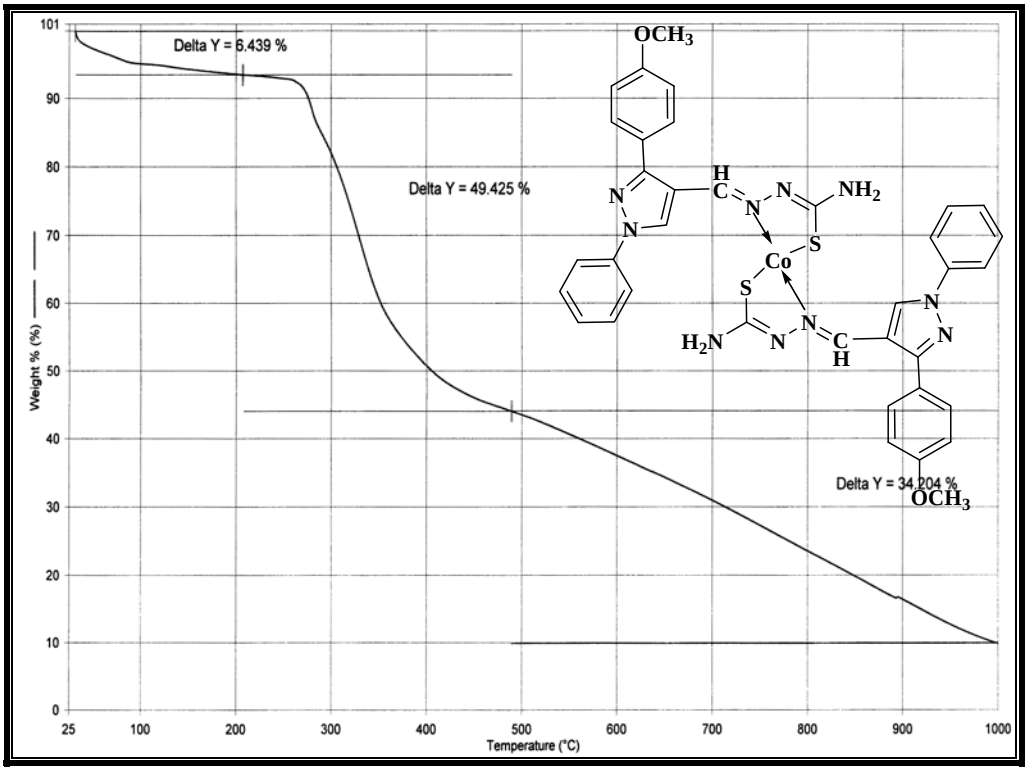


UV-Visible spectrum of RMT- 15



No.	P/V	Wavelength	Abs.	Description
1	●	746.00	0.036	
2	●	268.00	1.031	
3	●	212.00	0.752	
4	▲	694.00	0.034	
5	▲	248.00	0.000	

TGA spectrum of RMT- 15



Results & Discussion

The most important bands in the infrared spectra of the Cobalt(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Cobalt(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide exhibited a bands observed at 3277 cm^{-1}, 1053 cm^{-1} and 1249 cm^{-1} of -NH_2, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1589 cm^{-1} and aromatic -C-H and -C=C bands due to at 3180-2933 cm^{-1} and 1496 cm^{-1} respectively. The specific bands (Co-N) and (Co-S) observed at 524 cm^{-1} and 426 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Cobalt(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other -NH_2 protons signals observed as singlets at 8.11 ppm. The signals of the (-HC=N) protons which appear as singlets at 9.62 ppm in the complex. The signal as compare to ligands show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine

nitrogen to the metal centre. The signal of -OCH_3 protons observed as singlet at 3.88 ppm. The signals of the aromatic protons of the Co(II) complex appeared at δ 6.53-7.50 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ interaligand transition. There are two detected absorption bands at around 212 nm and 268 nm assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ interaligand transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 746 nm is assigned to a merges of $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ transition in tetrahedral geometry.

The TGA curves of the Cobalt(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Co(L_2)\,(H_2O)_n] \cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Co(L_2)\,(H_2O)_n] + nH_2O$$

$$[Co(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Co(L_2)] + (H_2O)_n$$

$$[Co(L_2)] \xrightarrow{180\text{-}300\ ^0C} [CoL] + L$$

$$[CoL] \xrightarrow{300\text{-}600\ ^0C} CoO + L$$

(Where n = 0, 1 or 2).

Magnetic moment measurements for the complexes were made at room temperature. The cobalt(II) complex show magnetic moment 4.32 BM, a value in

accordance with a high spin configuration showing the presence of tetrahedral environment around the cobalt(II) ion in the complex. The experimental values are higher than spin only value due to orbital angular momentum contribution in d^7 system.

All spectral characterization, elemental analysis and thermal analysis confirm the structure of Cobalt(II) complex of 1-((3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-methylene)thiosemicarbazide(RMT-15). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the tetrahedral type geometries of the present complex.

CHAPTER-II

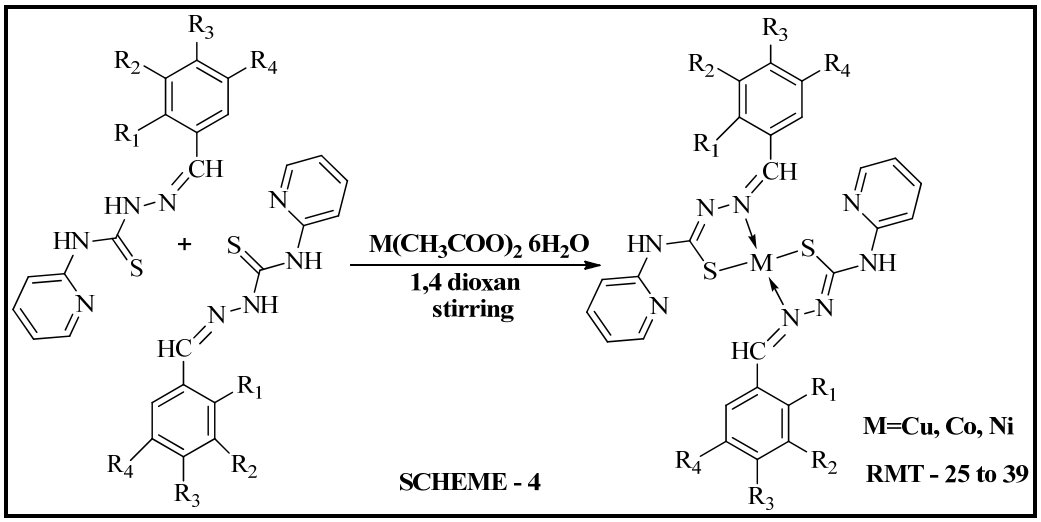
SYNTHESIS AND CHARACTERIZATION OF CU(II), NI(II) AND CO(II) COMPLEXES OF 1-SUBSTITUTED ARYLIDENE-4-(PYRIDIN-2-YL) THIOSEMICARBAZIDE

2.3.1 EXPERIMENTAL SECTION

Synthesis of metal complexes

General procedure for the synthesis of copper(II), nickel(II) and cobalt(II) complexes of 1-substituted arylidene-4-(pyridin-2-yl)thiosemicarbazide.

To a solution of 1-substituted arylidene-4-(pyridin-2-yl)thiosemicarbazide (0.02 mol) in methanol (60 mL) was added a solution of $M(acetate)_2 \cdot 4H_2O$ (0.01 mol) in distilled water (5-10 mL). The mixture was boiled with stirring for 1 hour. After 1 hour stopped the heating and reaction mixture stirred for 3 days at room temperature, and than 15-20 ml solvent was evaporated and cool the reaction mixture. The colored precipitate was collected by filtration, washed thoroughly with cold methanol and dried in vacuum.



SCHEME - 4

TABLE - IV

Comp. Code	M	R_1	R_2	R_3	R_4	Yield %	M. P. ºC	Λ_m (Ω^{-1} cm^2 mol^{-1})	μ_{eff} B. M.
RMT-25	Cu(II)					59	262	4.56	2.08
RMT-26	Ni(II)	-H	$-OCH_3$	-OH	-Br	62	>350	3.61	3.54
RMT-27	Co(II)					55	>350	4.08	4.36
RMT-28	Cu(II)					56	212	4.51	1.93
RMT-29	Ni(II)	-Cl	-H	-Cl	-H	59	196	4.36	3.18
RMT-30	Co(II)					70	240	4.78	4.06
RMT-31	Cu(II)					68	206	4.33	2.05
RMT-32	Ni(II)	-H	-H	$-OCH_3$	-H	71	>350	3.45	3.46
RMT-33	Co(II)					57	278	4.67	4.71
RMT-34	Cu(II)					60	>350	4.18	2.16
RMT-35	Ni(II)	-H	$-OCH_3$	$-OCH_3$	-H	65	302	4.92	3.34
RMT-36	Co(II)					71	>350	3.65	4.49
RMT-37	Cu(II)					53	>350	3.99	1.99
RMT-38	Ni(II)	-H	-OH	-H	-H	57	>350	4.54	3.31
RMT-39	Co(II)					52	244	3.21	4.12

2.3.2 SPECTRAL DATA OF THE SYNTHESIZED METAL COMPLEXES

[1] Copper(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(RMT-25).

Colour: Brown, **Anal. Calcd**. For $C_{28}H_{24}Br_2CuN_8O_4S_2$ (824.03 g/mol): C, 40.81%; H, 2.94%; N, 13.60%; S, 7.78%; Cu, 7.71%. **Found:** C, 40.93%; H, 2.99%; N, 13.49%; S, 7.65%; Cu, 7.80%; **ESI MS** (m/z): 821.0 $(CuL_2)+$; **IR (KBr, cm^{-1}):** *ν*(OH) 3483; *ν*(NH) 3313; *ν*(C=N) 1585; *ν*(N-N) 1045; *ν*(C=S) 1288; δ(C=S) 846; *ν*(Ar–C-H) 3148-3074; *ν*(Ar–C=C) 1504; *ν*(C-Br) 636; *ν*(Cu-N) 507; *ν*(Cu-S) 406.

[2] Nickel(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(RMT-26).

Colour: Green, **Anal. Calcd**. For $C_{28}H_{24}Br_2N_8NiO_4S_2$ (819.17 g/mol): C, 41.05%; H, 2.95%; N, 13.68%; S, 7.83%; Ni, 7.16%. **Found:** C, 40.91%; H, 2.87%; N, 13.61%; S, 7.92%; Ni, 7.22%; **ESI MS** (m/z): 815.2 $(NiL_2)+$; **IR**

(KBr, cm^{-1}): *ν*(OH) 3421; *ν*(NH) 3281; *ν*(C=N) 1577; *ν*(N-N) 1031; *ν*(C=S) 1236; δ(C=S) 835; *ν*(Ar–C-H) 3115-3084; *ν*(Ar–C=C) 1491; *ν*(C-Br) 617; *ν*(Ni-N) 507; *ν*(Ni-S) 422.

[3] Cobalt(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(pyridin-2-yl)thio-semicarbazide(RMT-27).

Colour: Green, **Anal. Calcd**. For $C_{28}H_{24}Br_2CoN_8O_4S_2$ (819.41 g/mol): C, 41.04%; H, 2.95%; N, 13.67%; S, 7.83%; Co, 7.19%. **Found:** C, 41.16%; H, 2.81%; N, 13.79%; S, 7.95%; Co, 7.07%; **ESI MS** (m/z): 820.0 (CoL_2)+; **IR (KBr, cm^{-1}):** *ν*(OH) 3404; *ν*(NH) 3298; *ν*(C=N) 1583; *ν*(N-N) 1035; *ν*(C=S) 1238; δ(C=S) 839; *ν*(Ar–C-H) 3119-3078; *ν*(Ar–C=C) 1481; *ν*(C-Br) 612; *ν*(Co-N) 513; *ν*(Co-S) 432.

[4] Copper(II) complex of 1-(2,4-dichlorobenzylidene)-4-(pyridin-2-yl)thio-semicarbazide(RMT-28).

Colour: Green, **Anal. Calcd**. For $C_{26}H_{18}Cl_4CuN_8S_2$ (711.96 g/mol): C, 43.86%; H, 2.55%; N, 15.74%; S, 9.01%; Cu, 8.93%. **Found:** C, 43.99%; H, 2.63%; N, 15.65%; S, 8.87%; Cu, 8.98%; **ESI MS** (m/z): 715.0 (CuL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH) 3331; *ν*(C=N) 1558; *ν*(N-N) 1049; *ν*(C=S) 1292; δ(C=S) 858; *ν*(Ar–C-H) 3159-2935; *ν*(Ar–C=C) 1518; *ν*(C-Cl) 761; *ν*(Cu-N) 520; *ν*(Cu-S) 410.

[5] Nickel(II) complex of 1-(2,4-dichlorobenzylidene)-4-(pyridin-2-yl)thiosemi-carbazide(RMT-29).

Colour: Redish, **Anal. Calcd**. For $C_{26}H_{18}Cl_4N_8NiS_2$ (707.11 g/mol): C, 44.16%; H, 2.57%; N, 15.85%; S, 9.07%; Ni, 8.30%. **Found:** C, 44.08%; H, 2.44%; N, 15.97%; S, 9.16%; Ni, 8.22%; **ESI MS** (m/z): 703.5 (NiL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH) 3362; *ν*(C=N) 1585; *ν*(N-N) 1051; *ν*(C=S) 1280; δ(C=S) 860; *ν*(Ar–C-H) 3105-3003; *ν*(Ar–C=C) 1487; *ν*(C-Cl) 777; *ν*(Ni-N) 516; *ν*(Ni-S) 406.

[6] Cobalt(II) complex of 1-(2,4-dichlorobenzylidene)-4-(pyridin-2-yl)thiosemi-carbazide(RMT-30).

Colour: Brown, **Anal. Calcd**. For $C_{26}H_{18}Cl_4CoN_8S_2$ (707.35 g/mol): C, 44.15%; H, 2.56%; N, 15.84%; S, 9.07%; Co, 8.33%. **Found:** C, 44.05%; H,

2.68%; N, 15.91%; S, 9.00%; Co, 8.42%; **ESI MS** (m/z): 705.2 (CoL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH) 3360; *ν*(C=N) 1581; *ν*(N-N) 1047; *ν*(C=S) 1305; δ(C=S) 864; *ν*(Ar–C-H) 3091-2987; *ν*(Ar–C=C) 1491; *ν*(C-Cl) 780; *ν*(Co-N) 486; *ν*(Co-S) 410.

[7] Copper(II) complex of 1-(4-methoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(RMT-31).

Colour: Green, **Anal. Calcd**. For $C_{28}H_{26}CuN_8O_2S_2$ (634.23 g/mol): C, 53.02%; H, 4.13%; N, 17.67%; S, 10.11%; Cu, 10.02%. **Found:** C, 53.11%; H, 4.22%; N, 17.56%; S, 10.03%; Cu, 9.95%; **ESI MS** (m/z): 635.2 (CuL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH) 3282; *ν*(C=N) 1579; *ν*(N-N) 1018; *ν*(C=S) 1261; δ(C=S) 862; *ν*(Ar–C-H) 3180-2999; *ν*(Ar–C=C) 1514; *ν*(Cu-N) 538; *ν*(Cu-S) 414.

[8] Nickel(II) complex of 1-(4-methoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(RMT-32).

Colour: Green, **Anal. Calcd**. For $C_{28}H_{26}N_8NiO_2S_2$ (629.38 g/mol): C, 53.43%; H, 4.16%; N, 17.80%; S, 10.19%; Ni, 9.33%. **Found:** C, 53.38%; H, 4.03%; N, 17.91%; S, 10.10%; Ni, 9.42%; **ESI MS** (m/z): 631.3 (NiL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH) 3306; *ν*(C=N) 1589; *ν*(N-N) 1020; *ν*(C=S) 1271; δ(C=S) 869; *ν*(Ar–C-H) 3188-3026; *ν*(Ar–C=C) 1491; *ν*(Ni-N) 518; *ν*(Ni-S) 422.

[9] Cobalt(II) complex of 1-(4-methoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(RMT-33).

Colour: Brown, **Anal. Calcd**. For $C_{28}H_{26}CoN_8O_2S_2$ (629.62 g/mol): C, 53.41%; H, 4.16%; N, 17.80%; S, 10.19%; Co, 9.36%. **Found:** C, 53.54%; H, 4.07%; N, 17.93%; S, 10.26%; Co, 9.24%; **ESI MS** (m/z): 625.0 (CoL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH) 3311; *ν*(C=N) 1552; *ν*(N-N) 1016; *ν*(C=S) 1261; δ(C=S) 864; *ν*(Ar–C-H) 3165-3026; *ν*(Ar–C=C) 1479; *ν*(Co-N) 520; *ν*(Co-S) 420.

[10] Copper(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(RMT-34).

Colour: Greenish, **Anal. Calcd**. For $C_{30}H_{30}CuN_8O_4S_2$ (694.29 g/mol): C, 51.90%; H, 4.36%; N, 16.14%; S, 9.24%; Cu, 9.15%. **Found:** C, 52.02%; H,

4.21%; N, 16.19%; S, 9.18%; Cu, 9.32%; **ESI MS** (m/z): 697.0 (CuL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH) 3402; *ν*(C=N) 1599; *ν*(N-N) 1028; *ν*(C=S) 1255; δ(C=S) 829; *ν*(Ar–C-H) 3111-2960; *ν*(Ar–C=C) 1489; *ν*(Cu-N) 518; *ν*(Cu-S) 412; **^{1}H-NMR (DMSO-d_6):** δppm 3.88 (s, 3H, OMe); 3.97 (s, 3H, OMe); 7.57 (tri, 2H, Ar-H); 7.70 (s, 1H, Ar-H); 7.87 (s, 1H, Ar-H); 8.06 (s, 1H, Ar-H); 8.15 (s, 1H, Ar-H); 8.28 (s, 1H, Ar-H); 8.65 (s, 1H, HC=N); 10.25 (s, 1H, NH); **UV-Vis:(DMF)** (λ_{max}/ nm): 250, 334, 744; **TGA wt. loss in %(temp.):** 2.60 (100°C); 4.87 (200°C); 40.28 (300°C); 54.33 (400°C); 78.27 (500°C); 91.04 (600°C); 91.25 (700°C); 91.46 (800°C); 91.07 (900°C).

[11] Nickel(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thio-semicarbazide(RMT-35).

Colour: Green, **Anal. Calcd**. For $C_{30}H_{30}N_8NiO_4S_2$ (689.43 g/mol): C, 52.26%; H, 4.39%; N, 16.25%; S, 9.30%; Ni, 8.51%. **Found:** C, 52.14%; H, 4.29%; N, 16.37%; S, 9.23%; Ni, 8.66%; **ESI MS** (m/z): 685.6 (NiL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH) 3421; *ν*(C=N) 1589; *ν*(N-N) 1037; *ν*(C=S) 1259; δ(C=S) 860; *ν*(Ar–C-H) 3178-3010; *ν*(Ar–C=C) 1491; *ν*(Ni-N) 522; *ν*(Ni-S) 406; **^{1}H-NMR (DMSO-d_6):** δppm 3.88 (s, 3H, OMe); 3.98 (s, 3H, OMe); 7.56 (tri, 2H, Ar-H); 7.71 (s, 1H, Ar-H); 7.85 (s, 1H, Ar-H); 8.05 (s, 1H, Ar-H); 8.13 (s, 1H, Ar-H); 8.28 (s, 1H, Ar-H); 8.64 (s, 1H, HC=N); 10.22 (s, 1H, NH); **UV-Vis:(DMF)** (λ_{max}/ nm): 268, 340, 684; **TGA wt. loss in %(temp.):** 4.37 (100°C); 9.36 (200°C); 46.67 (300°C); 57.88 (400°C); 63.71 (500°C); 81.91 (600°C); 89.75 (700°C); 89.67 (800°C); 90.70 (900°C).

[12] Cobalt(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thio-semicarbazide(RMT-36).

Colour: Brown, **Anal. Calcd**. For $C_{30}H_{30}CoN_8O_4S_2$ (689.67 g/mol): C, 52.25%; H, 4.38%; N, 16.25%; S, 9.30%; Co, 8.55%. **Found:** C, 52.33%; H, 4.47%; N, 16.11%; S, 9.38%; Co, 8.43%; **ESI MS** (m/z): 689.2 (CoL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH) 3421; *ν*(C=N) 1581; *ν*(N-N) 1024; *ν*(C=S) 1257; δ(C=S) 829; *ν*(Ar–C-H) 3188-3009; *ν*(Ar–C=C) 1492; *ν*(Co-N) 505; *ν*(Co-S) 416; **^{1}H-NMR (DMSO-d_6):** δppm 3.58 (s, 3H, OMe); 3.83 (s, 3H, OMe); 7.09 (m, 2H, Ar-H); 7.52 (m, 1H, Ar-H); 7.80 (m, 2H, Ar-H); 7.98 (d, 1H, *J* = 8.7 Hz, Ar-H); 8.49 (m, 1H,

Ar-H); 8.62 (s, 1H, HC=N); 10.26 (s, 1H, NH); **UV-Vis:(DMF)** (λ_{max}/ nm): 288, 342, 748; **TGA wt. loss in %(temp.):** 4.00 (100°C); 8.93 (200°C); 38.31 (300°C); 48.02 (400°C); 57.50 (500°C); 77.42 (600°C); 77.45 (700°C); 78.61 (800°C); 80.69 (900°C).

[13] Copper(II) complex of 1-(3-hydroxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(RMT-37).

Colour: Gray, **Anal. Calcd**. For $C_{26}H_{22}CuN_8O_2S_2$ (606.18 g/mol): C, 51.52%; H, 3.66%; N, 18.49%; S, 10.58%; Cu, 10.48%. **Found:** C, 51.40%; H, 3.53%; N, 18.36%; S, 10.68%; Cu, 10.57%; **ESI MS** (m/z): 610.1 (CuL_2)+; **IR (KBr, cm^{-1}):** *ν*(OH) 3435; *ν*(NH) 3303; *ν*(C=N) 1599; *ν*(N-N) 1016; *ν*(C=S) 1282; δ(C=S) 830; *ν*(Ar–C-H) 3167-3018; *ν*(Ar–C=C) 1479; *ν*(Cu-N) 518; *ν*(Cu-S) 439.

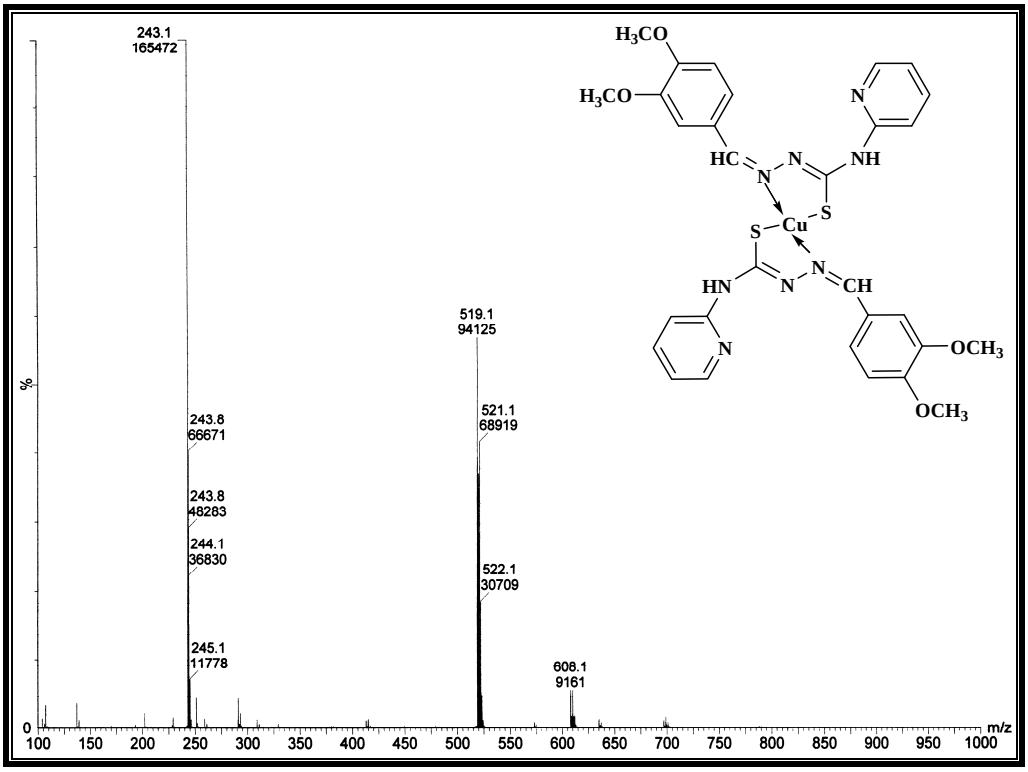
[14] Nickel(II) complex of 1-(3-hydroxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(RMT-38).

Colour: Yellow, **Anal. Calcd**. For $C_{26}H_{22}N_8NiO_2S_2$ (601.33 g/mol): C, 51.93%; H, 3.69%; N, 18.63%; S, 10.66%; Ni, 9.76%. **Found:** C, 52.02%; H, 3.75%; N, 18.70%; S, 10.58%; Ni, 9.66%; **ESI MS** (m/z): 603.0 (NiL_2)+; **IR (KBr, cm^{-1}):** *ν*(OH) 3444; *ν*(NH) 3252; *ν*(C=N) 1577; *ν*(N-N) 1045; *ν*(C=S) 1286; δ(C=S) 846; *ν*(Ar–C-H) 3142-3014; *ν*(Ar–C=C) 1491; *ν*(Ni-N) 489; *ν*(Ni-S) 416.

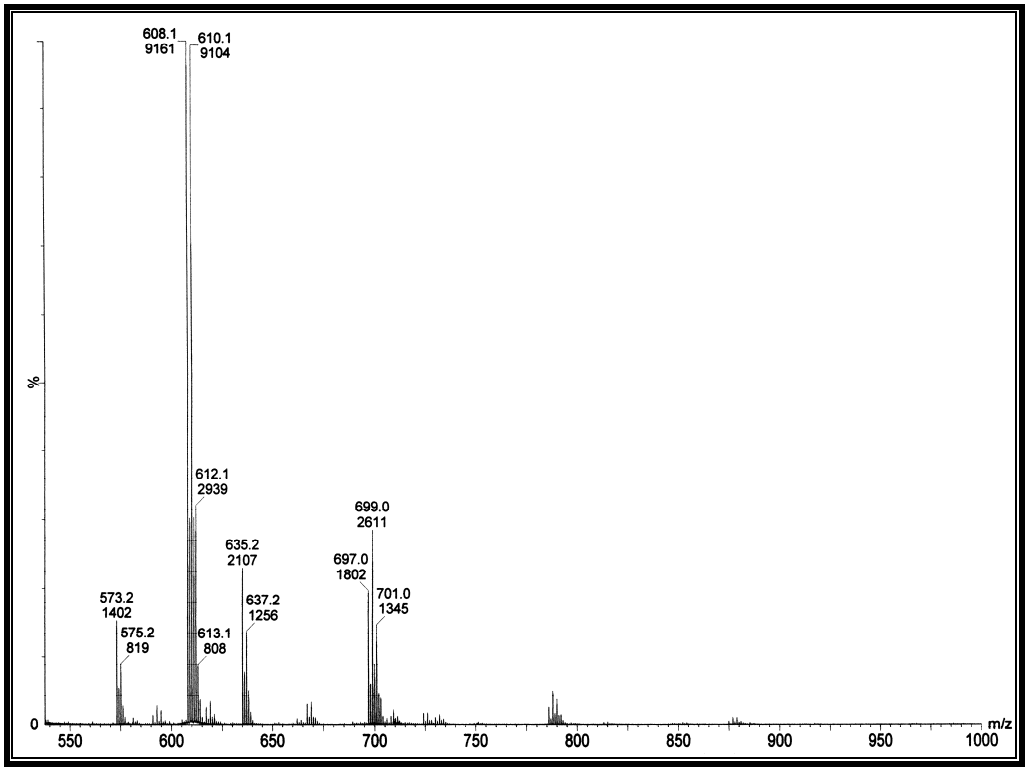
[15] Cobalt(II) complex of 1-(3-hydroxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(RMT-39).

Colour: Black, **Anal. Calcd**. For $C_{26}H_{22}CoN_8O_2S_2$ (601.57 g/mol): C, 51.91%; H, 3.69%; N, 18.63%; S, 10.66%; Co, 9.80%. **Found:** C, 51.98%; H, 3.53%; N, 18.71%; S, 10.74%; Co, 9.69%; **ESI MS** (m/z): 605.7 (CoL_2)+; **IR (KBr, cm^{-1}):** *ν*(OH) 3414; *ν*(NH) 3303; *ν*(C=N) 1608; *ν*(N-N) 1044; *ν*(C=S) 1282; δ(C=S) 846; *ν*(Ar–C-H) 3148-3022; *ν*(Ar–C=C) 1473; *ν*(Co-N) 528; *ν*(Co-S) 406.

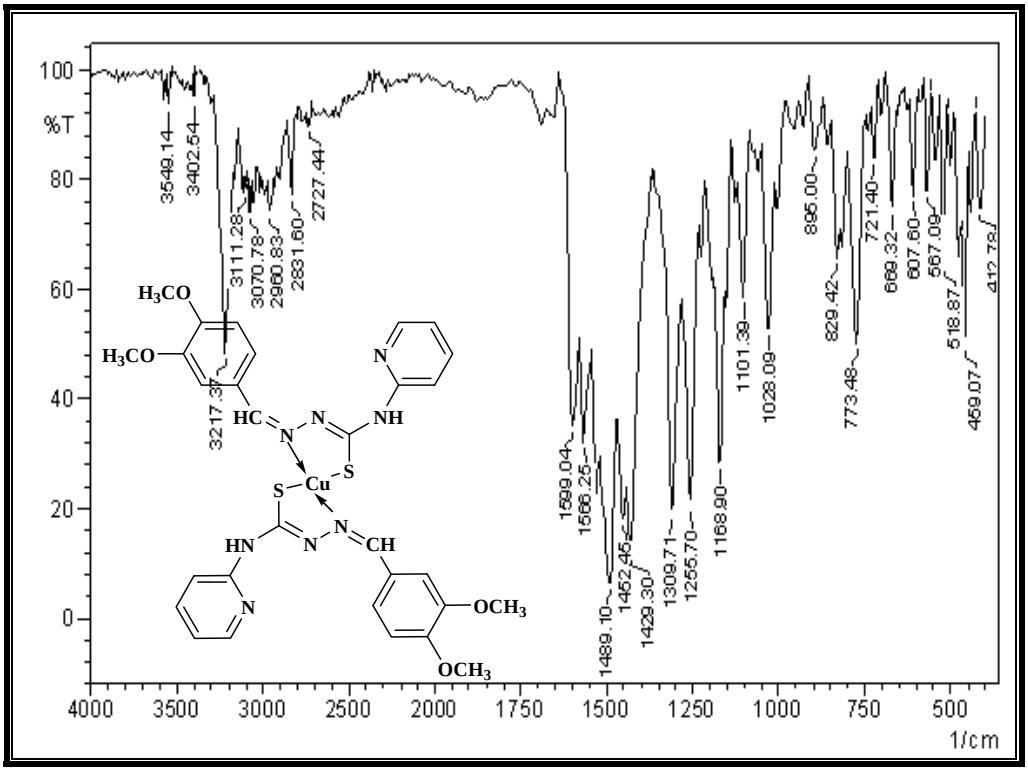
ESI Mass spectrum of RMT- 34



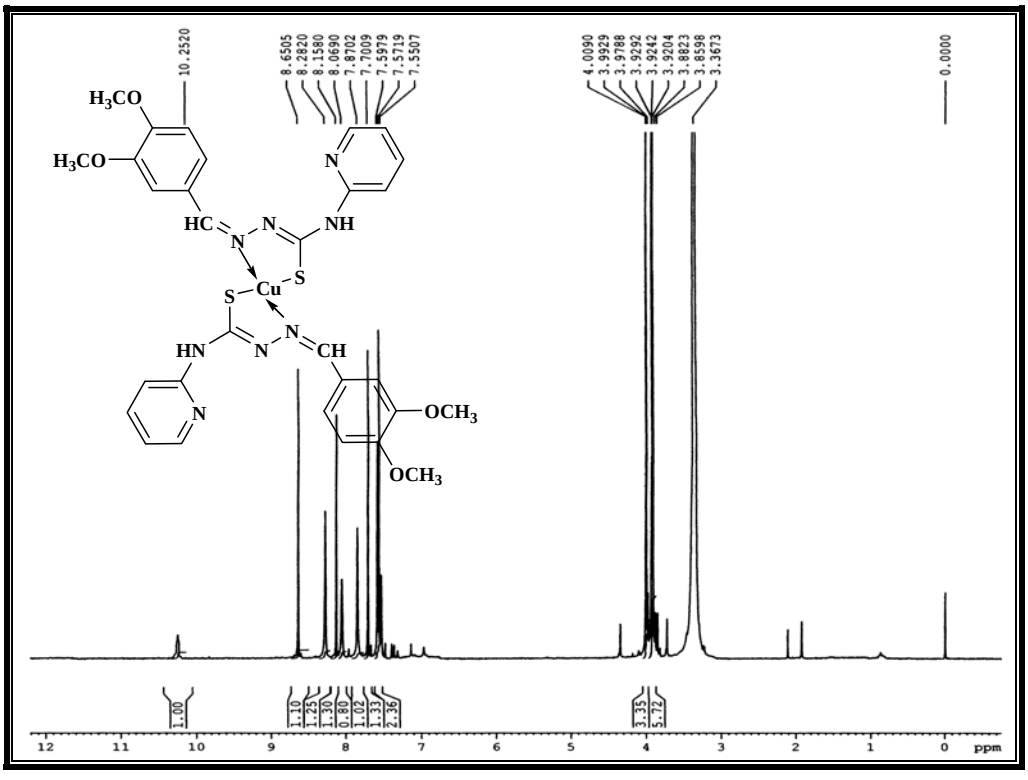
Expanded ESI Mass spectrum of RMT- 34



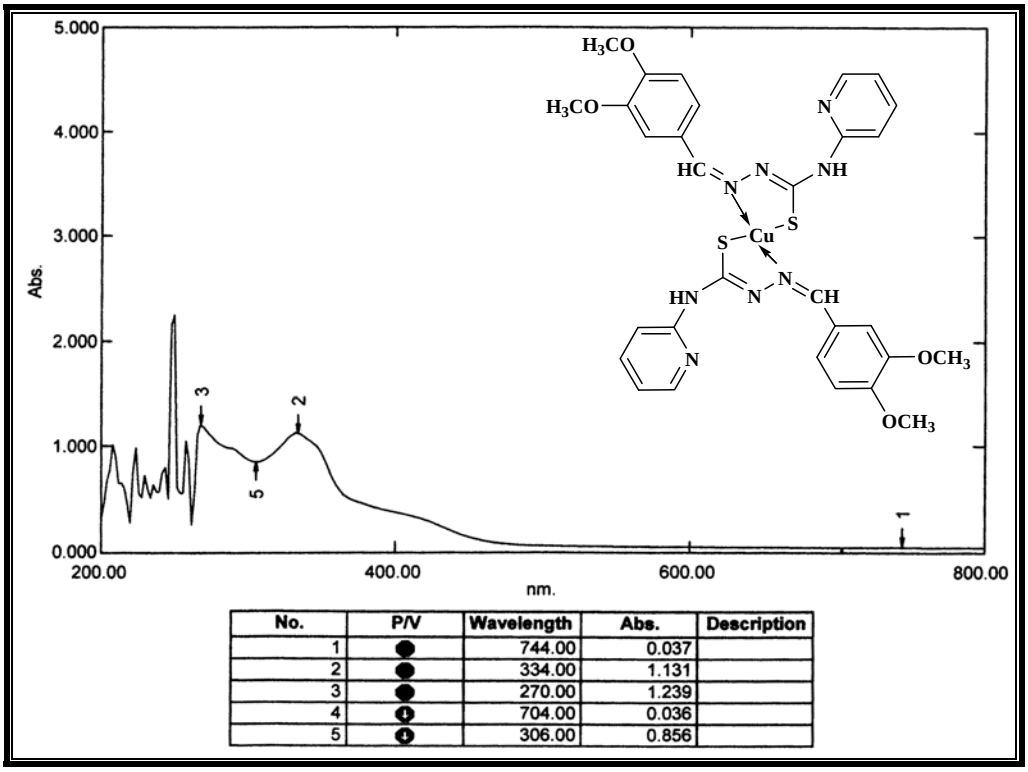
IR spectrum of RMT- 34



^{1}H NMR spectrum of RMT- 34

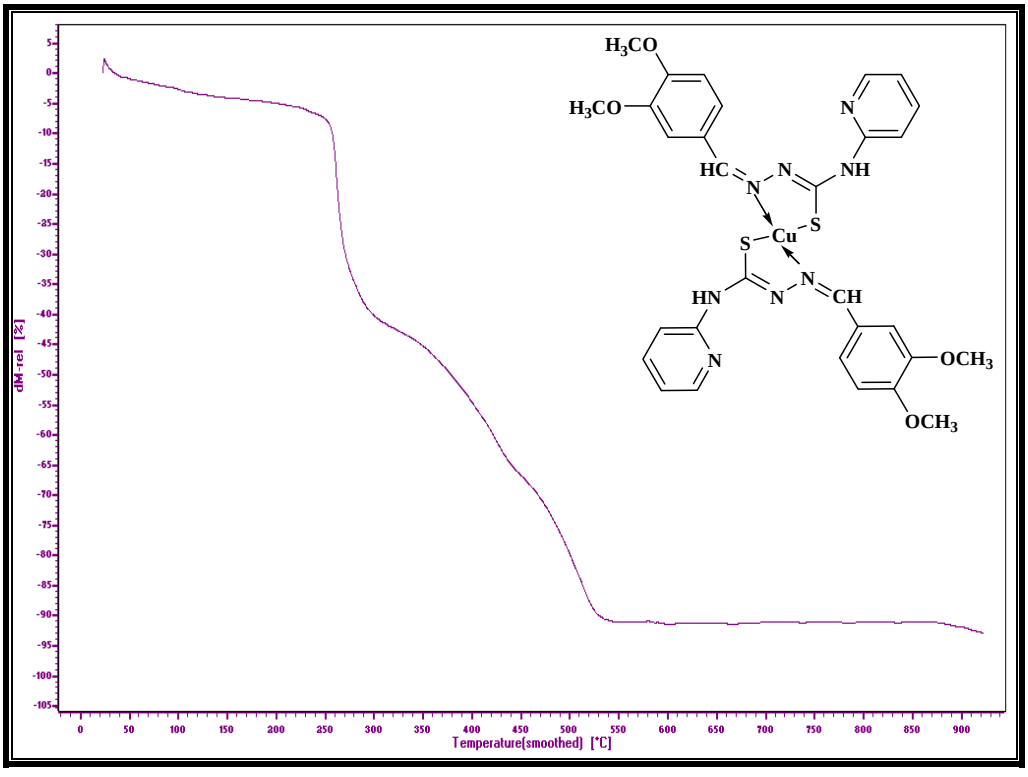


UV-Visible spectrum of RMT- 34



No.	P/V	Wavelength	Abs.	Description
1	●	744.00	0.037	
2	●	334.00	1.131	
3	●	270.00	1.239	
4	◆	704.00	0.036	
5	◆	306.00	0.856	

TGA spectrum of RMT- 34



Results & Discussion

The most important bands in the infrared spectra of the Copper(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Copper(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide exhibited a bands observed at 3402 cm^{-1}, 1028 cm^{-1} and 1255 cm^{-1} of -NH, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1599 cm^{-1} and aromatic -C-H and -C=C bands due to at 3111-2960 cm^{-1} and 1489 cm^{-1} respectively. The specific bands (Cu-N) and (Cu-S) observed at 518 cm^{-1} and 412 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Copper(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other -NH proton signal observed as singlet at 10.25 ppm. The signal of the (-HC=N) proton which appear as singlet at 8.65 ppm in the complex. The signal as compare to ligand show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine

nitrogen to the metal centre. The signals of -OCH_3 protons observed as singlet at 3.88 & 3.97 ppm. The signals of the aromatic protons of the Cu(II) complex appeared at δ 7.57-8.28 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ interaligand transition. There are two detected absorption bands at around 250 nm and 334 nm assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ interaligand transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 744 nm is assigned to a merges of $^2T_{2g} \leftarrow {}^2E_g$ transition in square planer geometry.

The TGA curves of the Copper(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Cu(L_2)\,(H_2O)_n] \cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Cu(L_2)\,(H_2O)_n] + nH_2O$$

$$[Cu(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Cu(L_2)] + (H_2O)_n$$

$$[Cu(L_2)] \xrightarrow{180\text{-}300\ ^0C} [CuL] + L$$

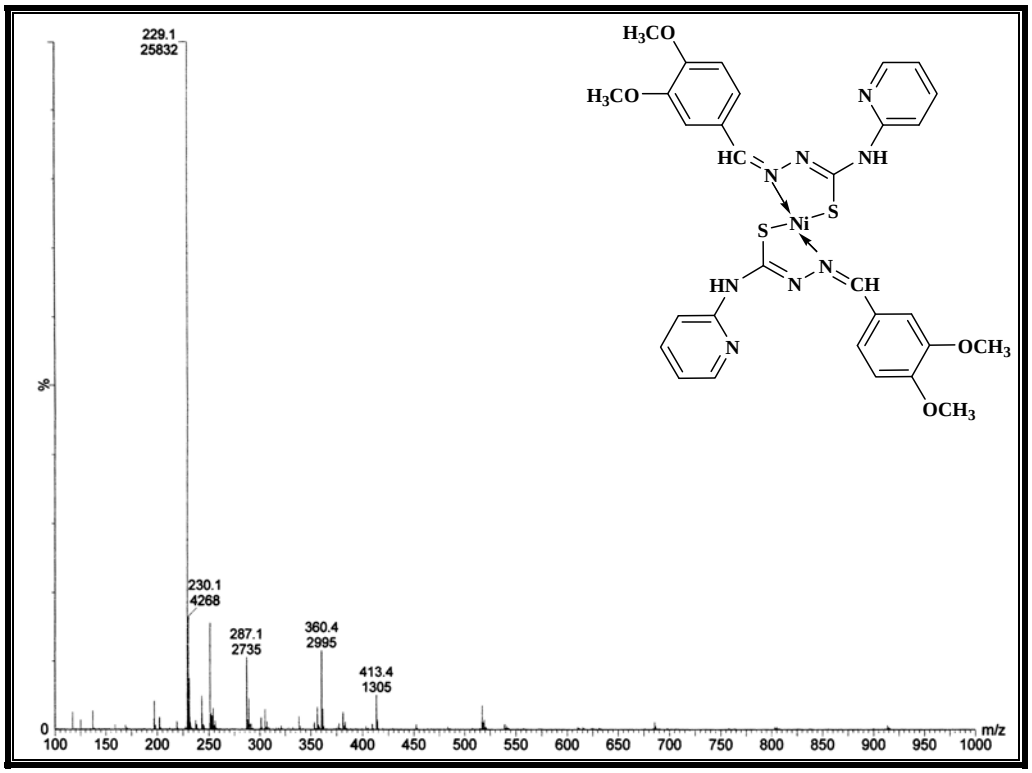
$$[CuL] \xrightarrow{300\text{-}600\ ^0C} CuO + L$$

(Where n = 0, 1 or 2).

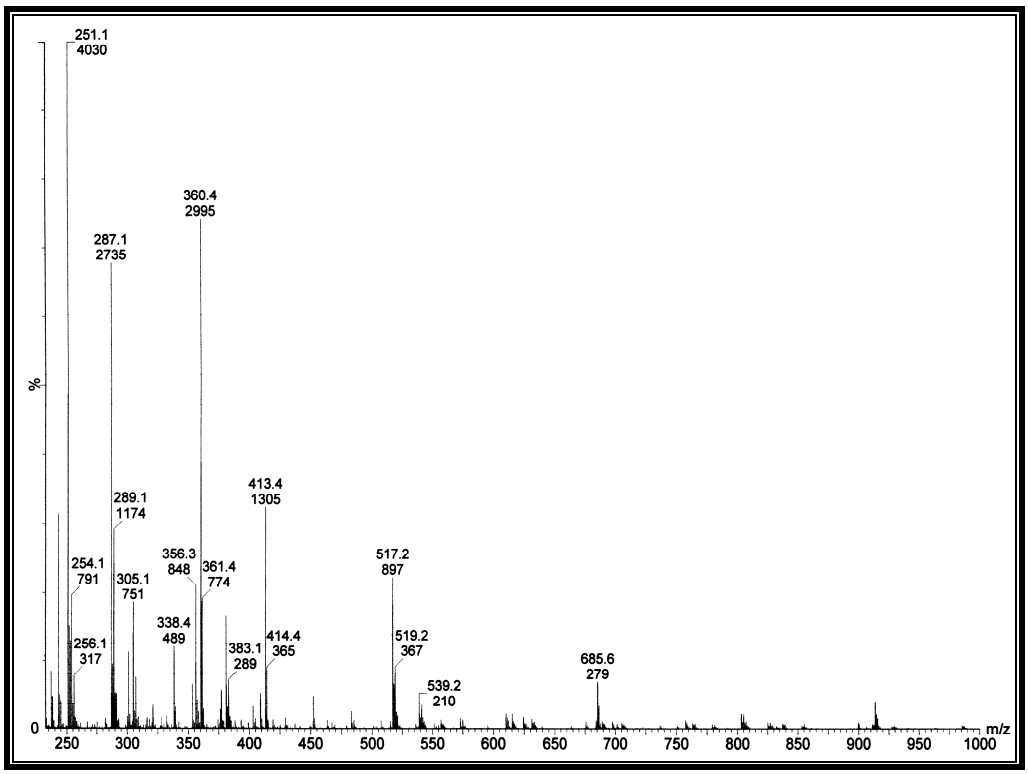
The room temperature magnetic moments for the copper(II) complex 1.74 BM correspond to the values normally observed for square-planar copper(II) compound. The room temperature value for μ_{eff} (2.16) (where μ_{eff} is the effective magnetic moment) is very close to the spin-only value of 1.73 B.M. for d^9.

All spectral characterization and thermal analysis confirms the structure of Copper(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl) thiosemicarbazide(RMT-34). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the square planer type geometries of the present complex.

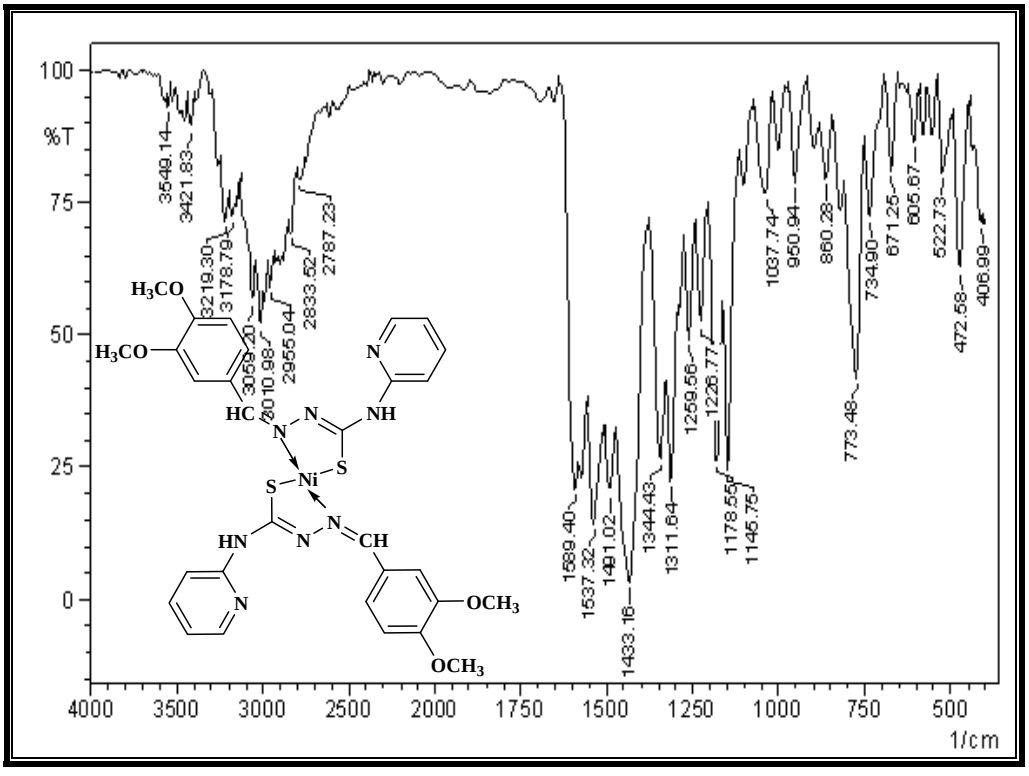
ESI Mass spectrum of RMT- 35



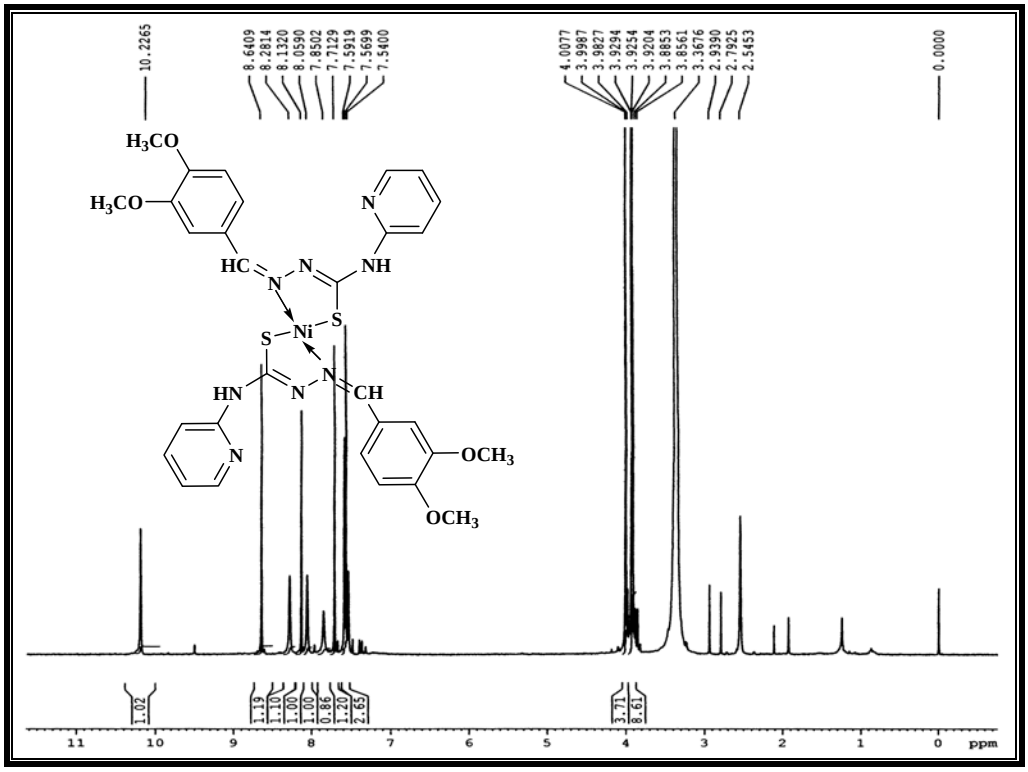
Expanded ESI Mass spectrum of RMT- 35



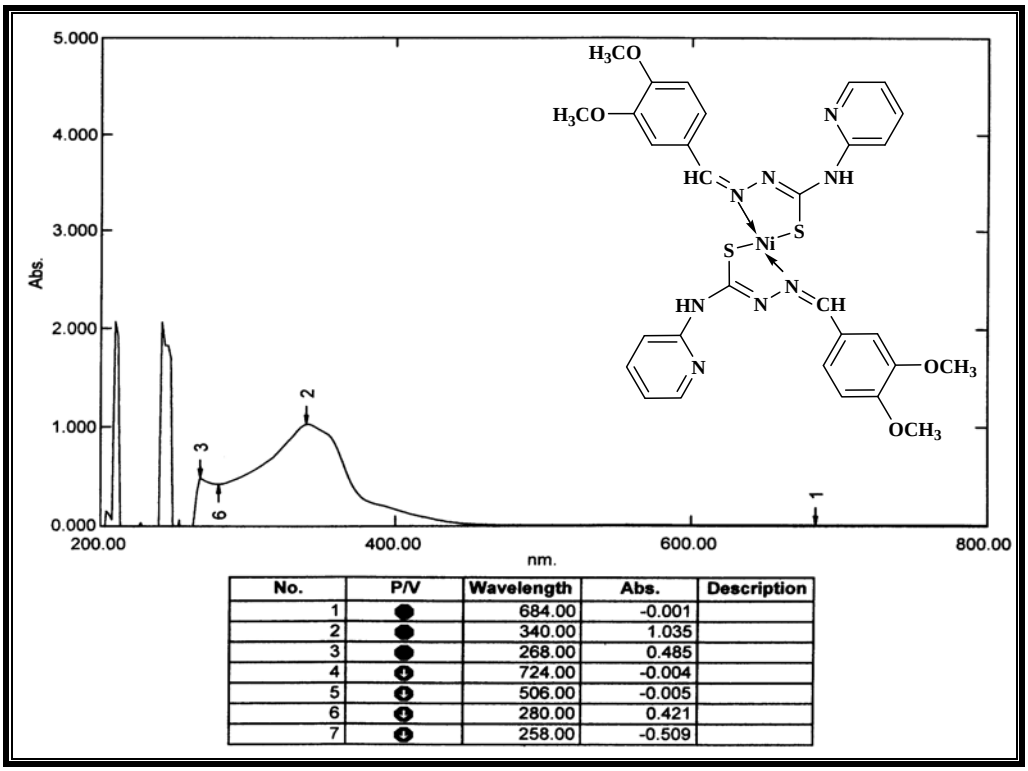
IR spectrum of RMT- 35



^{1}H NMR spectrum of RMT- 35

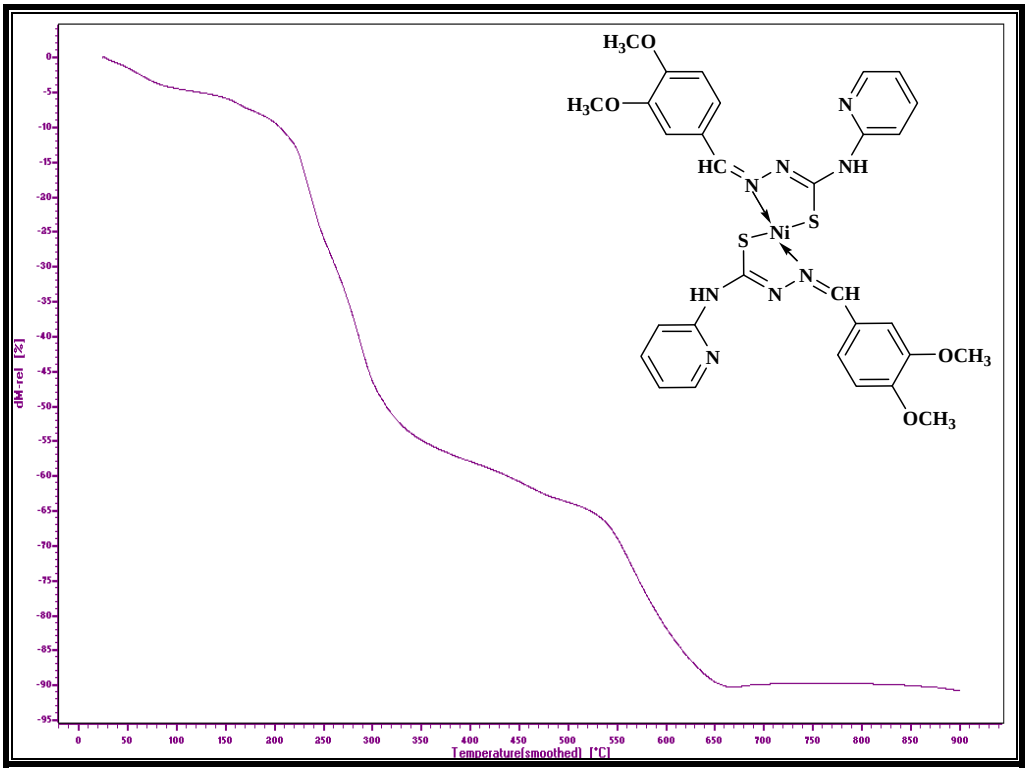


UV-Visible spectrum of RMT- 35



No.	P/V	Wavelength	Abs.	Description
1	●	684.00	-0.001	
2	●	340.00	1.035	
3	●	268.00	0.485	
4	▼	724.00	-0.004	
5	▼	506.00	-0.005	
6	▼	280.00	0.421	
7	▼	258.00	-0.509	

TGA spectrum of RMT- 35



Results & Discussion

The most important bands in the infrared spectra of the Nickel(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating

that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Nickel(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide exhibited a bands observed at 3421 cm^{-1}, 1037 cm^{-1} and 1259 cm^{-1} of -NH, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1589 cm^{-1} and aromatic -C-H and -C=C bands due to at 3178-3010 cm^{-1} and 1491 cm^{-1} respectively. The specific bands (Ni-N) and (Ni-S) observed at 522 cm^{-1} and 406 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Nickel(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other -NH proton signal observed as singlet at 10.22 ppm. The signal of the (-HC=N) proton which appear as singlet at 8.64 ppm in the complex. The signal as compare to ligands show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine nitrogen to the metal centre. The signals of -OCH_3 protons observed as singlet at 3.88 & 3.98 ppm. The signals of the aromatic protons of the Ni(II) complex appeared at δ 7.56-8.28 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi\rightarrow\pi^*$ and/or $n\rightarrow\pi^*$ interaligand transition. There are two detected absorption bands at around 268 nm assigned to $\pi\rightarrow\pi^*$ interaligand transition and 340 nm assigned to $^{3}T_{1g}(P)\leftarrow{}^{3}A_{2g}(F)$ transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 684 nm is assigned to a merges of $^{3}T_{1g}(F)\leftarrow{}^{3}A_{2g}(F)$ transition in tetrahedral geometry.

The TGA curves of the Nickel(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide was carried out within a temperature range from

room temperature up to 800 °C. The data from thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Ni(L_2)\,(H_2O)_n] \cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Ni(L_2)\,(H_2O)_n] + nH_2O$$

$$[Ni(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Ni(L_2)] + (H_2O)_n$$

$$[Ni(L_2)] \xrightarrow{180\text{-}300\ ^0C} [NiL] + L$$

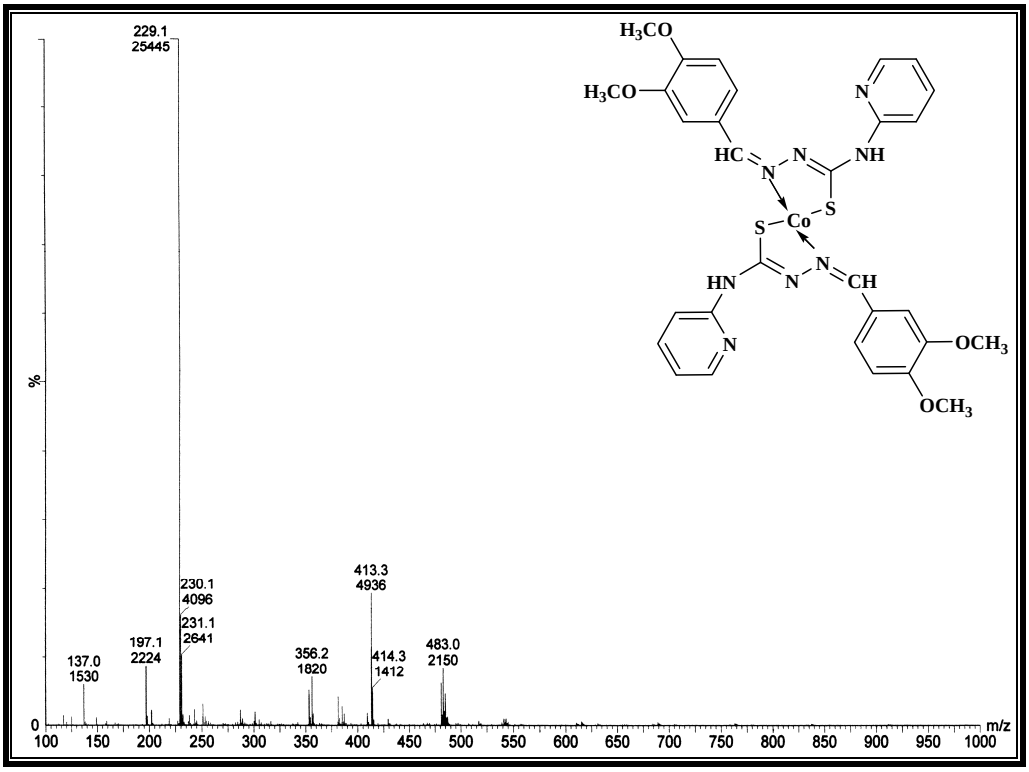
$$[NiL] \xrightarrow{300\text{-}600\ ^0C} NiO + L$$

(Where n = 0, 1 or 2).

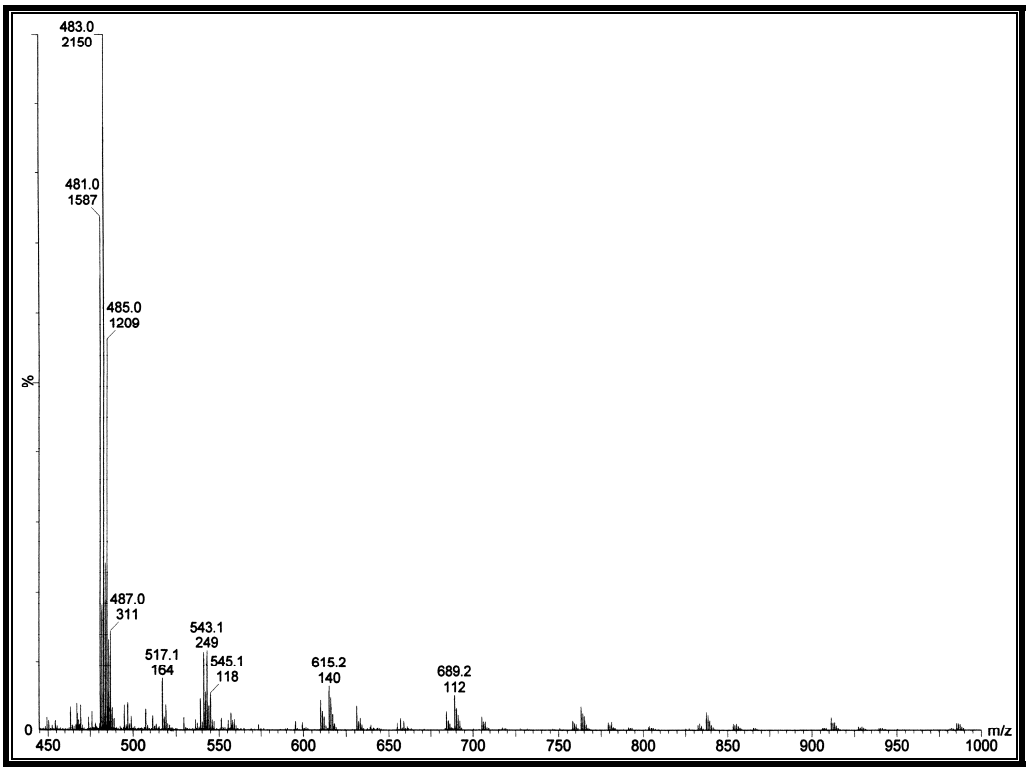
The magnetic moment of the nickel complex was found to be 3.34 B.M. which falls in the range generally observed for the four-coordinated Ni(II) complex. The magnetic data of the Ni(II) complex agree with a d^8 metal ion in an tetrahedral configuration.

All spectral characterization and thermal analysis confirms the structure of Nickel(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl) thiosemicarbazide(RMT-35). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the tetrahedral type geometries of the present complex.

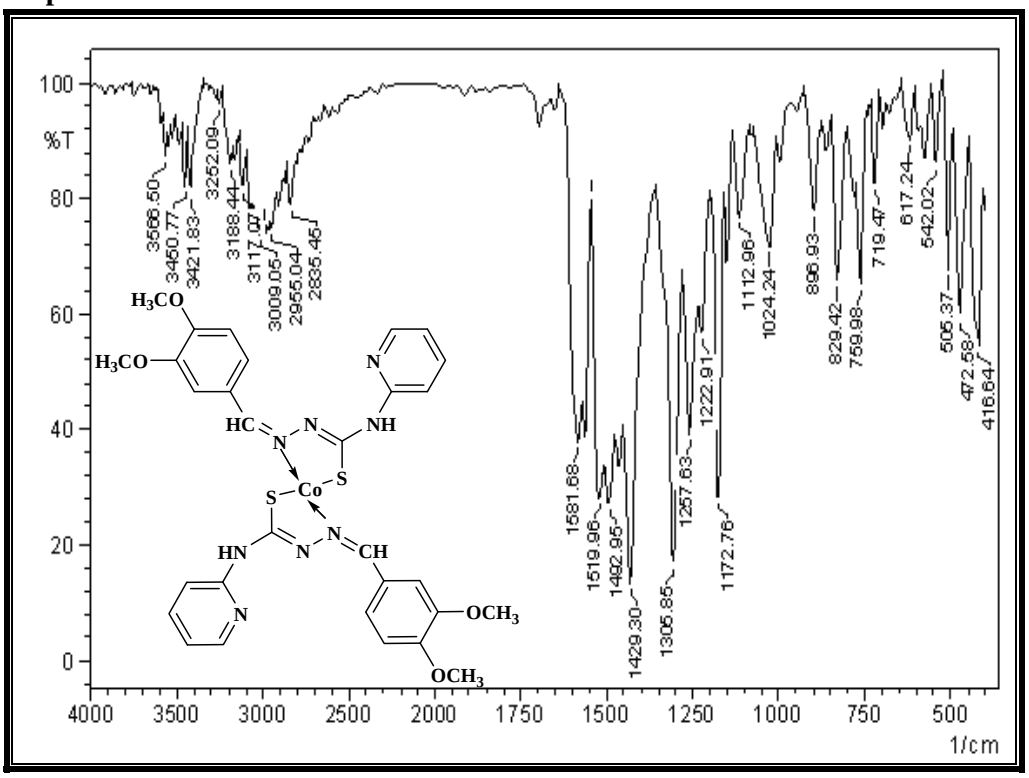
ESI Mass spectrum of RMT- 36



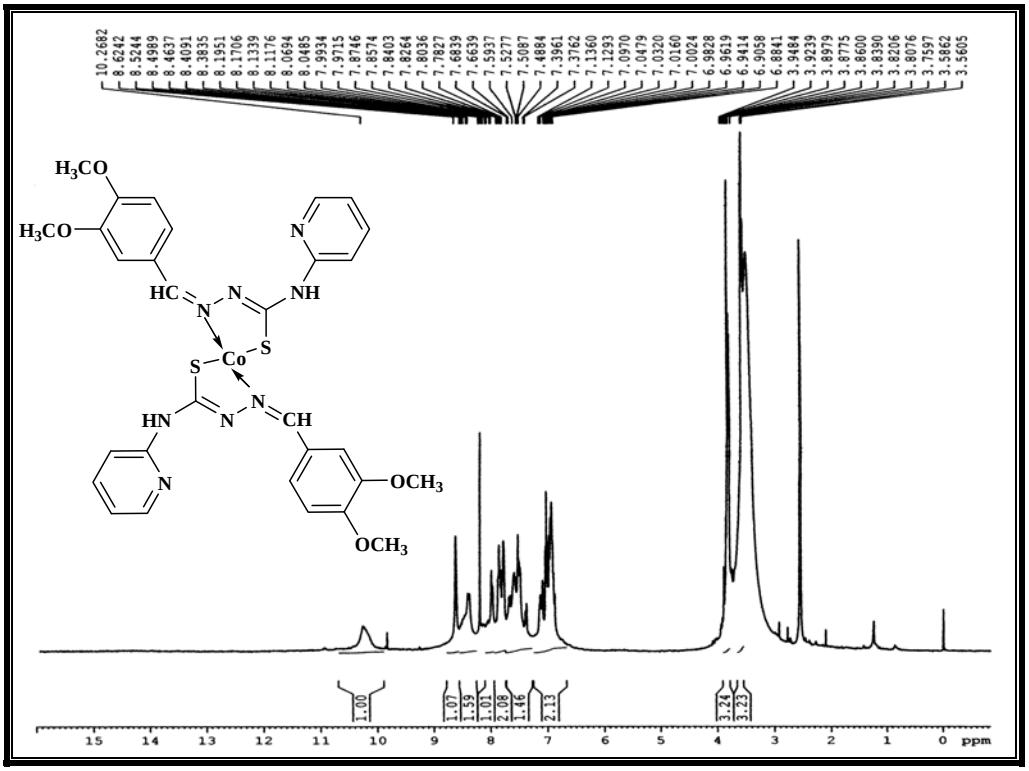
Expanded ESI Mass spectrum of RMT- 36



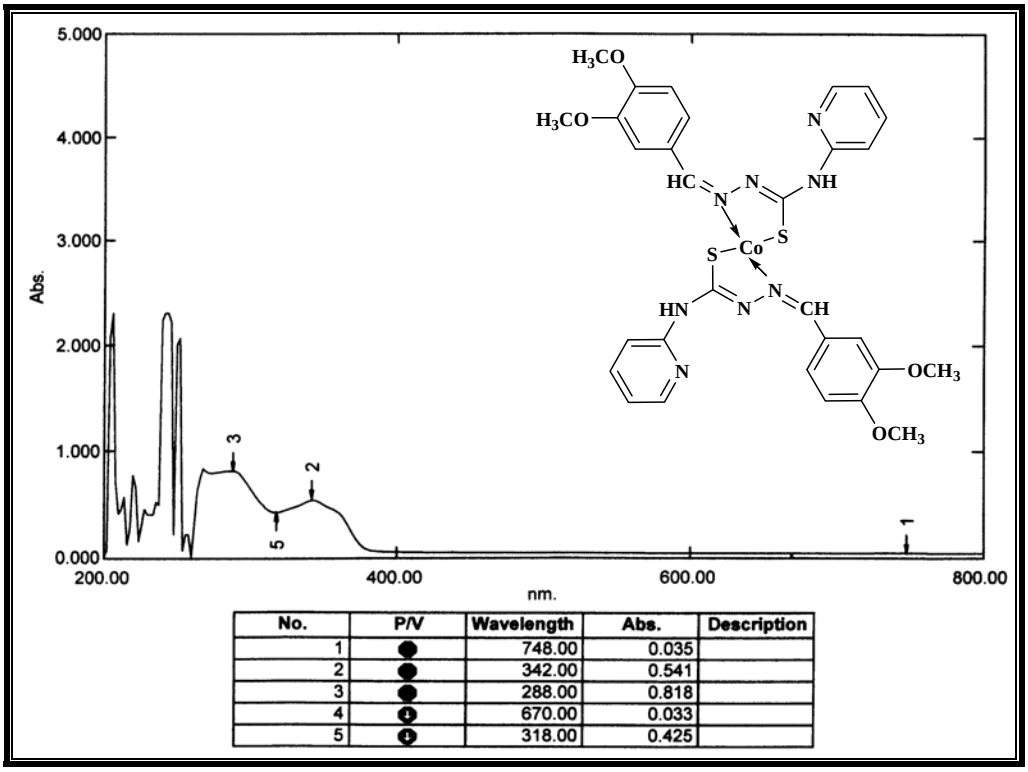
IR spectrum of RMT- 36



^{1}H NMR spectrum of RMT- 36

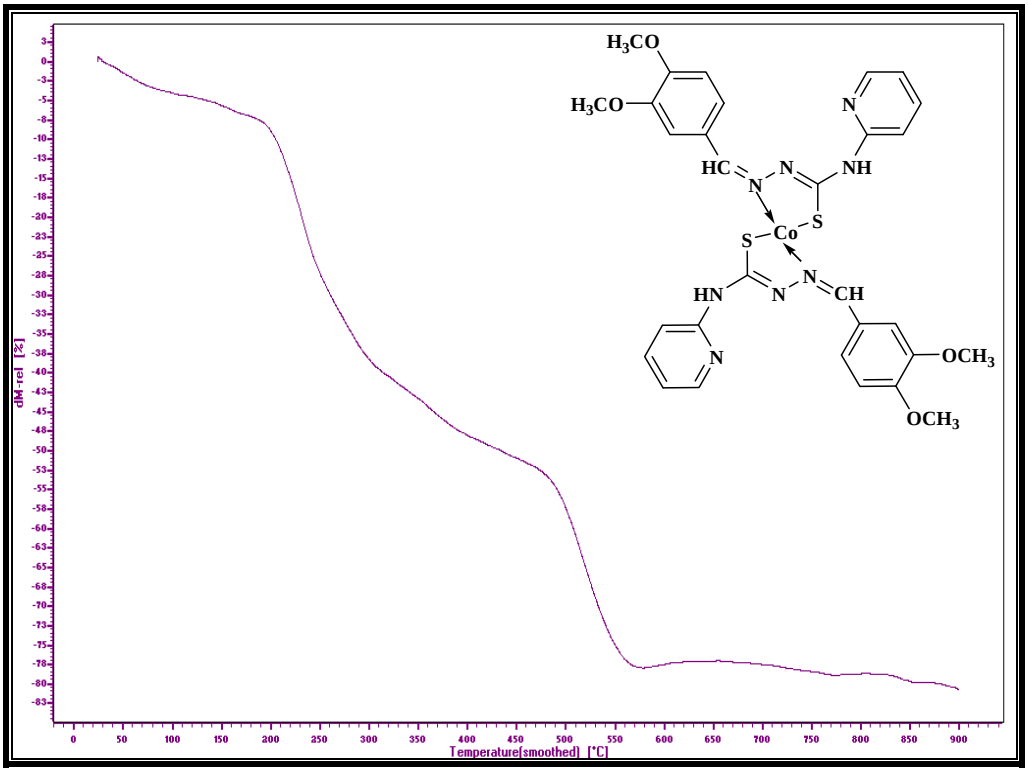


UV-Visible spectrum of RMT- 36



No.	P/V	Wavelength	Abs.	Description
1	●	748.00	0.035	
2	●	342.00	0.541	
3	●	288.00	0.818	
4	▲	670.00	0.033	
5	▲	318.00	0.425	

TGA spectrum of RMT- 36



Results & Discussion

The most important bands in the infrared spectra of the Cobalt(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Cobalt(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide exhibited a bands observed at 3421 cm^{-1}, 1024 cm^{-1} and 1257 cm^{-1} of -NH, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1581 cm^{-1} and aromatic -C-H and -C=C bands due to at 3188-3009 cm^{-1} and 1492 cm^{-1} respectively. The specific bands (Co-N) and (Co-S) observed at 505 cm^{-1} and 416 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Cobalt(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other -NH proton signal observed as singlet at 10.26 ppm. The signal of the (-HC=N) proton which appear as singlet at 8.62 ppm in the complex. The signal as compare to ligands show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine

nitrogen to the metal centre. The signal of -OCH_3 protons observed as singlet at 3.58 & 3.83 ppm. The signals of the aromatic protons of the Co(II) complex appeared at δ 7.09-8.49 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi \rightarrow \pi^*$ and/or $n \rightarrow \pi^*$ interaligand transition. There are two detected absorption bands at around around 288 nm assigned to $\pi \rightarrow \pi^*$ interaligand transition and 342 nm assigned to $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 748 nm is assigned to a merges of $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ transition in tetrahedral geometry.

The TGA curves of the Cobalt(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Co(L_2)\,(H_2O)_n] \cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Co(L_2)\,(H_2O)_n] + nH_2O$$

$$[Co(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Co(L_2)] + (H_2O)_n$$

$$[Co(L_2)] \xrightarrow{180\text{-}300\ ^0C} [CoL] + L$$

$$[CoL] \xrightarrow{300\text{-}600\ ^0C} CoO + L$$

(Where n = 0, 1 or 2).

Magnetic moment measurements for the complexes were made at room temperature. The cobalt(II) complex show magnetic moment 4.49 BM, a value in accordance with a high spin configuration showing the presence of tetrahedral environment around the cobalt(II) ion in the complex. The experimental values are higher than spin only value due to orbital angular momentum contribution in d^7 system.

All spectral characterization and thermal analysis confirms the structure of Cobalt(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide(RMT-36). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the tetrahedral type geometries of the present complex.

CHAPTER-III

SYNTHESIS AND CHARACTERIZATION OF CU(II), NI(II) AND CO(II) COMPLEXES OF 1-SUBSTITUTED ARYLIDENE-4-(4-BROMO-PHENYL) THIOSEMICARBAZIDE

2.4.1 EXPERIMENTAL SECTION

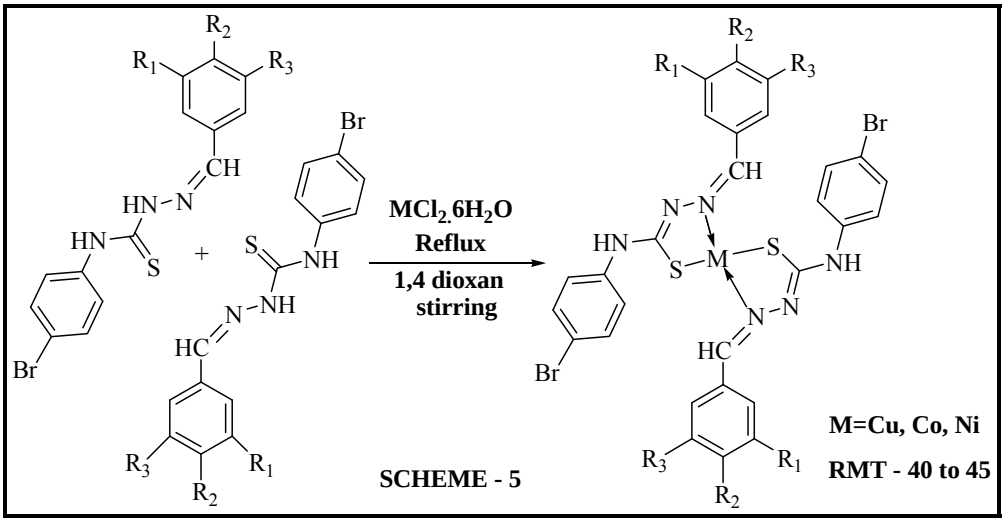
Synthesis of metal complexes

General procedure for the synthesis of Cu(II) and Co(II) metal complexes of 1-substituted arylidene-4-(4-bromophenyl) thiosemicarbazide

1-arylidene-4-(4-bromophenyl)thiosemicarbazide (0.02M) was dissolved in 1,4 dioxan than solid $M \cdot Cl_2 \bullet 6H_2O$ (0.01M)(where M = Cu & Co) was added to reaction mixture. The resulting reaction mixture was refluxed for 24 hours with continues stirring. After completion of the reaction the resulting solid was filtered and wash with cold dioxan and dried at room temperature.

General procedure for the synthesis of Ni(II) metal complexes of 1-substituted arylidene-4-(4-bromophenyl) thiosemicarbazide

1-arylidene-4-(4-bromophenyl)thiosemicarbazide (0.02M) was dissolved in 1,4 dioxan than solid $NiCl_2 \bullet 6H_2O$ (0.01M) was added to reaction mixture and maintain pH 6.8 to 7 by 40% NaOH. The resulting reaction mixture was refluxed for 5 hours with continues stirring. After completion of the reaction the resulting solid was filtered and wash with cold 1, 4 dioxan and dried at room temperature.



SCHEME - 5

TABLE - 5

Comp. Code	M	R_1	R_2	R_3	Yield %	M. P. ºC	Λ_m (Ω^{-1} cm^2 mol^{-1})	μ_{eff} B. M.
RMT-40	Cu(II)				59	294	4.50	1.97
RMT-41	Ni(II)	$-OCH_3$	-OH	-Br	71	320	4.83	3.19
RMT-42	Co(II)				64	274	3.10	4.86
RMT-43	Cu(II)				72	326	3.48	2.11
RMT-44	Ni(II)	$-OCH_3$	$-OCH_3$	-H	68	304	4.05	3.54
RMT-45	Co(II)				60	242	3.93	4.61

2.4.2 SPECTRAL DATA OF THE SYNTHESIZED METAL COMPLEXES

[1] Copper(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide(RMT-40).

Colour: Brown, **Anal. Calcd**. For $C_{30}H_{24}Br_4CuN_6O_4S_2$ (979.84 g/mol): C, 36.77%; H, 2.47%; N, 8.58%; S, 6.54%; Cu, 6.49%. **Found:** C, 36.70%; H, 2.61%; N, 8.49%; S, 6.45%; Cu, 6.63%; **ESI MS** (m/z): 985.3 $(CuL_2)+$; **IR (KBr, cm^{-1}):** *ν*(OH) 3504; *ν*(NH) 3389; *ν*(C=N) 1581; *ν*(N-N) 1047; *ν*(C=S) 1234; δ(C=S) 864; *ν*(Ar–C-H) 3091-2987; *ν*(Ar–C=C) 1491; *ν*(C-Br) 572; *ν*(Cu-N) 486; *ν*(Cu-S) 410; **^{1}H-NMR (DMSO-d_6):** δppm 3.63 (s, 3H, OMe); 7.39 (d, 2H, Ar-H); 7.46 (s, 1H, Ar-H); 7.50 (d, 2H, Ar-H); 7.61 (s, 1H, Ar-H); 8.01 (s, 1H, HC=N); 9.64 (s, 1H, OH); 10.10 (s, 1H, NH); **UV-Vis:(DMF)** (λ_{max}/ nm): 234, 266, 342, 678; **TGA wt. loss in %(temp.):** 8.66 (100°C); 18.06 (200°C); 29.97 (300°C); 52.41 (400°C); 55.86 (500°C); 58.63 (600°C); 59.59 (700°C); 60.94 (800°C); 65.31 (900°C).

[2] Nickel(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide(RMT-41).

Colour: Yellow, **Anal. Calcd**. For $C_{30}H_{24}Br_4N_6NiO_4S_2$ (974.99 g/mol): C, 36.96%; H, 2.48%; N, 8.62%; S, 6.58%; Ni, 6.02%. **Found:** C, 37.04%; H, 2.39%; N, 8.70%; S, 6.72%; Ni, 6.10%; **ESI MS** (m/z): 974.2 $(NiL_2)+$; **IR (KBr, cm^{-1}):** *ν*(OH) 3508; *ν*(NH) 3412; *ν*(C=N) 1566; *ν*(N-N) 1039; *ν*(C=S) 1286; δ(C=S) 817; *ν*(Ar–C-H) 3105-2983; *ν*(Ar–C=C) 1494; *ν*(C-Br) 596; *ν*(Ni-N) 495; *ν*(Ni-S) 408; **^{1}H-NMR (DMSO-d_6):** δppm 3.65 (s, 3H, OMe); 7.40 (d,

2H, *J* = 8.7 Hz, Ar-H); 7.49 (s, 1H, Ar-H); 7.56 (d, 2H, *J* = 8.6 Hz, Ar-H); 7.65 (s, 1H, Ar-H); 8.04 (s, 1H, HC=N); 9.67 (s, 1H, OH); 10.14 (s, 1H, NH); **UV-Vis:(DMF)** (λ_{max}/ nm): 270, 290, 332, 744; **TGA wt. loss in %(temp.):** 1.02 (100°C); 9.63 (200°C); 39.10 (300°C); 47.59 (400°C); 55.30 (500°C); 58.87 (600°C); 61.55 (700°C); 63.69 (800°C).

[3] Cobalt(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide(RMT-42).

Colour: Green, **Anal. Calcd**. For $C_{30}H_{24}Br_4CoN_6O_4S_2$ (975.23 g/mol): C, 36.95%; H, 2.48%; N, 8.62%; S, 6.58%; Co, 6.04%. **Found:** C, 36.79%; H, 2.56%; N, 8.53%; S, 6.66%; Co, 6.13%; **ESI MS** (m/z): 975.3 (CoL_2)+; **IR (KBr, cm^{-1}):** *ν*(OH) 3498; *ν*(NH) 3403; *ν*(C=N) 1599; *ν*(N-N) 1045; *ν*(C=S) 1288; δ(C=S) 833; *ν*(Ar–C-H) 3107-2974; *ν*(Ar–C=C) 1494; *ν*(C-Br) 605; *ν*(Co-N) 513; *ν*(Co-S) 412; **^{1}H-NMR (DMSO-d$_6$):** δppm 3.92 (s, 3H, OMe); 7.40 (s, 1H, Ar-H); 7.47 (d, 2H, *J* = 8.5 Hz, Ar-H); 7.59 (d, 3H, *J* = 8.5 Hz, Ar-H); 8.01 (s, 1H, HC=N); 9.71 (s, br, 1H, OH); 9.99 (s, 1H, NH); **UV-Vis:(DMF)** (λ_{max}/ nm): 268, 340, 564, 682; **TGA wt. loss in %(temp.):** 3.80 (100°C); 8.24 (200°C); 31.32 (300°C); 42.20 (400°C); 48.99 (500°C); 62.55 (600°C); 87.76 (700°C); 92.67 (800°C); 94.01 (900°C).

[4] Copper(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(4-bromophenyl) thiosemicarbazide(RMT-43).

Colour: Cream **Anal. Calcd**. For $C_{32}H_{30}Br_2CuN_6O_4S_2$ (850.1 g/mol): C, 45.21%; H, 3.56%; N, 9.89%; S, 7.54%; Cu, 7.48%. **Found:** C, 45.08%; H, 3.44%; N, 9.95%; S, 7.43%; Cu, 7.40%; **ESI MS** (m/z): 846.7 (CuL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH) 3238; *ν*(C=N) 1554; *ν*(N-N) 1022; *ν*(C=S) 1259; δ(C=S) 819; *ν*(Ar–C-H) 3134-2951; *ν*(Ar–C=C) 1510; *ν*(C-Br) 603; *ν*(Cu-N) 524; *ν*(Cu-S) 416.

[5] Nickel(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide(RMT-44).

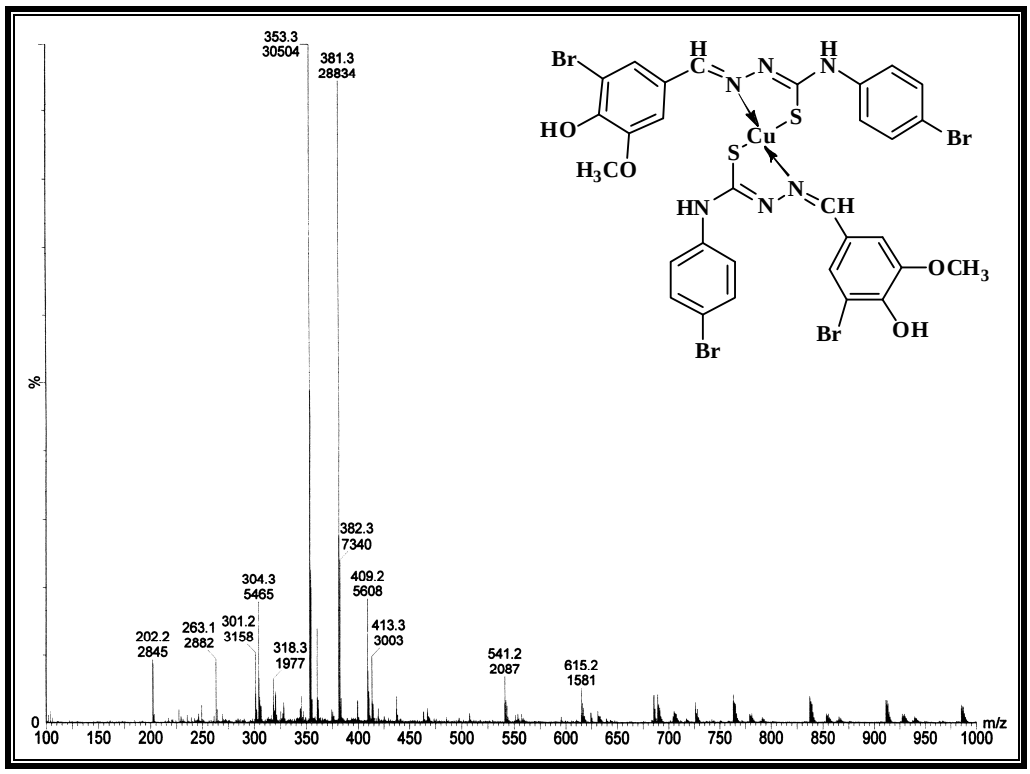
Colour: Brown, **Anal. Calcd**. For $C_{32}H_{30}Br_2N_6NiO_4S_2$ (845.25 g/mol): C, 45.47%; H, 3.58%; N, 9.94%; S, 7.59%; Ni, 6.94%. **Found:** C, 45.58%; H,

3.51%; N, 9.87%; S, 7.69%; Ni, 6.83%; **ESI MS** (m/z): 844.7 (NiL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH) 3304; *ν*(C=N) 1578; *ν*(N-N) 1027; *ν*(C=S) 1280; δ(C=S) 825; *ν*(Ar–C-H) 3146-3003; *ν*(Ar–C=C) 1498; *ν*(C-Br) 612; *ν*(Ni-N) 515; *ν*(Ni-S) 406.

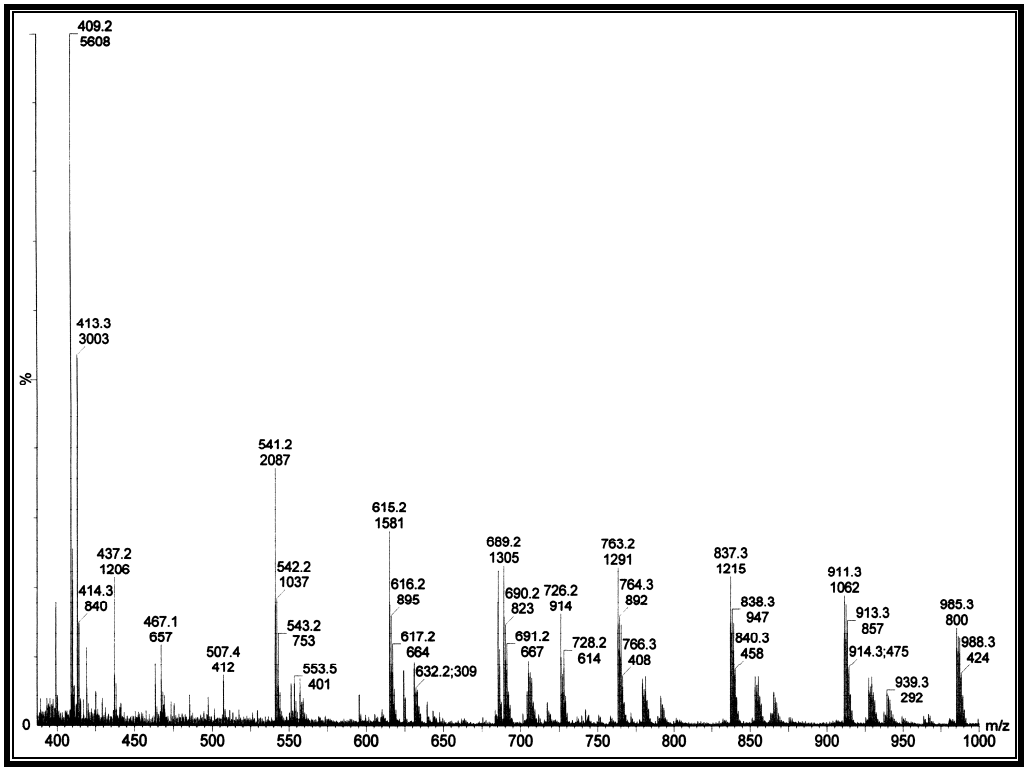
[6] Cobalt(II) complex of 1-(3,4-dimethoxybenzylidene)-4-(4-bromophenyl) thiosemicarbazide(RMT-45).

Colour: Green, **Anal. Calcd**. For $C_{32}H_{30}Br_2CoN_6O_4S_2$ (845.49 g/mol): C, 45.46%; H, 3.58%; N, 9.94%; S, 7.58%; Co, 6.97%. **Found:** C, 45.33%; H, 3.49%; N, 10.02%; S, 7.65%; Co, 7.05%; **ESI MS** (m/z): 845.1 (CoL_2)+; **IR (KBr, cm^{-1}):** *ν*(NH) 3308; *ν*(C=N) 1597; *ν*(N-N) 1016; *ν*(C=S) 1267; δ(C=S) 829; *ν*(Ar–C-H) 3088-3007; *ν*(Ar–C=C) 1514; *ν*(C-Br) 611; *ν*(Co-N) 518; *ν*(Co-S) 414.

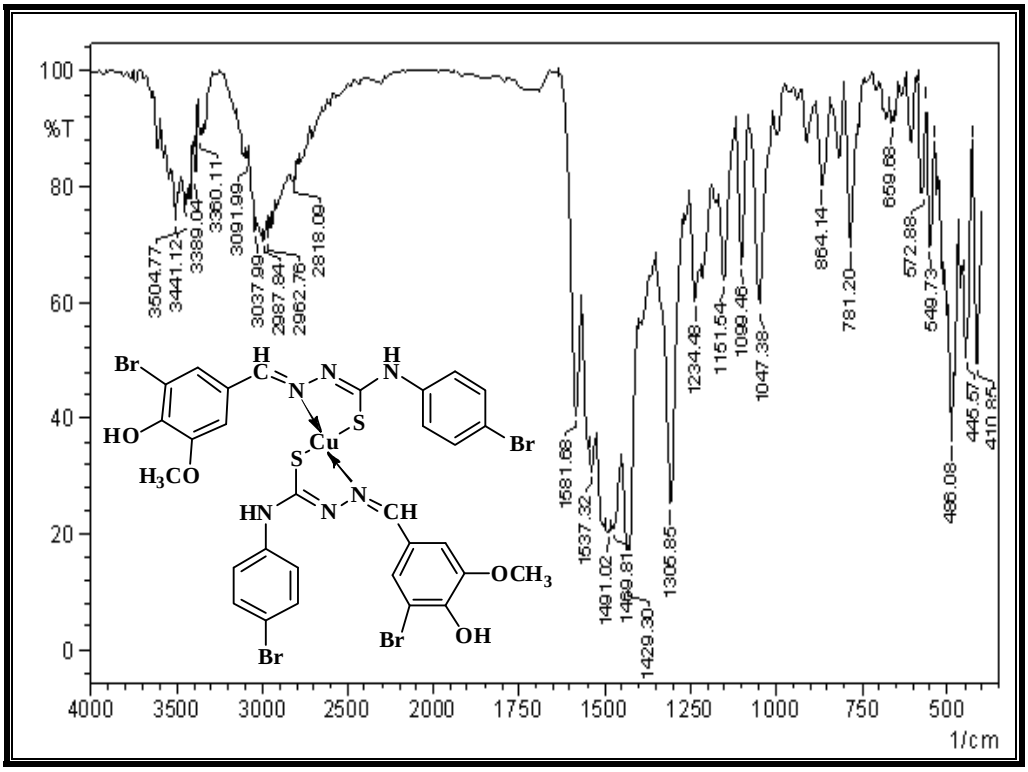
ESI Mass spectrum of RMT- 40



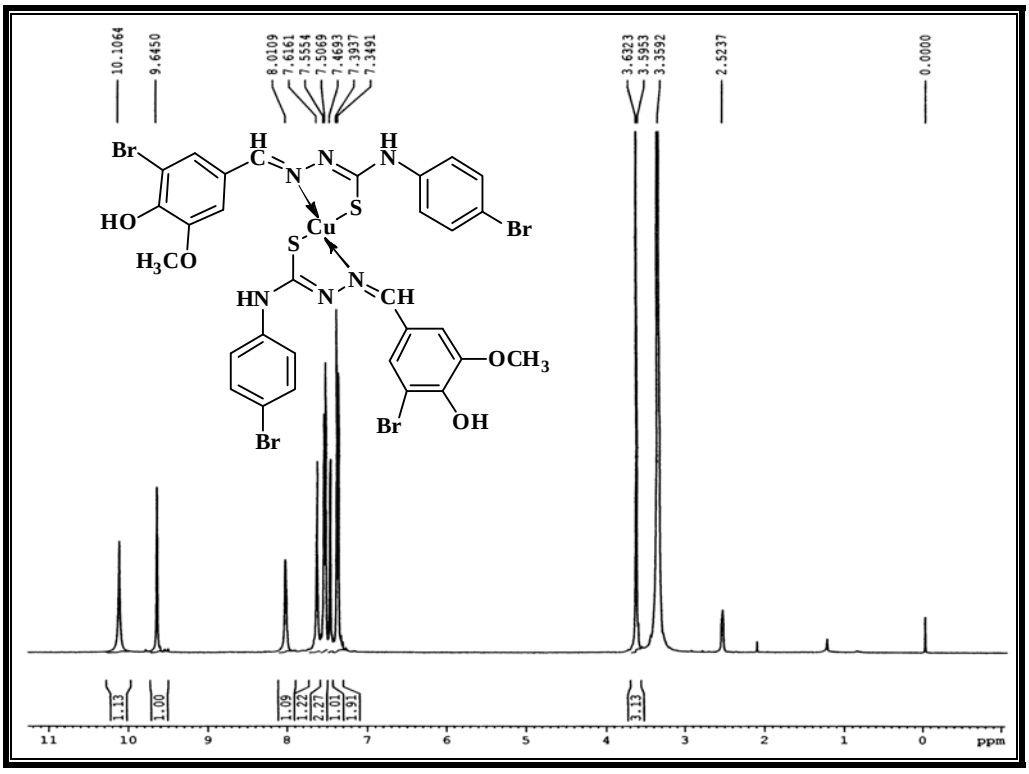
Expanded ESI Mass spectrum of RMT- 40



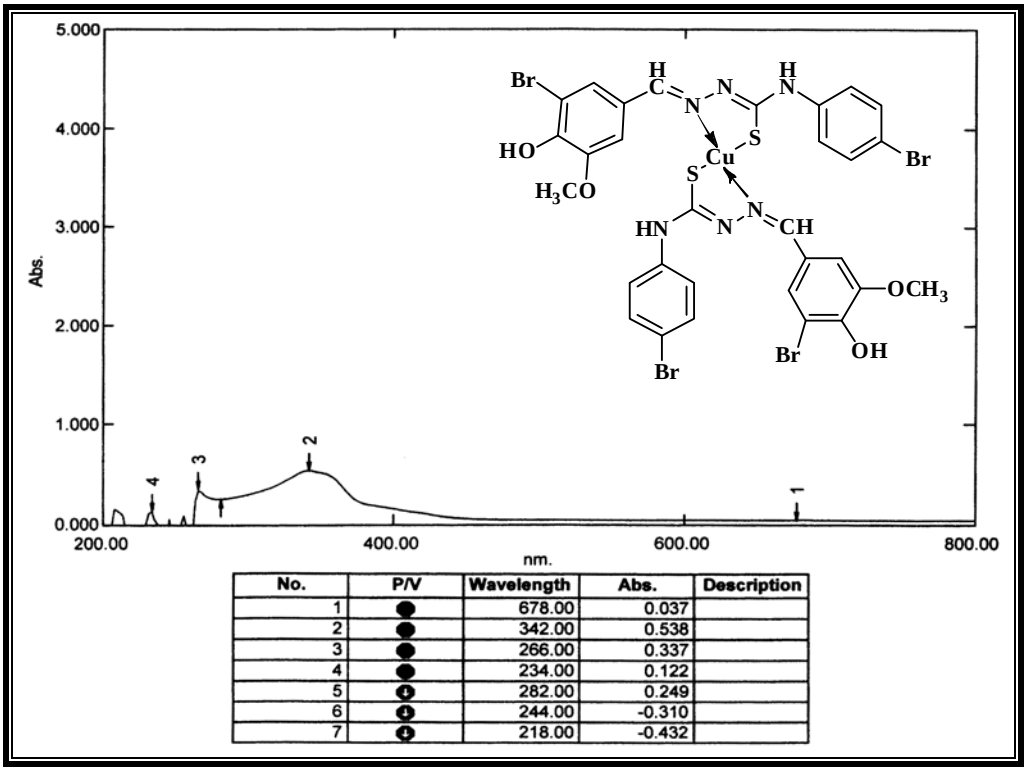
IR spectrum of RMT- 40



^{1}H NMR spectrum of RMT- 40

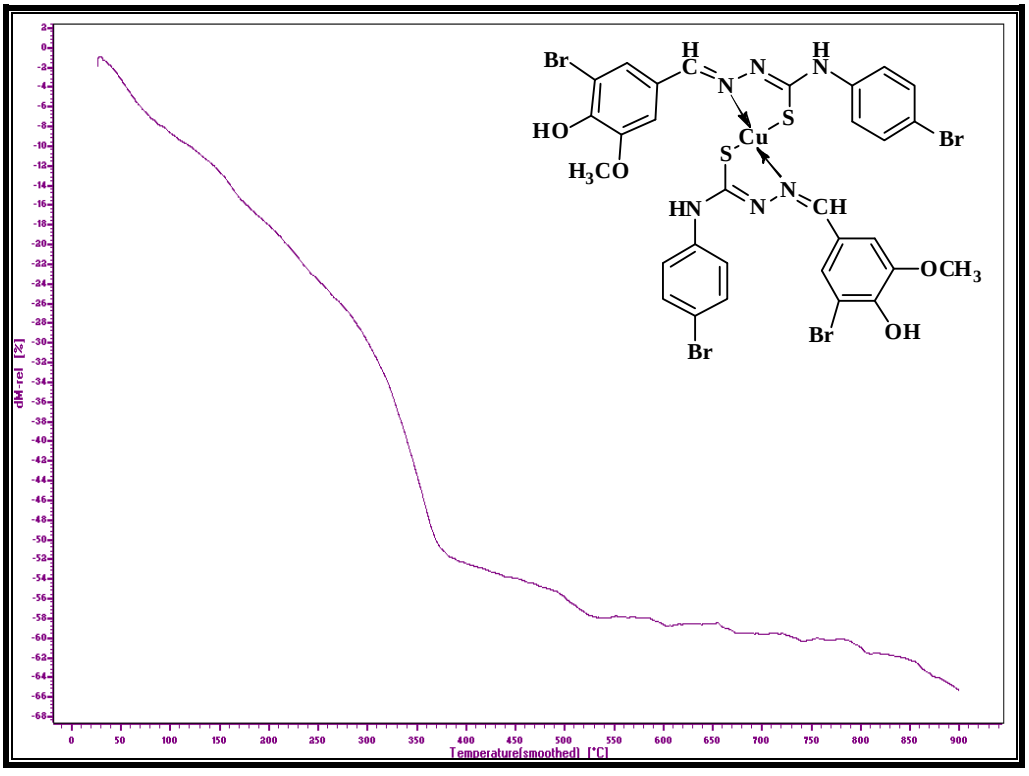


UV-Visible spectrum of RMT- 40



No.	P/V	Wavelength	Abs.	Description
1	●	678.00	0.037	
2	●	342.00	0.538	
3	●	266.00	0.337	
4	●	234.00	0.122	
5	▲	282.00	0.249	
6	▲	244.00	-0.310	
7	▲	218.00	-0.432	

TGA spectrum of RMT- 40



Results & Discussion

The most important bands in the infrared spectra of the Copper(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Copper(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide exhibited a bands observed at 3504 cm^{-1}, 3389 cm^{-1}, 1047 cm^{-1} and 1234 cm^{-1} of -OH, -NH, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1581 cm^{-1} and aromatic -C-H and -C=C bands due to at 3091-2987 cm^{-1} and 1491 cm^{-1} respectively. The specific bands (Cu-N) and (Cu-S) observed at 486 cm^{-1} and 410 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Copper(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other -NH proton signal observed as singlet at 10.10 ppm. The signal of the (-HC=N) proton which appear as singlet at 8.01 ppm in the complex. The signal as compare to ligand show a shift to up field in δ 0.03-

0.80ppm after complexation. This shift indicates the coordination of the imine nitrogen to the metal centre. The signals of -OCH_3 and -OH protons observed as singlet at 3.63 and 9.64 ppm, respectively. The signals of the aromatic protons of the Cu(II) complex appeared at δ 7.39-7.61 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi\rightarrow\pi^*$ and/or $n\rightarrow\pi^*$ interaligand transition. There are two detected absorption bands at around 266 nm and 342 nm assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ interaligand transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 678 nm is assigned to a merges of $^2T_{2g}\leftarrow{}^2E_g$ dtransition in square planer geometry.

The TGA curves of the Copper(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Cu(L_2)\,(H_2O)_n]\cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Cu(L_2)\,(H_2O)_n] + nH_2O$$

$$[Cu(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Cu(L_2)] + (H_2O)_n$$

$$[Cu(L_2)] \xrightarrow{180\text{-}300\ ^0C} [CuL] + L$$

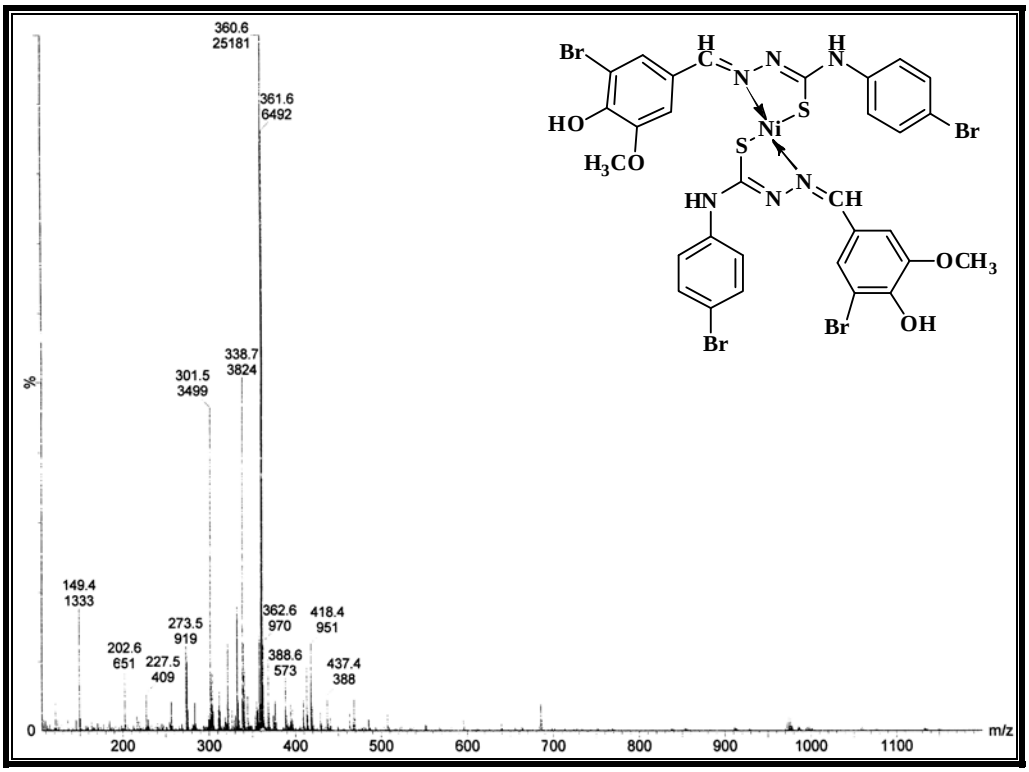
$$[CuL] \xrightarrow{300\text{-}600\ ^0C} CuO + L$$

(Where n = 0, 1 or 2).

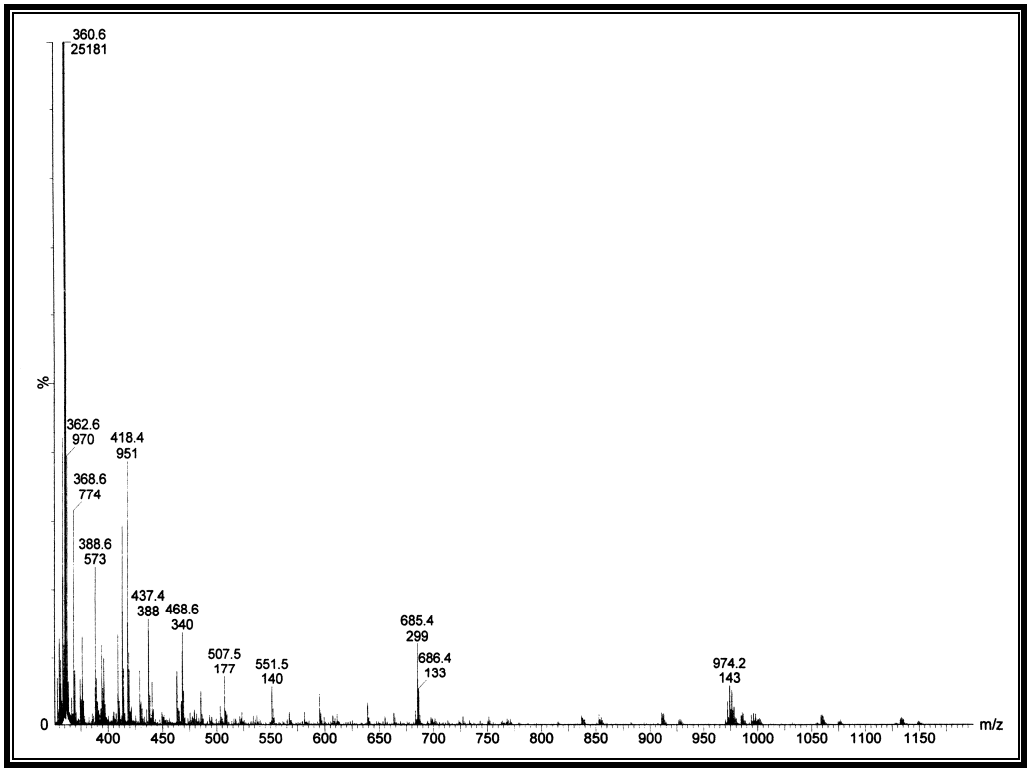
The room temperature magnetic moments for the copper(II) complex 1.74 BM correspond to the values normally observed for square-planar copper(II) compound. The room temperature value for μ_{eff} (1.97) (where μ_{eff} is the effective magnetic moment) is very close to the spin-only value of 1.73 B.M. for d^9.

All spectral characterization and thermal analysis confirms the structure of Copper(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide(RMT-40). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the square planer type geometries of the present complex.

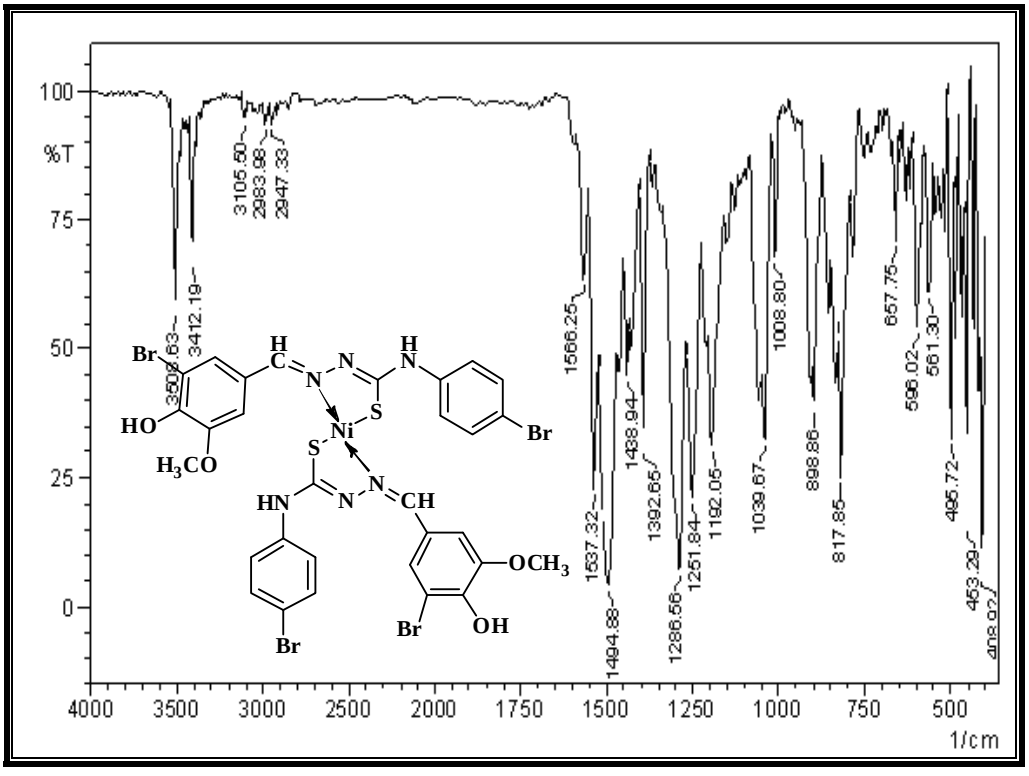
ESI Mass spectrum of RMT- 41



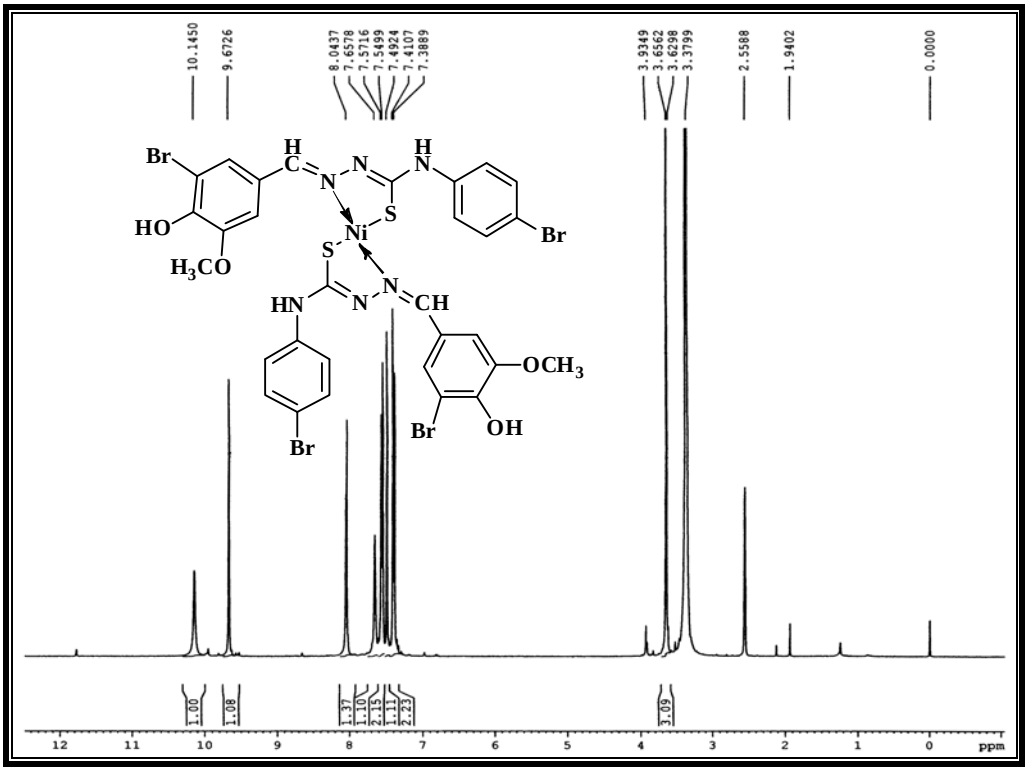
Expanded ESI Mass spectrum of RMT- 41



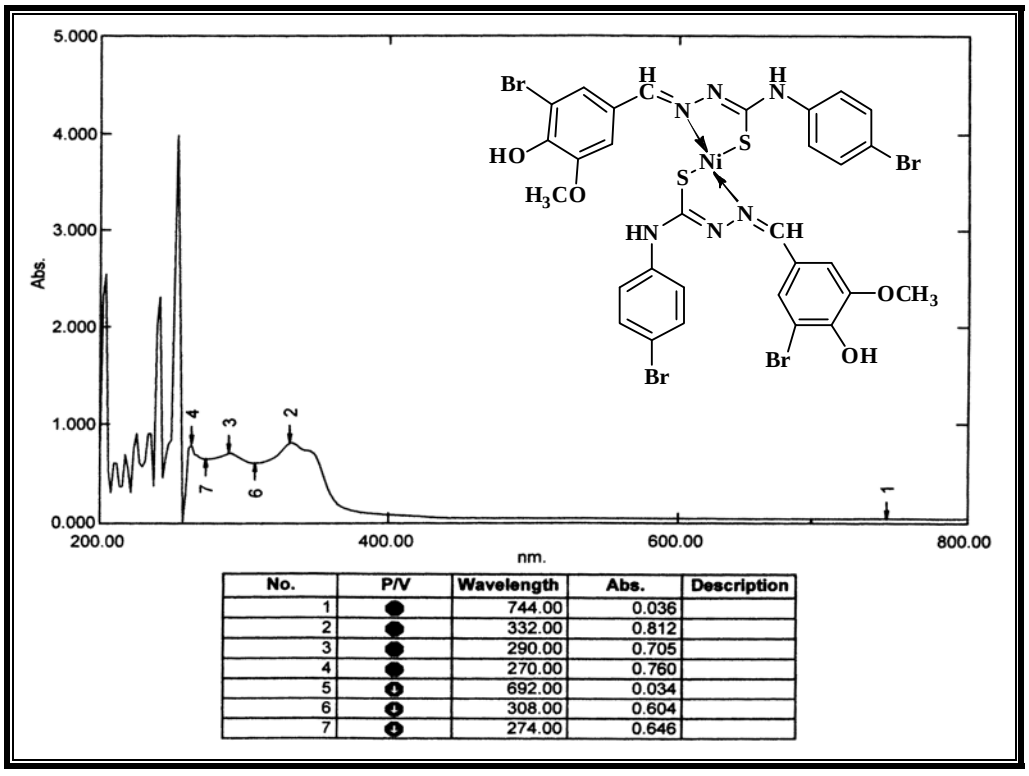
IR spectrum of RMT- 41



^{1}H NMR spectrum of RMT- 41

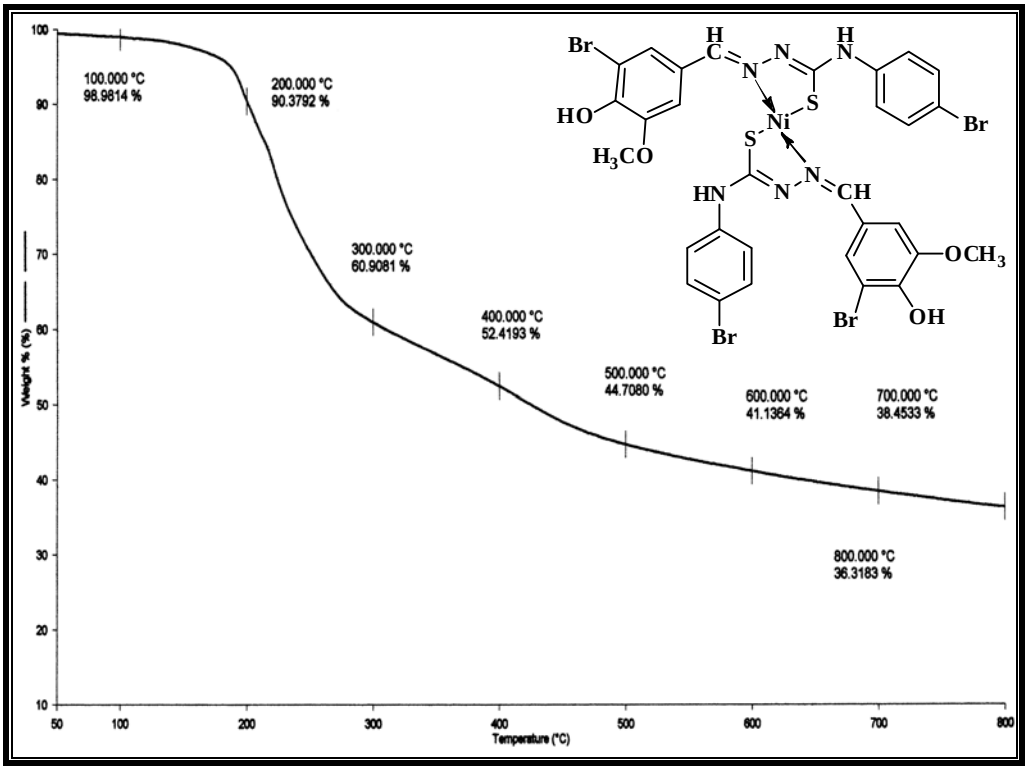


UV-Visible spectrum of RMT- 41



No.	P/V	Wavelength	Abs.	Description
1	●	744.00	0.036	
2	●	332.00	0.812	
3	●	290.00	0.705	
4	●	270.00	0.760	
5	◆	692.00	0.034	
6	◆	308.00	0.604	
7	◆	274.00	0.646	

TGA spectrum of RMT- 41



Results & Discussion

The most important bands in the infrared spectra of the Nickel(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating

that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Nickel(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide exhibited a bands observed at 3508 cm^{-1}, 3412 cm^{-1}, 1039 cm^{-1} and 1286 cm^{-1} of -OH, -NH, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1566 cm^{-1} and aromatic -C-H and -C=C bands due to at 3105-2983 cm^{-1} and 1494 cm^{-1} respectively. The specific bands (Ni-N) and (Ni-S) observed at 495 cm^{-1} and 408 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Nickel(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other -NH proton signal observed as singlet at 10.14 ppm. The signal of the (-HC=N) proton which appear as singlet at 8.04 ppm in the complex. The signal as compare to ligands show a shift to up field in δ 0.03-0.80ppm after complexation. This shift indicates the coordination of the imine nitrogen to the metal centre. The signals of -OCH_3 and -OH protons observed as singlet at 3.65 and 9.67 ppm, respectively. The signals of the aromatic protons of the Ni(II) complex appeared at δ 7.40-7.65 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi\rightarrow\pi^*$ and/or $n\rightarrow\pi^*$ interaligand transition. There are two detected absorption bands at around 270 nm assigned to $\pi\rightarrow\pi^*$ interaligand transition and 332 nm assigned to $^{3}T_{1g}(P)\leftarrow{}^{3}A_{2g}(F)$ transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 744 nm is assigned to a merges of $^{3}T_{1g}(F)\leftarrow{}^{3}A_{2g}(F)$ transition in tetrahedral geometry.

The TGA curves of the Nickel(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Ni(L_2)\,(H_2O)_n] \cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Ni(L_2)\,(H_2O)_n] + nH_2O$$

$$[Ni(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Ni(L_2)] + (H_2O)_n$$

$$[Ni(L_2)] \xrightarrow{180\text{-}300\ ^0C} [NiL] + L$$

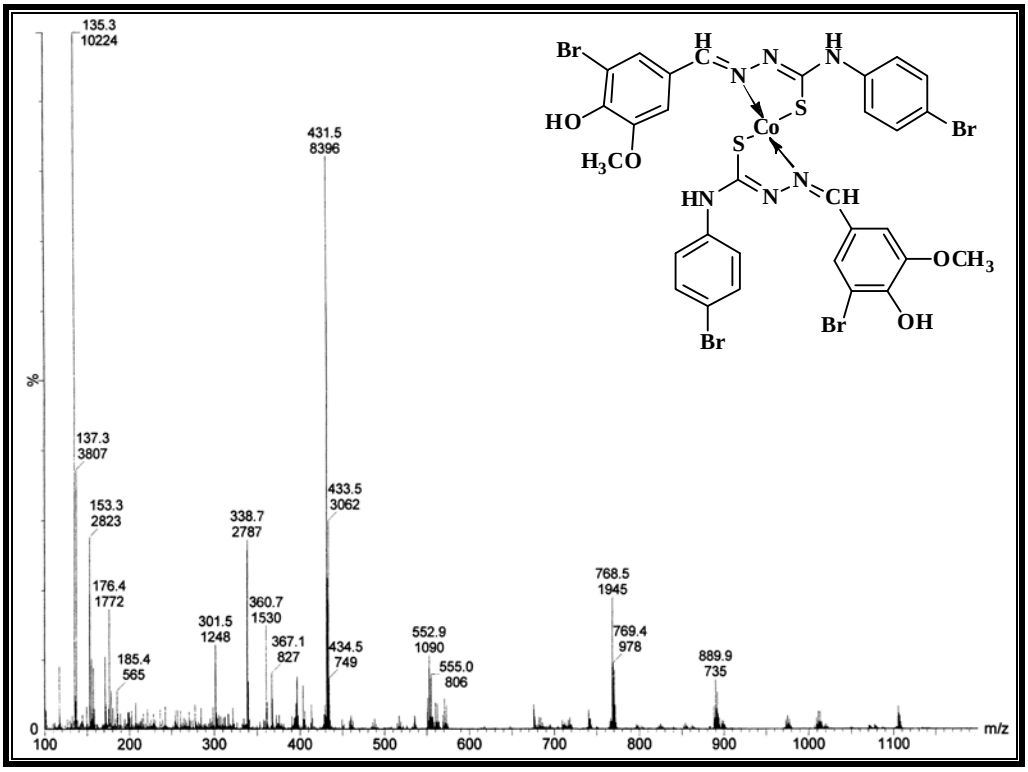
$$[NiL] \xrightarrow{300\text{-}600\ ^0C} NiO + L$$

(Where n = 0, 1 or 2).

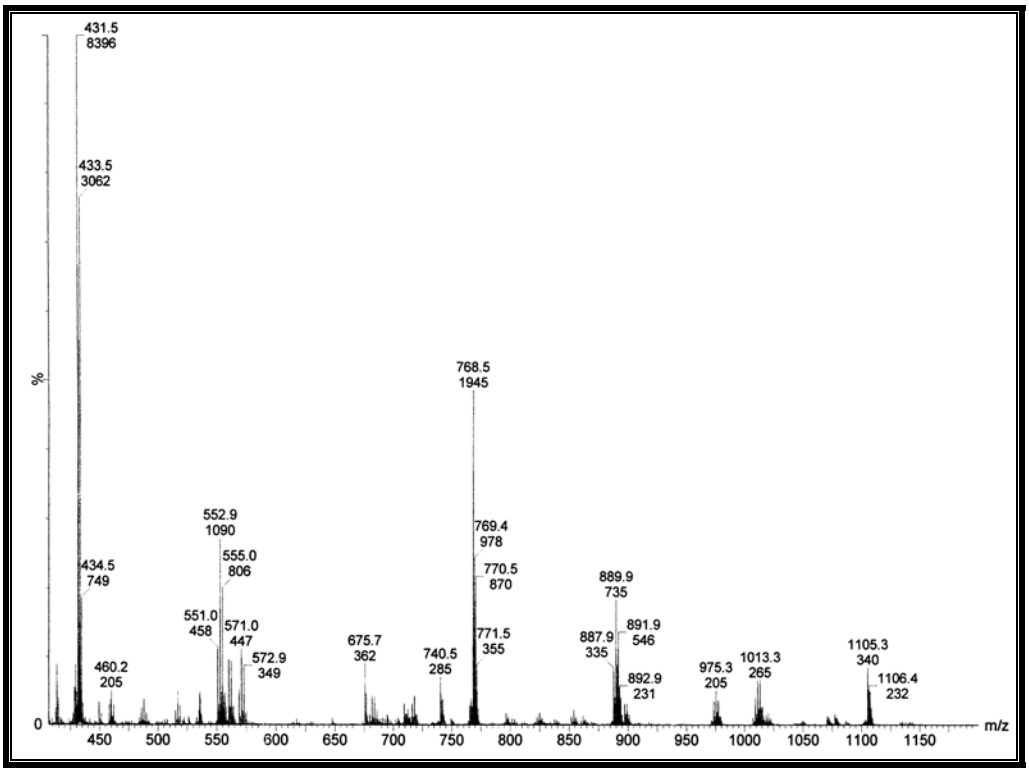
The magnetic moment of the nickel complex was found to be 3.19 B.M. which falls in the range generally observed for the four-coordinated Ni(II) complex. The magnetic data of the Ni(II) complex agree with a d^8 metal ion in an tetrahedral configuration.

All spectral characterization and thermal analysis confirms the structure of Nickel(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide(RMT-41). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the tetrahedral type geometries of the present complex.

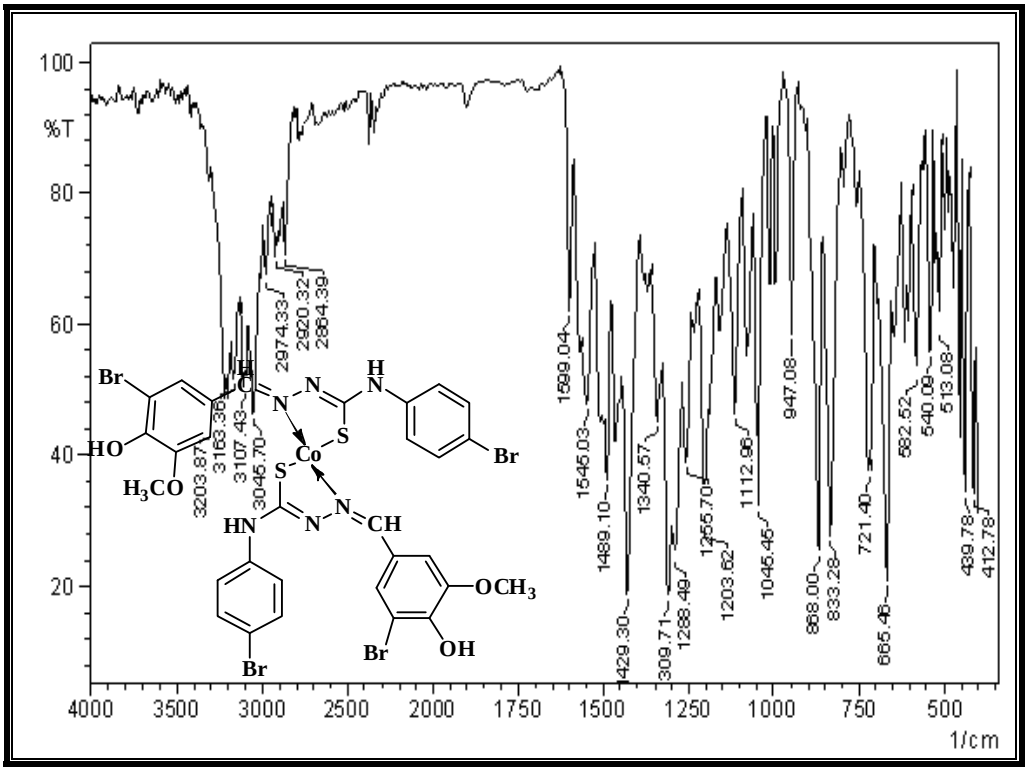
ESI Mass spectrum of RMT- 42



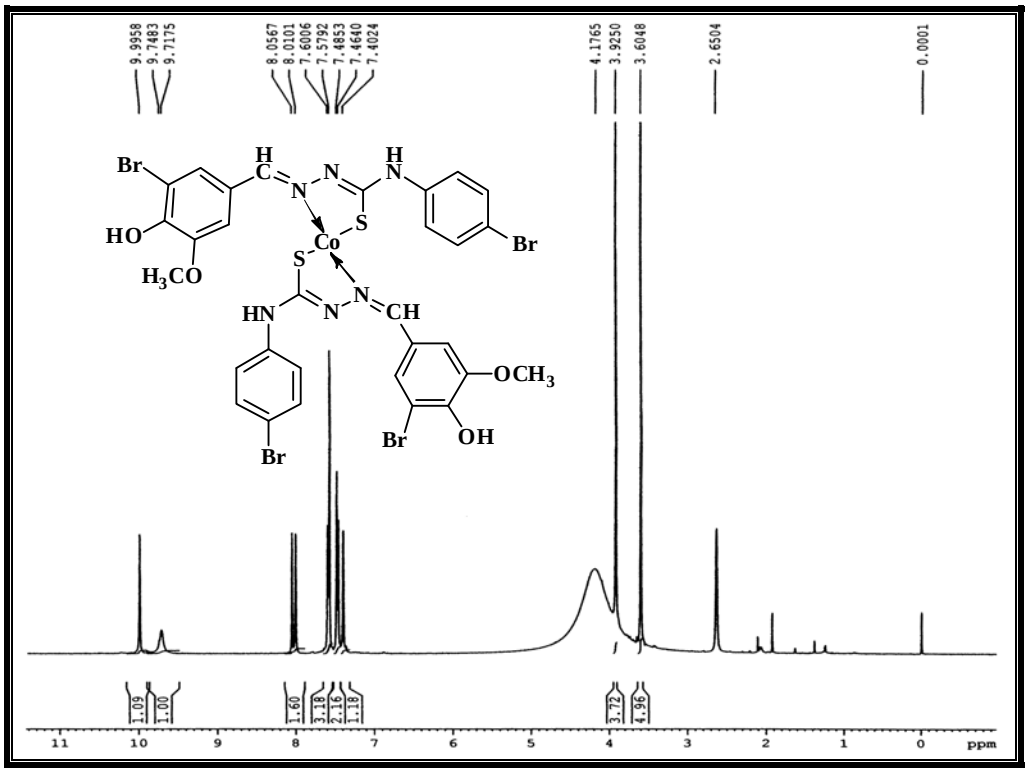
Expanded ESI Mass spectrum of RMT- 42



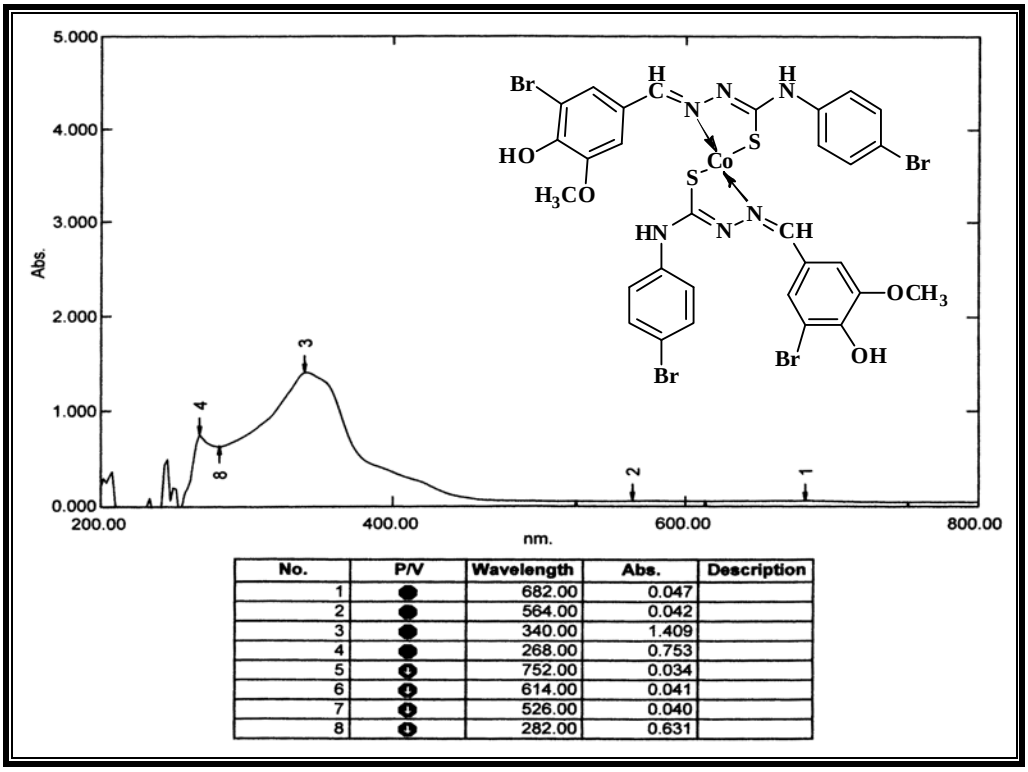
IR spectrum of RMT- 42



^{1}H NMR spectrum of RMT- 42

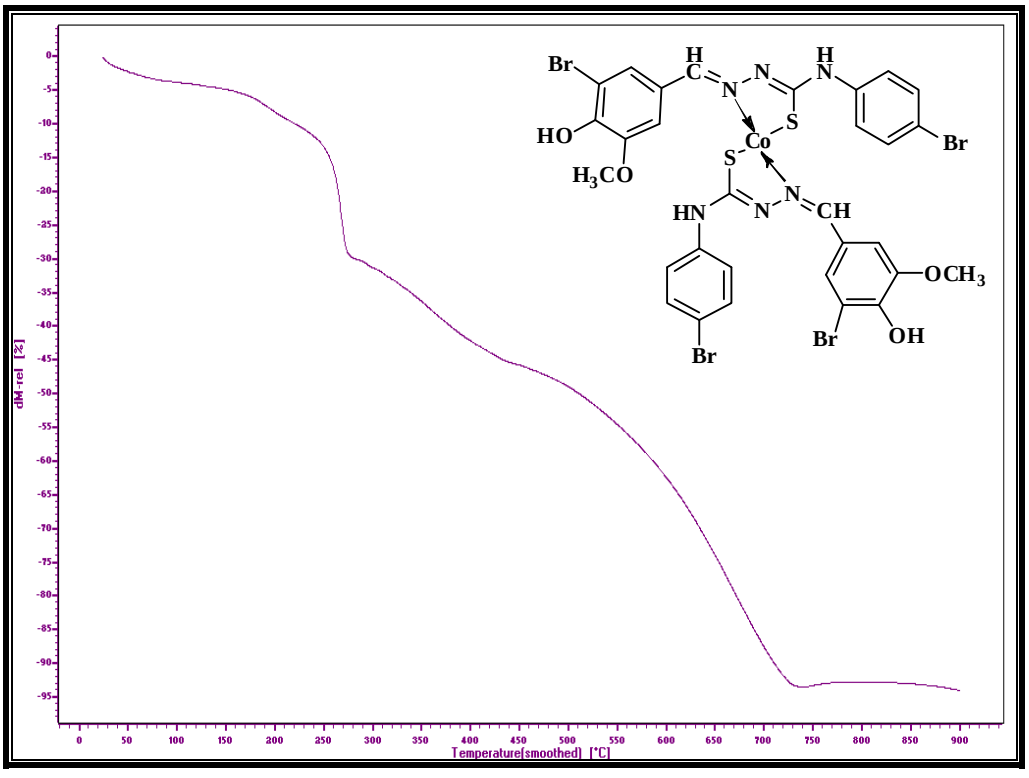


UV-Visible spectrum of RMT- 42



No.	P/V	Wavelength	Abs.	Description
1	●	682.00	0.047	
2	●	564.00	0.042	
3	●	340.00	1.409	
4	●	268.00	0.753	
5	◆	752.00	0.034	
6	◆	614.00	0.041	
7	◆	526.00	0.040	
8	◆	282.00	0.631	

TGA spectrum of RMT- 42



Results & Discussion

The most important bands in the infrared spectra of the Cobalt(II) complex of thiosemicarbazone are along within their tentative assignment. The position of these bands was helpful to detect the bonding sites of all ligand molecules interacted with metal. In principle, the ligand can exhibit thione-thiol tautomerism since it contains a thioamide NH-C=S functional group. The ν(S-H) band at 2556 cm^{-1} is absent from the IR spectra of the Schiff base ligands. At the same time the ν(N-H) band at 3440-3270 cm^{-1} is present, indicating that, in the solid state the ligands remain as the thione tautomer. Infrared spectra of the ligands show strong bands in the region 1590-1670 cm^{-1} which may be assigned to the symmetric ν(C=N) vibrations for all ligands. These frequencies are shifted towards lower wavenumber by ca. 15-30 cm^{-1} in spectra of all metal complexes, suggesting the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The metal–nitrogen bond was detected by appearing frequencies in the region 470-508 cm^{-1} from the IR data. Furthermore in the spectra of all ligands, the strong band observed at 762-829 cm^{-1} was shifted to lower wavenumber by ca. 10-15 cm^{-1} in all metal complexes, indicating that thione sulphur participate as a coordinating site. This prediction was confirmed by the presence of new band at 405-426 cm^{-1} which can be assigned to ν(M-S).

The IR spectra of the Cobalt(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide exhibited a bands observed at 3498 cm^{-1}, 3403 cm^{-1}, 1045 cm^{-1} and 1288 cm^{-1} of -OH, -NH, -N-N- and -C=S groups respectively. The (-CH=N-) group was observed at 1599 cm^{-1} and aromatic -C-H and -C=C bands due to at 3107-2974 cm^{-1} and 1494 cm^{-1} respectively. The specific bands (Co-N) and (Co-S) observed at 513 cm^{-1} and 412 cm^{-1} respectively. From the IR data, it can be inferred that the ligand involved in the complexation as a bidentate ligand which coordinated with metal ions through their thione sulphur and azomethine N atom.

In the ^{1}H-NMR spectra of the Cobalt(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide the signals of the =N-NH protons were observed as singlets at δ ~12.00ppm in the free ligand this signals disappears after complexation and other -NH proton signal observed as singlet at 9.99 ppm. The signal of the (-HC=N) proton which appear as singlet at 8.01 ppm in the complex. The signal as compare to ligands show a shift to up field in δ 0.03-0.80ppm

after complexation. This shift indicates the coordination of the imine nitrogen to the metal centre. The signals of -OCH_3 and -OH protons observed as singlet at 3.92 and 9.71 ppm, respectively. The signals of the aromatic protons of the Co(II) complex appeared at δ 7.40-7.59 ppm, and the resonance lines found correspond to the calculated multiplicity.

The electronic absorption spectra are often very helpful in the evaluation of results furnished by other methods of structural investigation. The bands in the range 200–450 nm can be assigned to $\pi\rightarrow\pi^*$ and/or $n\rightarrow\pi^*$ interaligand transition. There are two detected absorption bands at around around 268 nm assigned to $\pi\rightarrow\pi^*$ interaligand transition and 340 nm assigned to $^4T_{1g}(P)\leftarrow{}^4T_{1g}(F)$ transition, respectively, in the electronic spectra of all ligands. These transition also found in the spectra of the resulted complexes with small shifted and hyperchromically effect. The d-d transition of the complex was also recorded in visible region by concentrating the solution. The broad band in the region of 800-650 nm with maximum absorbance at 682 nm is assigned to a merges of $^4T_{2g}(F)\leftarrow{}^4T_{1g}(F)$ transition in tetrahedral geometry.

The TGA curves of the Cobalt(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide was carried out within a temperature range from room temperature up to 800 °C. The data from thermogravimetric analysis clearly indicated that the decomposition of the complex proceed in several steps. Hydration water molecules were lost in between 30 °C - 120 °C. The coordinated water molecules were liberated in between 120 °C - 180 °C, There is no change up to ~300 ºC after that there is a break in the curves due to evaporation of 0.5 molecule of organic ligand, the remaining ligand is removed from the coordination sphere at ~ 450 ºC. Finally the metal oxides were formed above 600 °C. The decomposition was complete at ≥600 °C for the complex. The degradation pathway for the complex may be represented as follows.

$$[Co(L_2)\,(H_2O)_n]\cdot nH_2O \xrightarrow{30\text{-}120\ ^0C} [\,Co(L_2)\,(H_2O)_n] + nH_2O$$

$$[Co(L_2)\,(H_2O)_n] \xrightarrow{120\text{-}180\ ^0C} [Co(L_2)] + (H_2O)_n$$

$$[Co(L_2)] \xrightarrow{180\text{-}300\ ^0C} [CoL] + L$$

$$[CoL] \xrightarrow{300\text{-}600\ ^0C} CoO + L$$

(Where n = 0, 1 or 2).

Magnetic moment measurements for the complexes were made at room temperature. The cobalt(II) complex show magnetic moment 4.86 BM, a value in accordance with a high spin configuration showing the presence of tetrahedral environment around the cobalt(II) ion in the complex. The experimental values are higher than spin only value due to orbital angular momentum contribution in d^7 system.

All spectral characterization and thermal analysis confirms the structure of Cobalt(II) complex of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide(RMT-42). A conductance of complex is shows that the complex is 1:2 non-electrolyte and the magnetic moment and UV-Visible studies suggest the tetrahedral type geometries of the present complex.

2.5 REFERENCES

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Stability constants of metal complexes

Section - C

3.1 THEORETICAL

3.1.1 Stability of co-ordination compounds

The stability of compounds means in a most general sense, the compounds exist under suitable conditions may be stored for a long period of time. However when the formation of complexes in solution is studied, two types of stabilities, thermodynamic stability and kinetic stability are considered.

In the language of thermodynamics, the equilibrium constants of a reaction are the measure of the heat released in the reaction and entropy change during reaction. The greater amount of heat evolved in the reaction, the most stable are the reaction products. Secondly, greater the increase in entropy during the reaction, greater is the stability of products. The kinetic stability of complexes refers to the sped with which transformation leading to the attainment of equilibrium will occur. Here we are mainly concerned with the thermodynamic stability of the complex compound.

3.1.2 Determination of stability constant of complexes

In complexes the term stability is employed in two ways (1) thermodynamic stability and kinetic stability. Thermodynamic stability deals with the bond energy, stability constant and redox potential. Kinetic stability deals with the rate of the reaction, mechanism of reaction, formation of intermediate complexes, and activation for the process etc.

The thermodynamic stability of a species is a measure of the extent to which the species will form or be transformed into other species under certain conditions, when the system has reached equilibrium.

Let metal ion (M^{n+}) combines with ligand (L) to form complex ML_n, then

$$M + nL \leftrightarrows ML_n$$

$$K = \frac{[ML_n]}{[M][L]^n}$$

Thus by knowing the value of [M], [L] and [ML_n] the value of K, stability constant of the complex ML_n, can be computed.

The knowledge of stability constant is needed for computing quantitatively the concentration of free metal ion, ligand and any of its complexes formed in the system, under different conditions of pH. These data are extensively employed in analytical chemistry, stereochemistry, and biochemistry and in the technology of non ferrous and rare metals, solvent extraction, ion exchange etc.

There are so many techniques for the computation of stability constants. Here only two methods are explained known as pH-metric method and spectrophotometric method.

3.1.3 Determination of stepwise stability constants by pH-metric method

As complexing processes are considered as occurring by a series of stages thus it is possible to express the formation (stability) constants referring specially to the addition of ligands in a stepwise manner as follows:

$M + L \leftrightarrows ML$	$K_1 = \frac{[ML]}{[M][L]}$	$\therefore [ML] = K_1[M][L]$	(a)
$ML + L \leftrightarrows ML_2$	$K_2 = \frac{[ML_2]}{[ML][L]}$	$\therefore [ML_2] = K_2[ML][L]$	(b)
$ML_2 + L \leftrightarrows ML_3$	$K_3 = \frac{[ML_3]}{[ML_2][L]}$	$\therefore [ML_3] = K_3[ML_2][L]$	(c)
……..	……		
…….	……		
…….	……		
$ML_{n-1} + L \leftrightarrows ML_n$	$K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$	$\therefore [ML_n] = [ML_{n-1}][L]$	(n)

The constants K_1, K_2, K_3,……K_n are called the stepwise stability constants. The stepwise constants are related to the overall stability constant by the simple related:

$\beta_1 = K_1$

$\beta_2 = K_1.K_2$

$\beta_3 = K_1.K_2.K_3$

$\beta_4 = K_1.K_2.K_3.K_4$

Therefore $\beta_n = K_1.K_2.K_3. \ldots\ldots K_n$ (1)

A large number of techniques of great diversity are now being employed for the determination of stepwise stability constants. The most generally utilised and probably the most accurate and reliable method for the determination of stability constant is based on the potentiometric measurement of hydrogen ion concentration. This depends on the fact that pH of the solution is directly affected by complex formation, which is accompanied by the displacement of a proton from the acidic ligand. The magnitude of the observed pH change may be employed to determine the stability constant of the metal complexes by Bjerrum's method, Calvin and Wilson's method.

Out of these techniques Bjerrum's method is better as used by Calvin and Wilson. Bjerrum suggested certain formation functions such as $\bar{n}_A$, $\bar{n}$, pL. These functions are employed to calculate the stepwise stability constans.

The formation function ($\bar{n}$) of a metal ligand (M, L) system can be defined as:

$$\bar{n} = \frac{\text{Total concentration of L bound to M}}{\text{Total concentration of M}}$$

$$\bar{n} = \frac{[ML] + 2[ML_2] + 3[ML_3] + ...}{[M] + [ML] + [ML_2] + [ML_3] + ...} \qquad (2)$$

Substitute the values of eq. (a), (b), (c) and (n) in (2)

$$\bar{n} = \frac{K_1[M][L] + 2K_2[ML][L] + 2K_3[ML_2][L] + ...}{[M] + K_1[M][L] + K_2[ML][L] + K_3[ML_2][L] + ...} \qquad (3)$$

Now substitute the value of eq. (a) and (b) in (3)

$$\bar{n} = \frac{K_1[M][L] + 2K_1K_2[M][L]^2 + 3K_2K_3[ML][L]^2 + ...}{[M] + K_1[M][L] + K_1K_2[M][L]^2 + K_2K_3[ML][L]^2 + ...} \qquad (4)$$

Now the value of eq. (a) substitute in (4)

$$\bar{n} = \frac{K_1[M][L] + 2K_1K_2[M][L]^2 + 3K_1K_2K_3[M][L]^3 + ...}{[M] + K_1[M][L] + K_1K_2[M][L]^2 + K_1K_2K_3[M][L]^3 + ...} \quad (5)$$

Now taking [M] common form eq. (5)

$$\bar{n} = \frac{K_1[L] + 2K_1K_2[L]^2 + 3K_1K_2K_3[L]^3 + ...}{1 + K_1[L] + K_1K_2[L]^2 + K_1K_2K_3[L]^3 + ...} \quad (6)$$

Now according to eq. (1) $\beta_n = K_1.K_2.K_3....K_n$, $\therefore$ b1 = K1, $\beta_2 = K_1.K_2$, $\beta_3 = K_1.K_2.K_3$, and so on, substitute in the (6)

$$\bar{n} = \frac{\beta[L] + 2\beta[L]^2 + 3\beta[L]^3 + ...}{1 + \beta[L] + \beta[L]^2 + \beta[L]^3 + ...}$$

$$\bar{n} = \frac{\sum_{i=0}^{n} i\beta_i[L]^i}{1 + \sum_{i=0}^{n} \beta_i[L]^i} \quad (7)$$

$$\bar{n} = \sum_{i=0}^{n} i(\bar{n} - 1)\beta_i[L]^i \quad (8)$$

In this same way for ligand-proton (L, H) system formation function $\bar{n}_A$ is defined as

$$\bar{n}_A = \frac{\text{Total concentrat ion of H bound to L}}{\text{Total concentrat ion of L not bound to M}}$$

$$\bar{n}_A = \frac{[HL] + 2[H_2L] + 3[H_3L] + ...}{[L] + [HL] + [H_2L] + [H_3L] + ...}$$

$$\bar{n}_A = \frac{K_1^H[H][L] + 2K_1^HK_2^H[H]^2[L] + 3K_1^HK_2^HK_3^H[H]^3[L] + ...}{[L] + K_1^H[H][L] + K_1^HK_2^H[H]^2[L] + K_1^HK_2^HK_3^H[H]^3[L] + ...}$$

$$\bar{n}_A = \frac{K_1^H[H] + 2K_1^H K_2^H [H]^2 + 3K_1^H K_2^H K_3^H [H]^3 + ...}{1 + K_1^H[H] + K_1^H K_2^H [H]^2 + K_1^H K_2^H K_3^H [H]^3 + ...}$$

$$\bar{n}_A = \frac{\beta_1^H[H] + 2\beta_2^H [H]^2 + 3\beta_3^H [H]^3 + ...}{1 + \beta_1^H[H] + \beta_2^H [H]^2 + \beta_3^H [H]^3 + ...}$$

$$\bar{n}_A = \frac{\sum_{i=0}^{n} i\beta_i^H [H]^i}{\sum_{i=0}^{n} \beta_i^H [H]^i} \qquad (9)$$

Now formation function $\bar{n}$ is

$$\bar{n} = \frac{T_{CL^\circ} - \text{Concentration of L not bound to M}}{T_{CM^\circ}}$$

Where T_{CL° = Total concentration of ligand L and T_{CM° = Total concentration of metal M

$\therefore\ \bar{n}\,T_{CM^\circ} = T_{CL^\circ}$ - Concentration of L not bound to M

$\therefore$ Concentration of L not bound to M = $T_{CL^\circ} - \bar{n}\,T_{CM^\circ}$ (10)

From the value of $\bar{n}_A$,

Total concentration of L not bound to M = $[L]\left(1 + \beta_1^H[H] + \beta_2^H[H]^2 + \beta_3^H[H]^3 + ...\right)$

$$M = [L]\sum_{i=0}^{n} \beta_i^H [H]^i \qquad (11)$$

Substitute the value of eq. (11) in (10)

$\therefore\ [L]\sum_{i=0}^{n} \beta_i^H [H]^i = T_{CL^\circ} - \bar{n}\,T_{CM^\circ}$

$$\therefore\ [L] = \frac{T_{CL^\circ} - \bar{n}T_{CM^\circ}}{\sum_{i=0}^{n} \beta_i^H [H]^i}$$

$$\therefore\ [L]^{-1} = \frac{\sum_{i=0}^{n} \beta_i^H [H]^i}{T_{CL^\circ} - \bar{n} T_{CM^\circ}} \qquad (12)$$

Taking log in eq. (12)

$$\log[L]^{-1} = \log_{10} \frac{\sum_{i=0}^{n} \beta_i^H [H]^i}{T_{CL^\circ} - \bar{n} T_{CM^\circ}}, \qquad \log[L]^{-1} = pL$$

$$\therefore\ pL = \log_{10} \frac{\sum_{i=0}^{n} \beta_i^H [H]^i}{T_{CL^\circ} - \bar{n} T_{CM^\circ}} \qquad (13)$$

Calvin and Wilson have demonstrated that pH measurements made during titrations with alkali solution of ligand in the presence and absence of metal ion could be employed to calculate the formation functions $\bar{n}_A$, $\bar{n}$ and pL and stability constants can be computed. Irving and Rossotti[1], titrated following solutions against standard sodium hydroxide solution N° keeping total volume V° constant.

1. X mL mineral acid ($HClO_4$) E°
2. A + X_1 mL ligand
3. B + X_2 mL metal ion

On plotting the pH value of the solution with the addition of sodium hydroxide solution three graphs are achieved.

The formation functions $\bar{n}_A$, $\bar{n}$ and pL can be computed from the following eqations:

$$\bar{n}_A = Y - \frac{(V_1 - V_2)(N^\circ - E^\circ)}{(V^\circ + V_1) T_{CL^\circ}} \qquad (14)$$

$$\bar{n} = \frac{(V_3 - V_2)(N^\circ + E^\circ)}{(V^\circ + V_1)(\bar{n}_A)(T_{CM^\circ})} \qquad (15)$$

$$pL = \log_{10} \frac{1 + K_1^H [H] + K_1^H K_2^H [H]^2 + ...}{T_{CL^\circ} - \bar{n} T_{CM^\circ}} \times \frac{V^\circ + V_3}{V^\circ}$$

$$pL = \log_{10} \frac{\sum_{n=0}^{n} \beta_n^H \cdot \frac{1}{(anti \log B)^n}}{T_{CL^\circ} - \bar{n} T_{CM^\circ}} \times \frac{V^\circ + V_3}{V^\circ} \quad (16)$$

Where,

Y = number of dissociable protons

V_1, V_2 and V_3 = volume of alkali employed bring the solution 1, 2 and 3 to same pH value

T_{CL° = total concentration of the ligand

T_{CM° = total concentration of metal ion

By the knowledge of $\bar{n}_A$, $\bar{n}$, pH and pL protonation and stepwise stability constants can be computed by different methods such as:

3.1.4 Determination of stoichiometric stability constant

A fairly large number of methods for computing stability constants from experimental data have been used by number of authors[2-4] Some of the more generally applicable Computational methods are as follows :

(1) Least square method[5]

From eq. (7)

$$\bar{n} = \frac{\sum_{i=0}^{n} i\beta_i [L]^i}{1 + \sum_{i=0}^{n} \beta_i [L]^i}$$

For i = 1; $\bar{n} = \frac{K_1[L]}{1 + K_1[L]}$ or $K_1 = \frac{\bar{n}}{(1 - \bar{n})[L]}$ (17)

or $\log K_1 = \log \frac{\bar{n}}{1 - \bar{n}} + pL$ (18)

for i = 2, $\bar{n} = \frac{K_2[L] + 2K_1K_2[L]^2}{1 + K_1[L] + K_1K_2[L]}$

or $\frac{\bar{n}}{(\bar{n} - 1)[L]} = \frac{(2 - \bar{n})[L]K_1K_2}{(\bar{n} - 1)} K_1$ (19)

or $K_2 = \frac{1}{[L]} \cdot \frac{\bar{n} + (\bar{n} - 1)K_1[L]}{(2 - \bar{n})K_1[L]}$

or $\log K_2 = pL + \log \frac{\bar{n} + (\bar{n} - 1)K_1[L]}{(2 - \bar{n})K_1[L]}$ (20)

The term $(\bar{n}$ -1)$K_1[L]$ is negligible when $\bar{n} > 0.5$

Hence, $\log K_2 = 2pL + \log \frac{\bar{n}}{(2 - \bar{n})K_1}$ (21)

The equations (18) and (20) are straight line equations. Thus by plotting different values of $\bar{n}$ and [L] straight line will be achieved. Thus the values of K_1 and K_2 can be computed.

(2) Half integral method[2] / Interplotation at half $\bar{n}$ values[6]

By putting the value $\bar{n} = 0.5$ in equation (18) we obtain

$\log K_1 = pL$

Similarly by putting the value $\bar{n} = 1.5$ in the equation (20) we obtain

$\log K_2 = pL$

It means if we plot a graph between $\bar{n}$ and pL then the corresponding values of pL at $\bar{n}$ equal to 0.5 and 1.5 gives log K_1 and log K_2 respectively.

In the same manner if $\bar{n}H$ is plotted against pH the values of log K_1^H, log K_2^H etc. can be computed.

(3) Linear plot method[2]

Eq. (6) for N = 2 system may be written in form

$$yp_1 + xp_2 = 1 \quad (22)$$

Where x and y are function of $\bar{n}$ and [L] and the parameter p_1 and p_2 are related to the stability constants. The six possible transformation of eq. (6) are

$$\frac{1-\bar{n}}{\bar{n}} \cdot [L] \cdot \beta_1 + \frac{2-\bar{n}}{\bar{n}} \cdot [L]^2 \cdot \beta_2 = 1 \quad (23)$$

$$\frac{\bar{n}}{(1-\bar{n})} \cdot \frac{1}{[L]} \cdot \frac{1}{\beta_2} + \frac{(\bar{n}-2)}{1-\bar{n}} \cdot [L] \cdot \beta_2 / \beta_1 = 1 \quad (24)$$

$$\frac{\bar{n}}{(2-\bar{n})[L]^2} \cdot \frac{1}{\beta_2} + \frac{(\bar{n}-1)}{(2-\bar{n})[L]} \cdot \beta_1 / \beta_2 = 1 \quad (25)$$

The other three transformations are obtained mearly be interchanging the values of x and y in the above equation. Eq. (22) can be rearranged as

$$y = -\frac{p_2}{p_1} x + \frac{1}{p_1} \quad (26)$$

Thus if y is plotted against x, a straight line of slope $-p_2/p_1$ and intercept $1/p_1$ should result. Such plots had been used by several authors[7,8]. They were quite convenient in cases where the measurements spread over a rather narrow range of free ligand concentration.

(4) Point wise calculation method[9]

Hearon and Gilbert have suggested the following methods for point wise calculation of K_1 and K_2.

Here $\beta_2 = K_1K_2$ is obtained graphically from a number of independent experiments. K_1 is then calculated at several points using eq. (6) in the form of

$$K_1 = \frac{(2-\bar{n}).K_1K_2[L]^2 - \bar{n}}{(\bar{n}-1).[L]} \quad (27)$$

And pointwise calculation of K_2 is made using the relation.

$$K_1K_2 = \frac{K_1[L] - \bar{n}(1+K_1[L])}{(\bar{n}-2)[L]} \quad (28)$$

3.1.4 Thermodynamic constants

The stability constants of the metal complexes are related to thermodynamic properties such as free energy charge (ΔG), enthalpy (ΔH) and entropy change (ΔS). These values can be computed by usual equations:

$$\Delta G = -2.303\ RT \log K \tag{29}$$

$$\Delta H = 2.303R \frac{T_2 T_1}{T_2 - T_1} \log \frac{K_2}{K_1} \tag{30}$$

$$\Delta S = \frac{(\Delta H - \Delta G)}{T} \tag{31}$$

Where, K_2 and K_1 are the stability constants at the absolute temperatures T_2 and T_1 respectively.

3.1.5 Limitations to applicability of computation methods

The assumptions made in deriving the formation function viz. absence of metal ion hydrolysis, poly nuclear complex formation, anion complexing etc. sets limits to the applicability of computation methods described above, in addition to those arising from the particular conditions under which the methods hold. Accordingly, the methods for detecting the presence of these neglected factors and also correcting for them, if possible, have been suggested by some workers.

Irvin and rossotti[6] associate the absence of perfect symmetry about the mid point of the formation curve with the presence of poly nuclear species; formation of several types of complexes when ligands have several coordination sites and with incomplete formation of one of the complexes. The symmetry of the formation curve, therefore, can be of great value in revealing such factors.

Rossotti and Rossotti[7] have suggested that $\bar{n}$ would be independent of $T_{CM}°$ in absence of polynuclear complex formation. Where only one polynuclear species is formed, determination of $\bar{n}$ at different values of $T_{CM}°$ and then extra potation to low values of $T_{CM}°$ has been recommended.

Mathematical methods of computing mononuclear stability constant, even when polynuclear species are present, have been suggested[10,11] but these seem to have been applied only to complexes arising in metal ion hydrolysis.

Metal ion hydrolysis, if it occurs in the pH range of complex formation, would result in higher than the true values of stability constants. Fraiser et al.[12] Studied hydrolysis of several bivalent metal ions in dioxane-water and have shown that, for these ions, computations made in the pH range 3 – 6 are least deviated by metal ion hydrolysis. Use of high ligand-metal ratio has been recommended to depress the pH range of complex formation if necessary.

We have studied the proton ligand stability constants and metal ligand stability constants at 30° ± 0.2°C temperatures for synthesized ligands and metal complexes by the Calvin Bjerrum titration technique adopted by Irvin and Rossotti.

Proton-ligand stability constants of the ligands at 30° ± 0.2°C

Ligand	$\log pK_1^H$	$\log pK_2^H$	$\log \beta^H$
TRM – 1	10.66	3.11	13.77
TRM – 12	11.15	2.88	14.03
TRM - 14	10.94	3.22	14.16

Metal ligand stability constant of M(TRM - 1)$_2$ at 30° ± 0.2°C

Chelates	Stability Constant	Computational Methods			
		a	b	c	d
Cu(TRM-1)$_2$	$\log K_1$	8.62	8.63	8.60	8.64
	$\log K_2$	4.73	4.71	4.76	4.72
	$\log \beta_2$	13.35	13.34	13.36	13.36
Ni(TRM-1)$_2$	$\log K_1$	9.02	8.98	8.99	8.96
	$\log K_2$	5.61	5.62	5.62	5.66
	$\log \beta_2$	14.63	14.63	14.61	14.62
Co(TRM-1)$_2$	$\log K_1$	8.61	8.60	8.61	8.63
	$\log K_2$	5.35	5.36	5.37	5.36
	$\log \beta_2$	13.95	13.96	13.98	13.99

Metal ligand stability constant of M(TRM - 12)$_2$ at 30° ± 0.2°C

Chelates	Stability Constant	Computational Methods			
		a	b	c	d
Cu(TRM-12)$_2$	$\log K_1$	9.11	9.12	9.13	9.15
	$\log K_2$	6.06	6.06	6.07	6.04
	$\log \beta_2$	15.17	15.18	15.20	15.19
Ni(TRM-12)$_2$	$\log K_1$	8.85	8.86	8.84	8.82
	$\log K_2$	5.26	5.28	5.29	5.33
	$\log \beta_2$	14.11	14.14	14.13	14.15
Co(TRM-12)$_2$	$\log K_1$	8.37	8.36	8.37	8.35
	$\log K_2$	5.34	5.31	5.32	5.35
	$\log \beta_2$	13.71	13.67	13.69	13.70

Metal ligand stability constant of M(TRM - 14)$_2$ at 30° ± 0.2°C

Chelates	Stability Constant	Computational Methods			
		a	**b**	**c**	**d**
Cu(TRM-14)$_2$	$\log K_1$	9.71	9.70	9.69	9.73
	$\log K_2$	4.83	4.82	4.84	4.82
	$\log \beta_2$	14.54	14.52	14.53	14.55
Ni(TRM-14)$_2$	$\log K_1$	9.42	9.43	9.44	9.44
	$\log K_2$	4.52	4.53	4.54	4.52
	$\log \beta_2$	13.94	13.96	13.98	13.96
Co(TRM-14)$_2$	$\log K_1$	9.83	9.85	9.88	9.82
	$\log K_2$	5.60	5.60	5.54	5.62
	$\log \beta_2$	15.43	15.45	15.42	15.44

(a) Interpolation at half $\bar{n}$ values

(b) Least square method

(c) Linear plot method

(d) Point wise calculation method

3.2 EXPERIMENTAL

pH of solutions to calculate the proton ligand stability constants and metal ligand stability constants were measured with a EQUIP-TRONICS instrument (Model EQ-614) equipped with a combined electrode and magnetic stirrer pH-meter (accuracy ± 0.005 units) with a combined glass electrode assembly of pH range 0 to 14. This instrument has been built in an internal electronic voltage supply with a temperature compensator covering the range from 0 to 100°C. The instrument was calibrated with buffer solution of known pH before starting the pH titrations.

1. Sodium nitrate-$NaNo_3$	1.0 M
2. Sodium hydroxide-NaOH	0.5 M & 0.1 M
3. Nitric acid-HNO_3	0.1 M
4. Ligand solution	0.1 M
5. Metal solution (Cu, Ni and Co)	0.1 M

Nitric acid and Sodium hydroxide were standardized by titrating with 0.1 N NaOH and 0.05 M succinic acid solution respectively.

Calvin Bjerrum pH titration

The following sets of solutions were prepared for pH titration.

Set 1 : 0.8 mL 0.1 M HNO_3 + 11.2 mL distilled water + 24.0 mL dioxane + 4.0 mL 1 M $NaNO_3$.

Set 2 : 0.8 mL 0.1 M HNO_3 + 11.2 mL distilled water + 22.0 mL dioxane + 2.0 mL 0.1 M ligand solution + 4.0 mL 1 M $NaNO_3$.

Set 3 : 0.8 mL 0.1 M HNO_3 + 10.8 mL distilled water + 22.0 mL dioxane + 2.0 mL 0.1 M ligand solution + 4.0 mL 1 M $NaNO_3$ + 0.4 mL 0.1 M metal solution.

The total volume (V°) of the every set is 40 mL. The ligand solutions were prepared in Dioxane : Water ratio 60 : 40 (V/V).

Solutions mentioned above sets were allowed to stand at a 30°C ± 0.2°C temperature for few minutes then titrated against standard alkali solution (NaOH 0.5 N) under an inert atmosphere of nitrogen. The change in the pH of the solution with each addition of alkali was recorded are given in TABLE.

The pH titration reading of acid, acid + ligand (TRM - 1) and acid + ligand (TRM - 1) + metal ions.

$N° = 0.5$, $E° = 0.02$ M, $V° = 40.0$ ml, $T_{CL}° = 5 \times 10^{-3}$ M, $T_{CM}° = 1 \times 10^{-3}$ M, $t = 30 \pm 0.2°C$, $u° = 0.1$ M

Solvent = Dioxane : water 60 : 40 (v/v).

Vol. of alkali added	Acid	Acid + ligand	Acid + ligand + metal ions		
			Cu^{+2}	Ni^{+2}	Co^{+2}
0.00	1.70	1.70	1.70	1.70	1.70
0.50	1.80	1.85	1.85	1.85	1.85
1.00	2.00	2.35	2.45	2.32	2.40
1.20	2.30	2.71	2.62	2.70	2.60
1.30	2.35	2.90	2.85	2.88	2.81
1.40	2.50	3.25	3.20	3.23	3.21
1.50	2.75	3.75	3.75	3.55	3.65
1.52	2.82	3.90	3.85	3.95	3.77
1.54	2.90	4.00	3.96	4.10	3.83
1.56	3.01	4.19	4.07	4.16	4.00
1.58	3.10	4.40	4.20	4.21	4.25
1.60	3.20	4.52	4.25	4.25	4.50
1.62	3.55	4.61	4.50	4.52	4.62
1.64	4.35	4.75	4.52	4.65	4.80
1.66	8.40	5.00	5.02	4.77	4.98
1.68	10.25	8.50	5.24	5.00	5.25
1.70	11.20	8.98	5.72	5.25	5.74
1.75	11.75	9.70	6.26	6.01	6.59
1.80	12.10	10.30	7.78	6.56	7.60
1.85	12.25	10.76	8.69	8.56	8.48
1.90	12.30	11.00			8.95
1.95	12.41	11.18	9.04	9.24	9.39
2.00	12.50	11.40	9.50		

1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide

(TRM- 1) at 30° ± 0.2°C

B	**$V_1 - V_2$**	$\bar{n}_A$	$\log \frac{2-\bar{n}_A}{\bar{n}_A - 1}$	$\log PK_2^H$
2.50	0.321	1.8042	-0.6135	3.1135
2.75	0.279	1.6967	-0.3613	3.1113
3.00	0.226	1.5640	-0.1118	3.1118
3.25	0.171	1.4252	0.1311	3.1188
3.50	0.116	1.2901	0.3887	3.1113
3.75	0.075	1.1876	0.6366	3.1134
4.00	0.046	1.1149	0.8865	3.1135
4.25	0.027	1.0680	1.1339	3.1161
4.50	0.016	1.0394	1.3877	3.1123
4.75	0.009	1.0226	1.6377	3.1152
5.00	0.005	1.0128	1.8845	3.1155

Average $\log PK_2^H$ = 3.1138

B	**$V_2 - V_1$**	$\bar{n}_A$	$\log \frac{\bar{n}_A}{1-\bar{n}_A}$	$\log PK_1^H$
9.25	0.015	0.9626	1.4122	10.6612
9.50	0.026	0.9355	1.1613	10.6013
9.75	0.044	0.8908	0.9111	10.6611
10.00	0.072	0.8208	0.612	10.6612
10.25	0.112	0.7204	0.4114	10.6614
10.50	0.163	0.5920	0.1615	10.6615
10.75	0.221	0.4493	-0.0883	10.6617
11.00	0.275	0.3142	-0.3398	10.6610
11.25	0.318	0.2049	-0.5889	10.6611
11.50	0.350	0.1267	-0.8384	10.6616

Average $\log PK_1^H$ = 10.6613

Copper + 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide (TRM- 1) at 30° ± 0.2°C

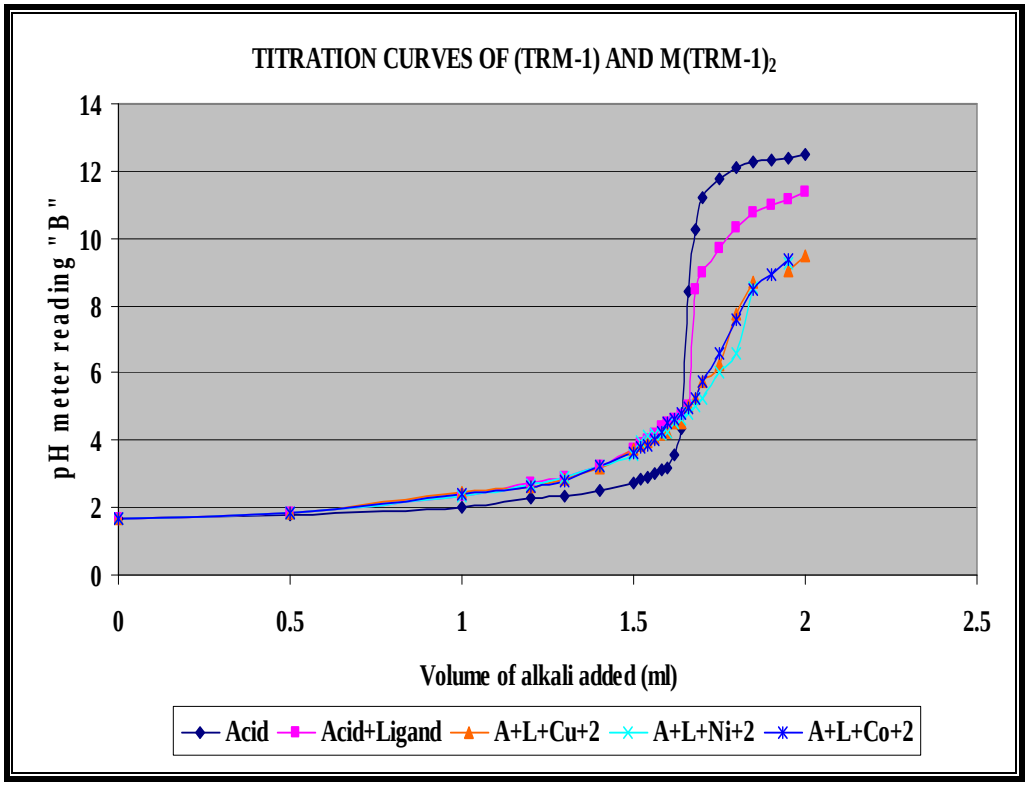
B	V_3	V_2	V_3-V_2	$\bar{n}$	pL
4.50	1.602	1.593	0.009	0.0958	11.7559
4.75	1.614	1.600	0.014	0.1749	11.0227
5.00	1.636	1.618	0.018	0.1957	10.2819
5.25	1.665	1.637	0.028	0.3183	9.5419
5.50	1.678	1.640	0.038	0.4745	8.8043
5.75	1.698	1.643	0.055	0.6868	8.0651
6.00	1.711	1.647	0.064	0.7992	7.3253
6.25	1.730	1.650	0.080	0.9985	6.5865
6.50	1.751	1.654	0.097	1.2107	5.8486
6.75	1.765	1.660	0.105	1.3106	5.1863
7.00	1.778	1.663	0.115	1.4352	4.7307
7.25	1.789	1.666	0.123	1.5351	3.6388
7.50	1.800	1.670	0.130	1.6225	2.8988
7.75	1.810	1.673	0.137	1.7096	2.1617
8.00	1.820	1.682	0.138	1.8145	1.8094
8.25	1.838	1.688	0.150	1.8832	0.4843

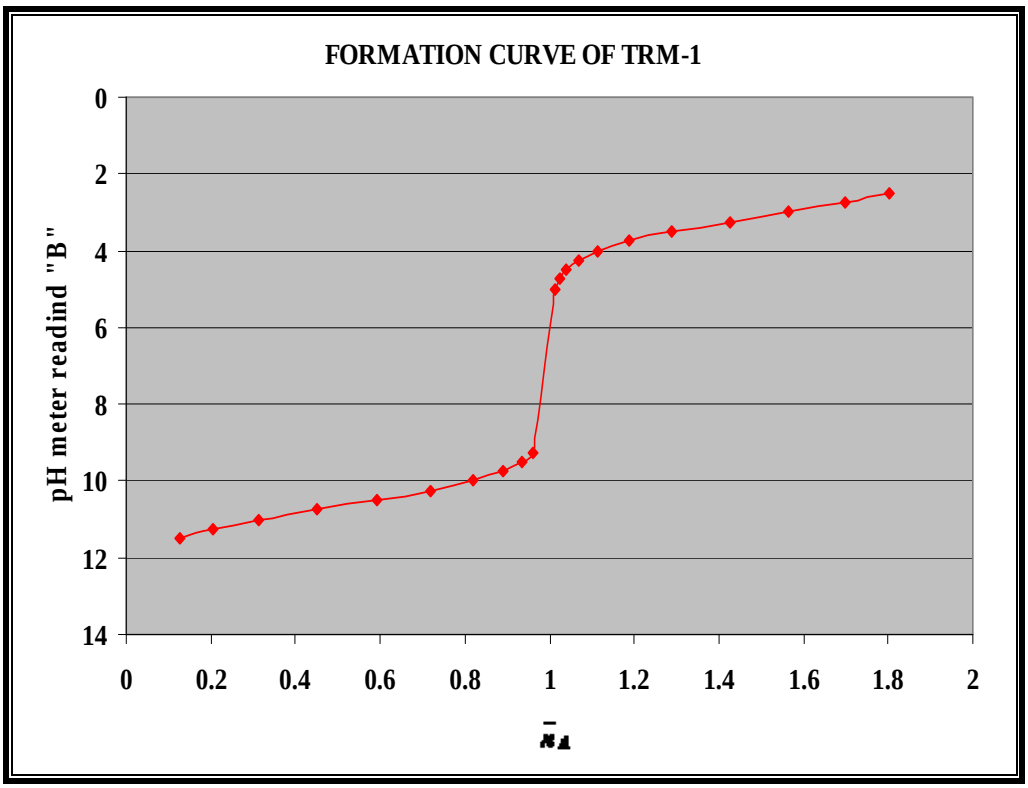
Nickel + 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide (TRM- 1) at 30° ± 0.2°C

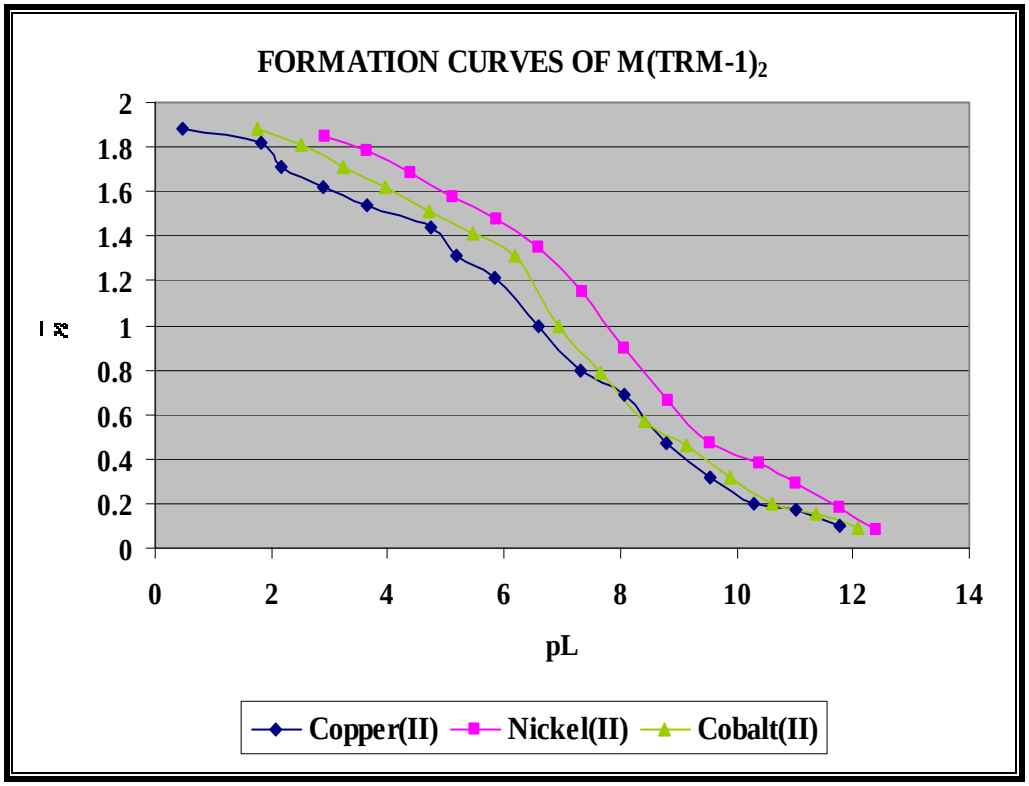
B	V_3	V_2	V_3-V_2	$\bar{n}$	pL
4.25	1.595	1.588	0.007	0.0784	12.4071
4.50	1.611	1.593	0.018	0.1830	11.7650
4.75	1.627	1.600	0.027	0.2859	11.0228
5.00	1.651	1.618	0.033	0.3784	10.3881
5.25	1.675	1.637	0.038	0.4683	9.5508
5.50	1.696	1.640	0.056	0.6591	8.8150
5.75	1.721	1.643	0.078	0.8995	8.0785
6.00	1.745	1.647	0.098	1.1481	7.3414
6.25	1.765	1.650	0.115	1.3477	6.6034
6.50	1.778	1.654	0.124	1.4725	5.8648
6.75	1.789	1.660	0.129	1.5723	5.1298
7.00	1.801	1.663	0.138	1.6846	4.3914
7.25	1.813	1.666	0.147	1.7845	3.6541
7.50	1.823	1.670	0.153	1.8460	2.9206

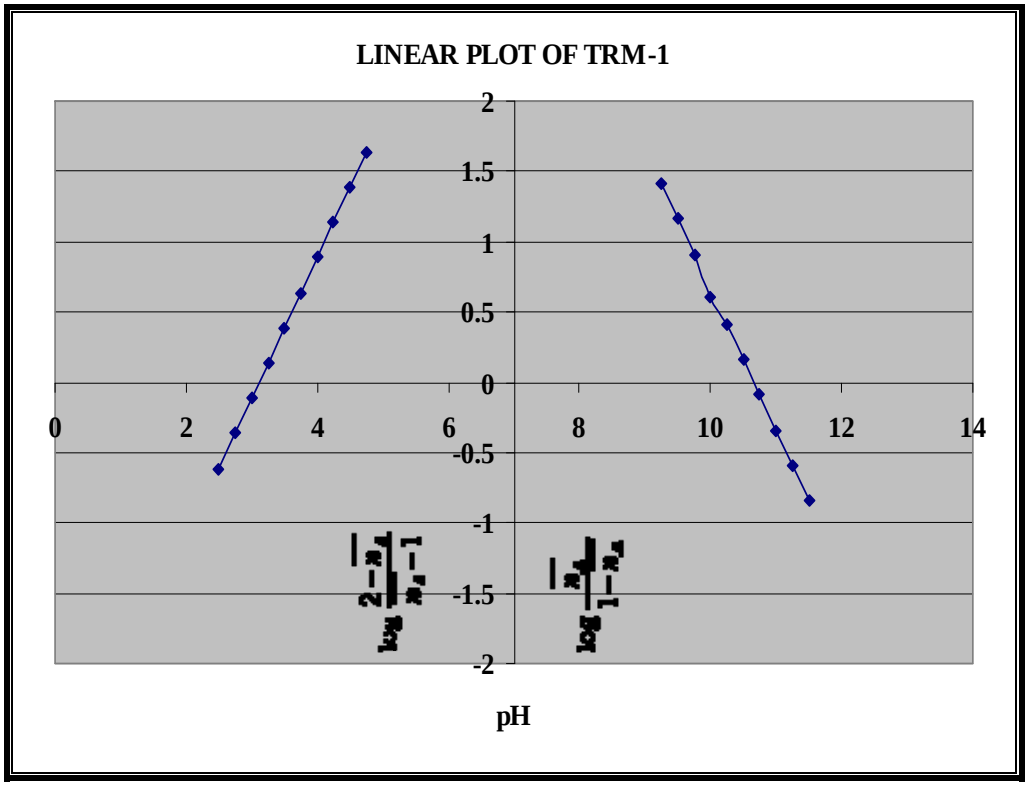
Cobalt + 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)thiosemicarbazide (TRM- 1) at 30° ± 0.2°C

B	V_3	V_2	V_3-V_2	$\bar{n}$	pL
4.50	1.601	1.593	0.008	0.0903	12.0930
4.75	1.613	1.600	0.013	0.1499	11.3530
5.00	1.637	1.618	0.019	0.1968	10.6161
5.25	1.664	1.637	0.027	0.3205	9.8789
5.50	1.677	1.640	0.037	0.4623	9.1416
5.75	1.688	1.643	0.045	0.5744	8.4010
6.00	1.709	1.647	0.062	0.7866	7.6630
6.25	1.724	1.650	0.074	0.9989	6.9238
6.50	1.755	1.654	0.101	1.3081	6.1850
6.75	1.771	1.660	0.111	1.4105	5.4498
7.00	1.781	1.663	0.118	1.5110	4.7095
7.25	1.793	1.666	0.127	1.6226	3.9700
7.50	1.803	1.670	0.133	1.7096	3.2321
7.75	1.815	1.673	0.142	1.8090	2.4984
8.00	1.833	1.682	0.151	1.8828	1.7600


TITRATION CURVES OF (TRM-1) AND M(TRM-1)2
pH meter reading "B"
14
12
10
8
6
4
2
0
0
0.5
1
1.5
2
2.5
Volume of alkali added (ml)
Acid
Acid+Ligand
A+L+Cu+2
A+L+Ni+2
A+L+Co+2


FORMATION CURVE OF TRM-1
pH meter readind "B"
0
2
4
6
8
10
12
14
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2


FORMATION CURVES OF M(TRM-1)2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
pL
Copper(II)
Nickel(II)
Cobalt(II)


LINEAR PLOT OF TRM-1
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0
2
4
6
8
10
12
14
pH

The pH titration reading of acid, acid + ligand (TRM - 12) and acid + ligand (TRM - 12) + metal ions.

$N^\circ = 0.5$, $E^\circ = 0.02$ M, $V^\circ = 40.0$ ml, $T_{CL}^\circ = 5 \times 10^{-3}$ M, $T_{CM}^\circ = 1 \times 10^{-3}$ M, $t = 30 \pm 0.2^\circ$C, $u^\circ = 0.1$ M

Solvent = Dioxane : water 60 : 40 (v/v).

Vol. of alkali added	Acid	Acid + ligand	Acid + ligand + metal ions		
			Cu^{+2}	Ni^{+2}	Co^{+2}
0.00	1.70	1.70	1.70	1.70	1.70
0.50	1.80	1.85	1.85	1.85	1.85
1.00	2.00	2.35	2.32	2.35	2.30
1.20	2.30	2.65	2.56	2.65	2.66
1.30	2.35	2.86	2.80	2.85	2.86
1.40	2.50	3.22	3.15	3.22	3.18
1.50	2.75	3.62	3.55	3.62	3.52
1.52	2.82	3.73	3.68	3.72	3.64
1.54	2.90	3.80	3.76	3.81	3.68
1.56	3.01	3.88	3.83	3.87	3.77
1.58	3.10	3.99	3.91	3.93	3.84
1.60	3.20	4.20	4.01	4.00	3.99
1.62	3.55	4.26	4.27	4.30	4.25
1.64	4.35	5.00	4.52	4.47	4.52
1.66	8.40	6.45	4.75	4.85	4.75
1.68	10.25	8.25	5.14	5.15	5.30
1.70	11.20	9.60	5.26	5.25	5.65
1.75	11.75	10.16	7.18	6.66	7.30
1.80	12.10	10.51	8.40	6.92	7.41
1.85	12.25	10.85	8.62	8.80	8.06
1.90	12.30	11.10		9.88	
1.95	12.41	11.41	9.24	9.14	8.90
2.00	12.50	11.65			

1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide

(TRM- 12) at 30° ± 0.2°C

B	**$V_1 - V_2$**	$\bar{n}_A$	$\log \frac{2-\bar{n}_A}{\bar{n}_A - 1}$	$\log PK_2^H$
2.50	0.285	1.7065	-0.3826	2.8826
2.75	0.248	1.5756	-0.1331	2.8831
3.00	0.170	1.4327	0.1178	2.8822
3.25	0.124	1.3001	0.3878	2.8826
3.50	0.078	1.1946	0.6177	2.8823
3.75	0.045	1.1194	0.8679	2.8821
4.00	0.028	1.0702	1.1180	2.8820
4.25	0.015	1.0415	1.5677	2.8823
4.50	0.009	1.0235	1.6177	2.8821
4.75	0.005	1.0130	1.8676	2.8824
5.00	0.002	1.0085	2.1180	2.8820

Average $\log PK_2^H$ = 2.8823

B	**$V_2 - V_1$**	$\bar{n}_A$	$\log \frac{\bar{n}_A}{1-\bar{n}_A}$	$\log PK_1^H$
9.25	0.005	0.9876	1.9022	11.1522
9.50	0.007	0.9732	1.6524	11.1524
9.75	0.015	0.9619	1.4028	11.1528
10.00	0.026	0.9342	1.1526	11.1526
10.25	0.044	0.8886	0.9021	11.1521
10.50	0.073	0.8178	0.6522	11.1522
10.75	0.114	0.7163	0.4023	11.1523
11.00	0.165	0.5868	0.1524	11.1524
11.25	0.223	0.4441	-0.0958	11.1525
11.50	0.276	0.3101	-0.3473	11.1527

Average $\log PK_1^H$ = 11.1524

Copper + 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide (TRM- 12) at 30° ± 0.2°C

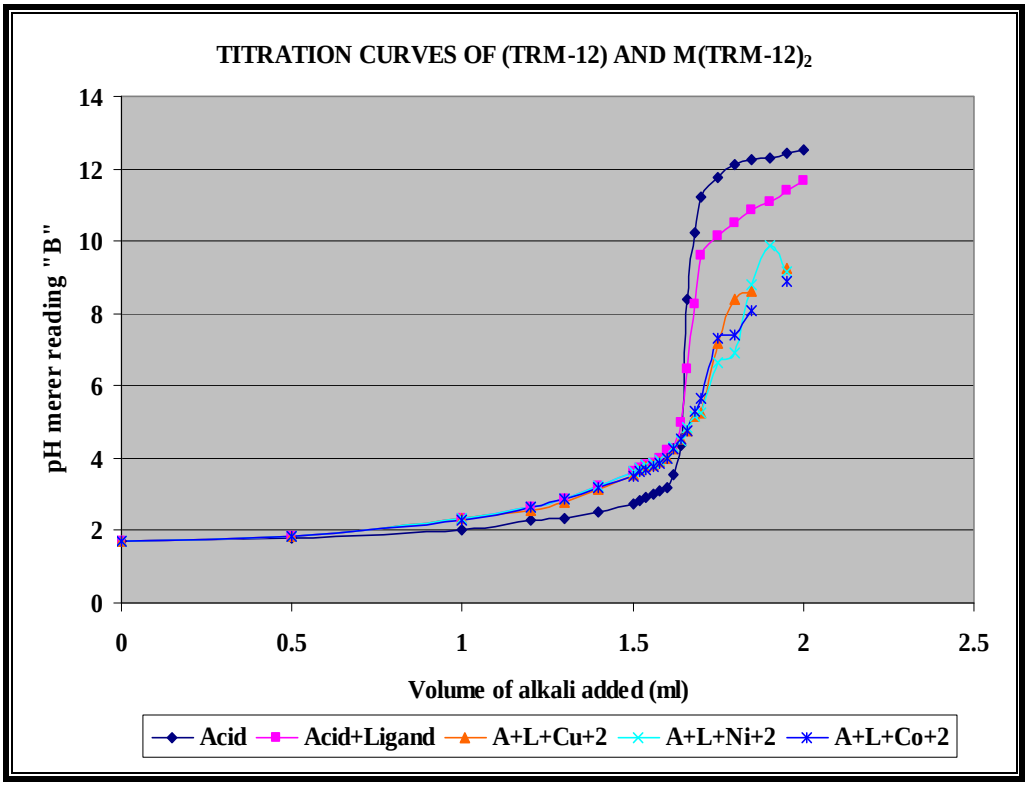
B	V_3	V_2	V_3-V_2	$\bar{n}$	pL
4.50	1.618	1.610	0.008	0.0803	13.1822
4.75	1.628	1.618	0.010	0.1045	12.5161
5.00	1.640	1.625	0.015	0.1687	11.7522
5.25	1.650	1.630	0.02	0.2378	11.0892
5.50	1.663	1.633	0.03	0.3745	10.3302
5.75	1.678	1.638	0.04	0.4995	9.5866
6.00	1.704	1.642	0.062	0.7742	8.8483
6.25	1.732	1.647	0.085	1.0623	8.1174
6.50	1.753	1.650	0.103	1.2859	7.3933
6.75	1.764	1.653	0.111	1.3998	6.6732
7.00	1.780	1.658	0.122	1.5223	5.9348
7.25	1.790	1.660	0.130	1.6225	4.8875
7.50	1.800	1.662	0.138	1.7221	4.4595
7.75	1.810	1.665	0.145	1.8288	3.7188
8.00	1.815	1.668	0.147	1.9306	2.9064

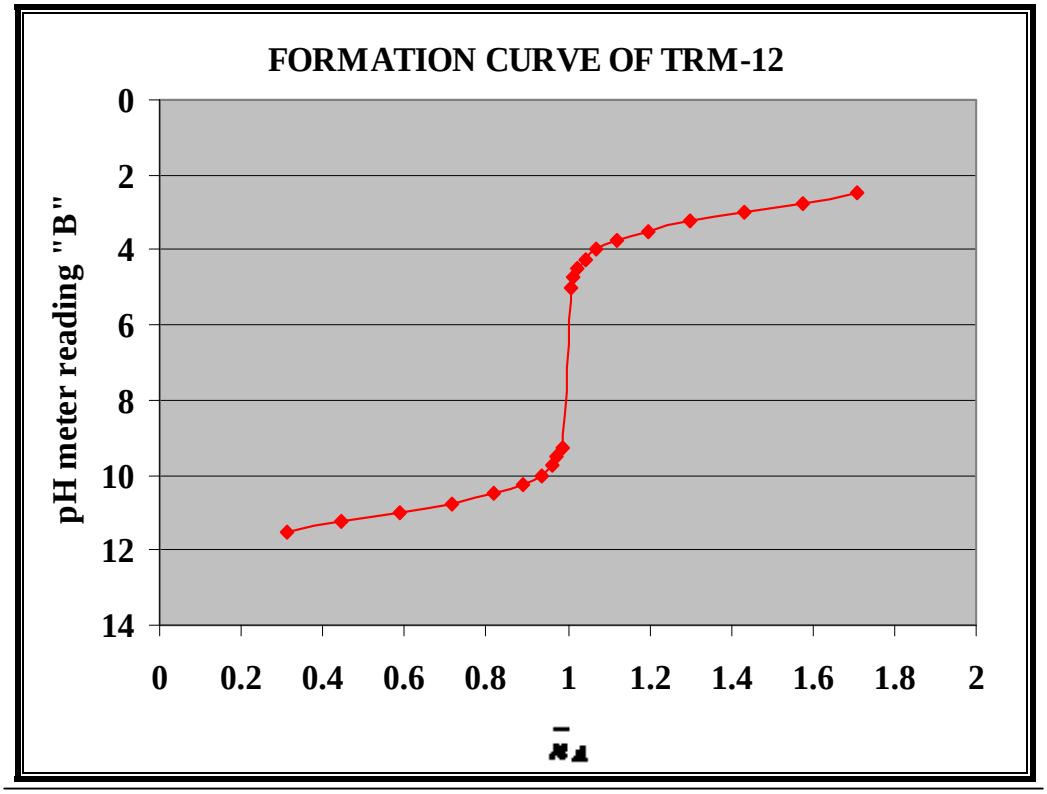
Nickel + 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide (TRM- 12) at 30° ± 0.2°C

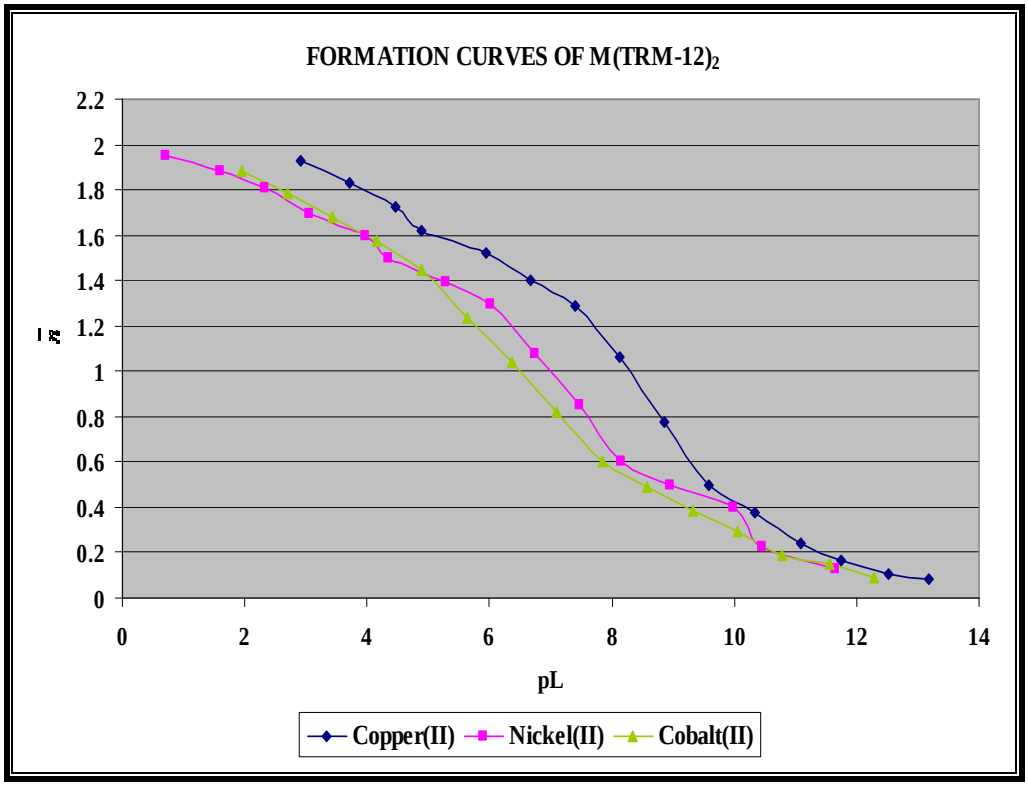
B	V_3	V_2	V_3-V_2	$\bar{n}$	pL
4.50	1.622	1.610	0.012	0.1290	11.6621
4.75	1.639	1.618	0.021	0.2284	10.4464
5.00	1.655	1.625	0.030	0.3995	9.9820
5.25	1.671	1.630	0.041	0.5001	8.9534
5.50	1.685	1.633	0.052	0.5994	8.1458
5.75	1.709	1.638	0.071	0.8488	7.4780
6.00	1.730	1.642	0.088	1.0810	6.7468
6.25	1.755	1.647	0.108	1.2935	6.0050
6.50	1.762	1.650	0.112	1.3976	5.2739
6.75	1.776	1.653	0.123	1.4995	4.3400
7.00	1.790	1.658	0.132	1.5990	3.9755
7.25	1.801	1.660	0.141	1.6987	3.0626
7.50	1.808	1.662	0.146	1.8115	2.3293
7.75	1.815	1.665	0.150	1.8833	1.5960
8.00	1.822	1.668	0.154	1.9481	0.6957

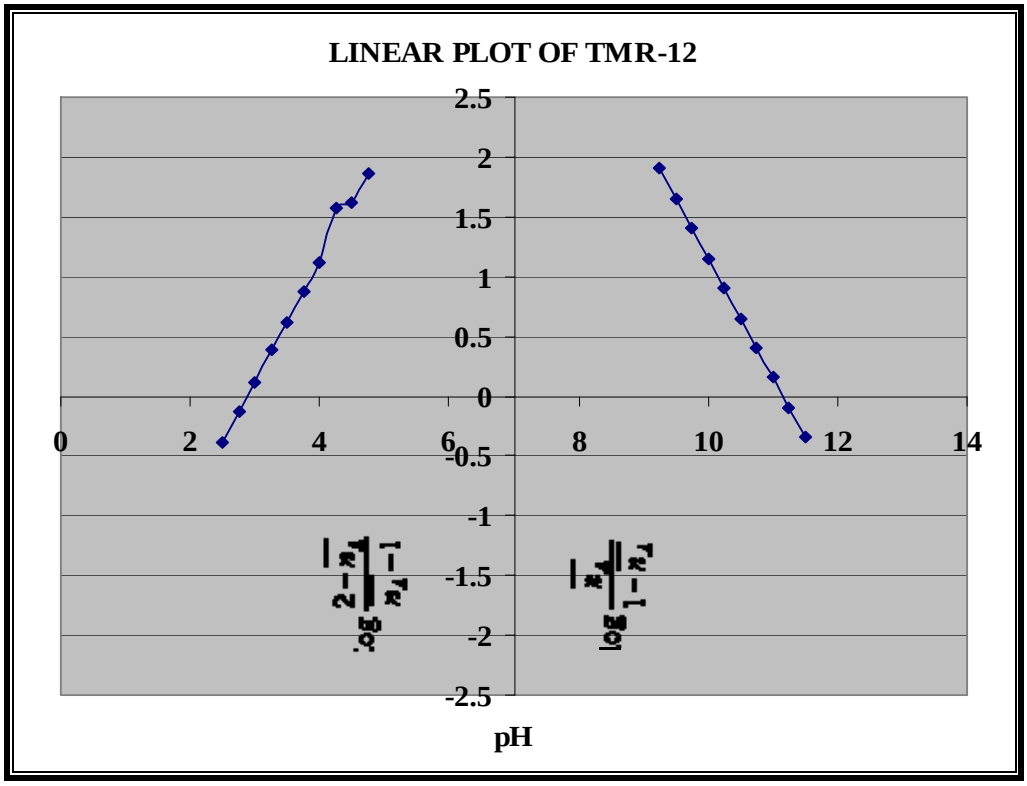
Cobalt + 1-(3,4-dimethoxybenzylidene)-4-(pyridin-2-yl)thiosemicarbazide (TRM- 12) at 30° ± 0.2°C

B	V_3	V_2	V_3-V_2	$\bar{n}$	pL
4.50	1.618	1.610	0.008	0.0880	12.2837
4.75	1.632	1.618	0.014	0.1509	11.5465
5.00	1.643	1.625	0.018	0.1875	10.7884
5.25	1.658	1.630	0.028	0.2956	10.0580
5.50	1.667	1.633	0.034	0.3850	9.3206
5.75	1.678	1.638	0.040	0.4875	8.5827
6.00	1.690	1.642	0.048	0.6025	7.8424
6.25	1.718	1.647	0.071	0.8217	7.1040
6.50	1.740	1.650	0.090	1.0369	6.3649
6.75	1.758	1.653	0.105	1.2361	5.6289
7.00	1.779	1.658	0.121	1.4471	4.8936
7.25	1.793	1.660	0.133	1.5725	4.1591
7.50	1.802	1.662	0.140	1.6822	3.4262
7.75	1.811	1.665	0.146	1.7825	2.6913
8.00	1.819	1.668	0.151	1.8803	1.9579


TITRATION CURVES OF (TRM-12) AND M(TRM-12)2
pH merer reading "B"
14
12
10
8
6
4
2
0
0
0.5
1
1.5
2
2.5
Volume of alkali added (ml)
Acid
Acid+Ligand
A+L+Cu+2
A+L+Ni+2
A+L+Co+2


FORMATION CURVE OF TRM-12
pH meter reading "B"
0
2
4
6
8
10
12
14
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2


FORMATION CURVES OF M(TRM-12)2
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
pL
Copper(II)
Nickel(II)
Cobalt(II)


LINEAR PLOT OF TMR-12
2.5
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
-2.5
0
2
4
6
8
10
12
14
pH

The pH titration reading of acid, acid + ligand (TRM - 14) and acid + ligand (TRM - 14) + metal ions.

$N° = 0.5$, $E° = 0.02$ M, $V° = 40.0$ ml, $T_L° = 5 \times 10^{-3}$ M, $T_M° = 1 \times 10^{-3}$ M, $t = 30 \pm 0.2°C$, $u° = 0.1$ M

Solvent = Dioxane : water 60 : 40 (v/v).

Vol. of alkali added	Acid	Acid + ligand	Acid + ligand + metal ions		
			Cu^{+2}	Ni^{+2}	Co^{+2}
0.00	1.68	1.69	1.68	1.69	1.69
0.50	1.80	1.86	1.85	1.85	1.86
1.00	2.03	2.35	2.36	2.35	2.32
1.20	2.21	2.72	2.63	2.60	2.64
1.30	2.35	2.81	2.81	2.82	2.86
1.40	2.54	3.16	3.13	3.11	3.15
1.50	2.75	3.60	3.50	3.48	3.46
1.52	2.81	3.66	3.66	3.63	3.54
1.54	2.90	3.77	3.72	3.78	3.70
1.56	2.99	3.84	3.84	3.85	3.82
1.58	3.08	3.98	3.91	3.92	3.93
1.60	3.20	4.26	4.12	4.19	4.14
1.62	3.52	4.50	4.38	4.45	4.45
1.64	4.35	4.78	4.78	4.69	4.69
1.66	8.41	5.02	5.14	5.03	5.02
1.68	10.25	5.14	5.35	5.26	5.15
1.70	11.22	5.25	5.71	5.52	5.29
1.75	11.79	6.09	6.53	6.55	6.06
1.80	12.06	6.80	7.59	7.62	6.81
1.85	12.23	8.21	8.56	8.71	8.23
1.90	12.30	8.30	9.00	8.95	8.30
1.95	12.36	8.44			
2.00	12.42				8.58

1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl) thiosemicarbazide (TRM- 14) at 30° ± 0.2°C

B	**$V_1 - V_2$**	$\bar{n}_A$	$\log \frac{2-\bar{n}_A}{\bar{n}_A - 1}$	$\log PK_2^H$
2.50	0.337	1.8425	-0.7283	3.2283
2.75	0.301	1.7496	-0.4763	3.2263
3.00	0.249	1.6222	-0.2166	3.2166
3.25	0.195	1.4871	0.0224	3.2274
3.50	0.138	1.3445	0.2794	3.2206
3.75	0.092	1.2309	0.5246	3.2254
4.00	0.057	1.1432	0.7768	3.2232
4.25	0.034	1.0863	1.0252	3.2248
4.50	0.020	1.0504	1.2748	3.2252
4.75	0.012	1.0289	1.5258	3.2242
5.00	0.006	1.0164	1.7760	3.2240

Average $\log PK_2^H$ = 3.2241

B	**$V_2 - V_1$**	$\bar{n}_A$	$\log \frac{\bar{n}_A}{1-\bar{n}_A}$	$\log PK_1^H$
9.25	0.008	0.9794	1.6902	10.9402
9.50	0.014	0.9648	1.6407	10.9403
9.75	0.024	0.9856	1.1934	10.9434
10.00	0.041	0.8965	0.9408	10.9408
10.25	0.068	0.8599	0.6908	10.9408
10.50	0.108	0.7311	0.4332	10.9332
10.75	0.157	0.6088	0.1906	10.9406
11.00	0.241	0.3985	0.0576	10.9422
11.25	0.269	0.3295	-0.3092	10.9408
11.50	0.314	0.2150	-0.5595	10.9405

Average $\log PK_1^H$ = 10.9403

Copper + 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide (TRM- 14) at 30° ± 0.2°C

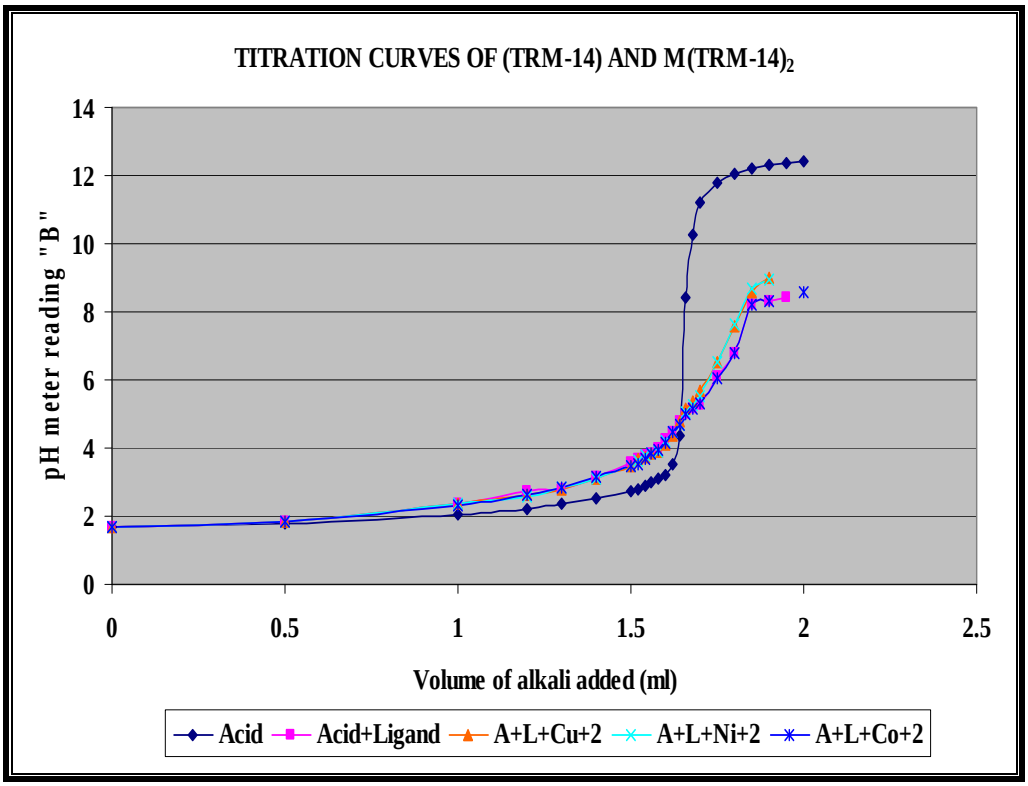
B	V_3	V_2	V_3-V_2	$\bar{n}$	pL
4.50	1.630	1.620	0.010	0.1078	13.4479
4.75	1.640	1.625	0.015	0.1882	12.3956
5.00	1.652	1.630	0.022	0.2748	11.4773
5.25	1.666	1.636	0.030	0.3740	11.0109
5.50	1.680	1.640	0.040	0.4992	10.2961
5.75	1.699	1.644	0.055	0.6870	9.5544
6.00	1.713	1.648	0.065	0.8124	8.8158
6.25	1.730	1.650	0.080	0.9985	7.9773
6.50	1.741	1.653	0.088	1.0983	7.3760
6.75	1.755	1.658	0.097	1.2100	6.2529
7.00	1.775	1.670	0.105	1.3111	5.8404
7.25	1.790	1.672	0.118	1.4725	4.9230
7.50	1.799	1.676	0.123	1.5350	4.1891
7.75	1.809	1.679	0.130	1.6232	3.4870
8.00	1.817	1.680	0.137	1.7099	2.9117
8.25	1.827	1.682	0.145	1.8102	2.2709

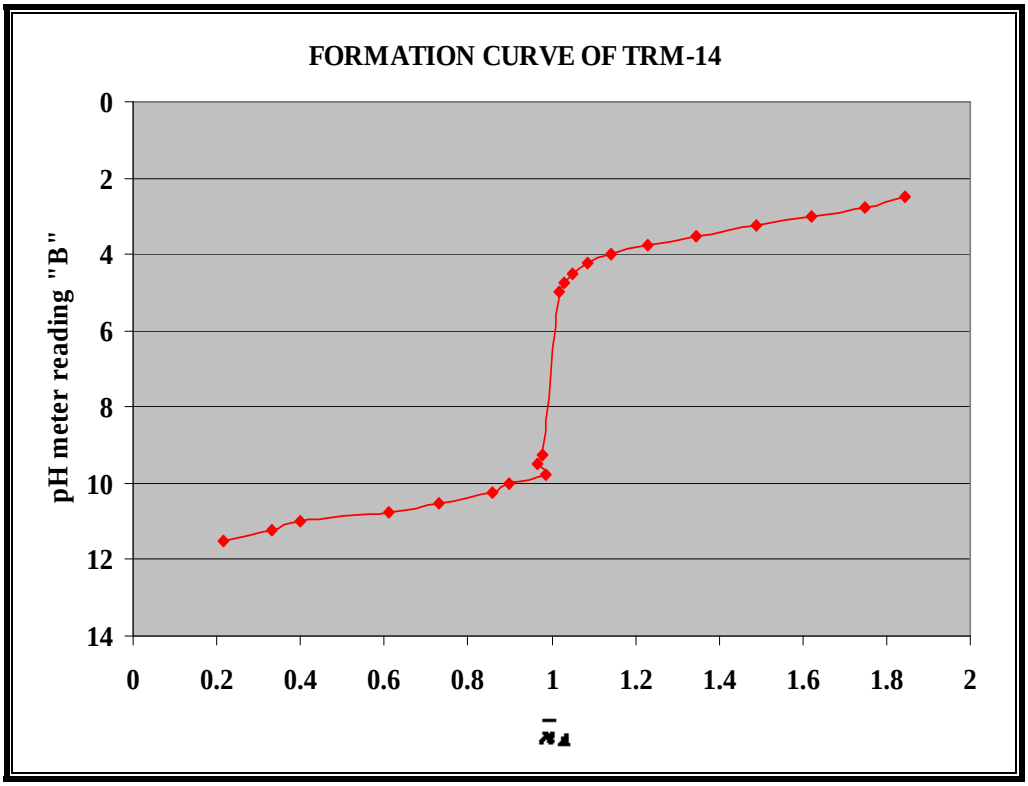
Nickel + 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide (TRM- 14) at 30° ± 0.2°C

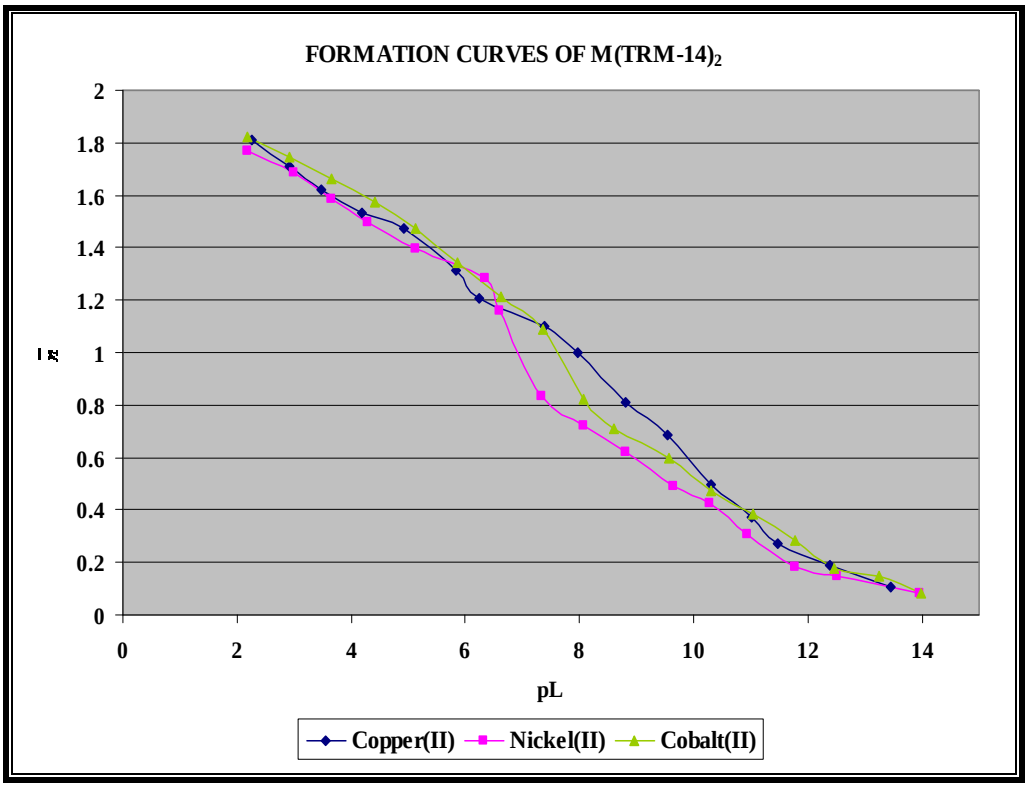
B	V_3	V_2	V_3-V_2	$\bar{n}$	pL
4.50	1.629	1.620	0.009	0.0821	13.9491
4.75	1.636	1.625	0.011	0.1506	12.5056
5.00	1.649	1.630	0.019	0.1863	11.7674
5.25	1.665	1.636	0.029	0.3102	10.9328
5.50	1.674	1.640	0.034	0.4245	10.2877
5.75	1.690	1.644	0.046	0.4886	9.6497
6.00	1.702	1.648	0.054	0.6237	8.8101
6.25	1.710	1.650	0.060	0.7244	8.0683
6.50	1.723	1.653	0.070	0.8363	7.3305
6.75	1.756	1.658	0.098	1.1589	6.5940
7.00	1.770	1.670	0.100	1.2850	6.3528
7.25	1.779	1.672	0.107	1.3976	5.1221
7.50	1.791	1.676	0.115	1.4980	4.2839
7.75	1.806	1.679	0.127	1.5849	3.6470
8.00	1.814	1.680	0.134	1.6836	2.9899
8.25	1.825	1.682	0.143	1.7708	2.1706

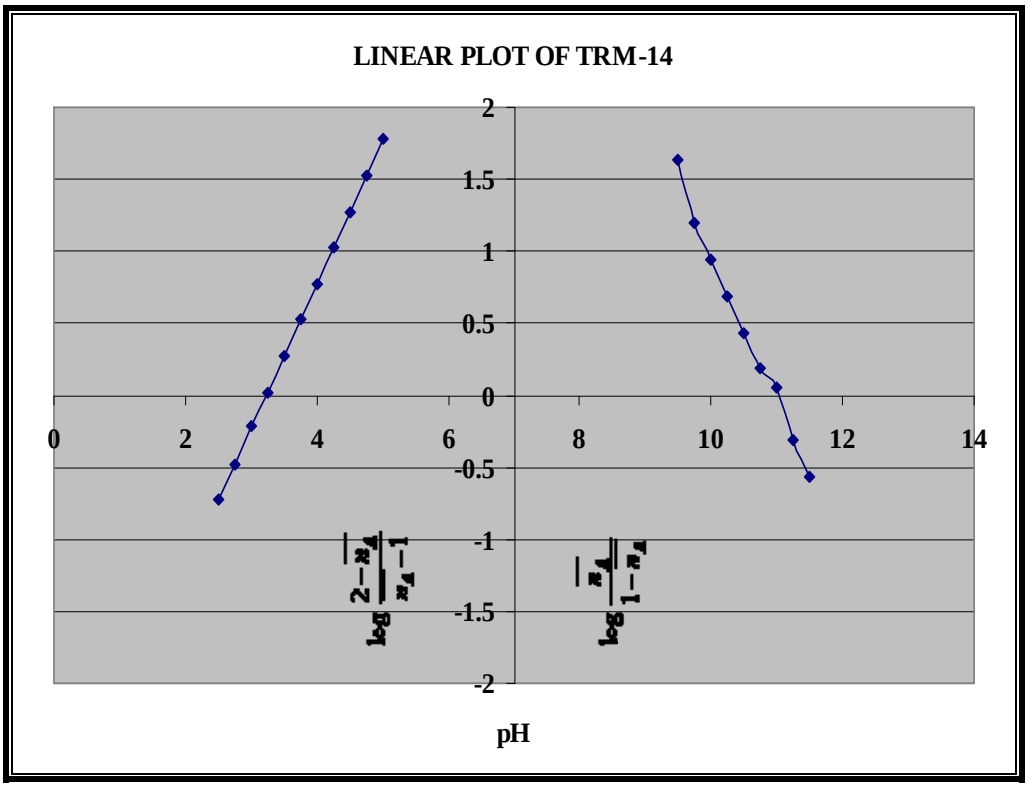
Cobalt + 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl)thiosemicarbazide (TRM- 14) at 30° ± 0.2°C

B	V_3	V_2	V_3-V_2	$\bar{n}$	pL
4.25	1.610	1.603	0.007	0.0810	13.9956
4.50	1.632	1.620	0.012	0.1506	13.2548
4.75	1.642	1.625	0.017	0.1779	12.4523
5.00	1.655	1.630	0.025	0.2820	11.7756
5.25	1.676	1.636	0.040	0.3873	11.0338
5.50	1.684	1.640	0.044	0.4756	10.2957
5.75	1.697	1.644	0.053	0.6005	9.5588
6.00	1.705	1.648	0.057	0.7109	8.6130
6.25	1.708	1.650	0.058	0.8240	8.0821
6.50	1.742	1.653	0.089	1.0860	7.3501
6.75	1.760	1.658	0.102	1.2116	6.6202
7.00	1.778	1.670	0.108	1.3418	5.8667
7.25	1.791	1.672	0.119	1.4729	5.1388
7.50	1.801	1.676	0.125	1.5714	4.4093
7.75	1.810	1.679	0.131	1.6611	3.6525
8.00	1.822	1.680	0.142	1.7479	2.9267
8.25	1.834	1.682	0.152	1.8231	2.1810


TITRATION CURVES OF (TRM-14) AND M(TRM-14)2
pH meter reading "B"
14
12
10
8
6
4
2
0
0
0.5
1
1.5
2
2.5
Volume of alkali added (ml)
Acid
Acid+Ligand
A+L+Cu+2
A+L+Ni+2
A+L+Co+2


FORMATION CURVE OF TRM-14
pH meter reading "B"
0
2
4
6
8
10
12
14
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2


FORMATION CURVES OF M(TRM-14)2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
2
4
6
8
10
12
14
pL
Copper(II)
Nickel(II)
Cobalt(II)


LINEAR PLOT OF TRM-14
2
1.5
1
0.5
0
-0.5
-1
-1.5
-2
0
2
4
6
8
10
12
14
pH

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Biological activities of ligands and their metal complexes

Section - D

4.1 INTRODUCTION

Thiosemicarbazones and their metal complexes possess a range of biological applications. Heterocyclic thiosemicarbazones exercise their beneficial therapeutic properties in mammalian cells by inhibiting ribonucleotide reductase, a key enzyme in the synthesis of DNA precursors. The non heme iron subunit has been shown to be inhibited or inactivated by thiosemicarbazones. Their ability to provide this inhibitory action is thought to be due to coordination of iron *via* their N-N-S tridentate ligating system, either by a performed iron complexes binding to the enzyme or by the free ligand complexing with the iron charged enzyme[1]. Studies of iron and copper complexes have shown that they can be more active in cell destruction as well as in the inhibition of DNA synthesis, than the uncomplexed thiosemicarbazones. Further, 5-hydroxy 2-formyl pyridine thiosemicarbazone has been shown to cause lesions in DNA. Therefore, there may be a second site of action in addition to inhibition of ribonucleotide reductase.

The antimicrobial activity of thiosemicarbazones against mycobacterium tuberculosis *in vitro* and later confirmed *in vivo.* Since the causative organism of leprosy, one of the world's six major disease, thiosemicarbazones have also been used as second line drug in the chemotherapy of leprosy. Besides this they were also inhibit growth of both fungi and protozoa[2]. Wiles and Supunchuk reported that heterocyclic derivatives of thiosemicarbazide are active against the growth of *Aspergillus niger* and *Chactomiumglobsum* in concentrations as low as 10 μg/mL. Since then, several workers have reported the antimicrobial activity of thiosemicarbazones against selected plant pathogenic and saprophytic fungi[3]. The antiviral effect of thiosemicarbazones was first demonstrated by Hamre *et al* who showed that p-aminobenzaldehyde-3-thisemicarbazone and several of its derivatives were active against vaccinia virus in mice[4]. These studies were extended to include thiosemicarbazones of isatin, benzene, thiophene, pyridine and quinoline derivatives, which also showed activity against vaccinia - induced encephalitis. Later Bauer and co-workers isolated isatin-3-thiosemicarbazone having greatest activity against vaccinia virus. Thiosemicarbazones have also been tested against a variety of other viral infections including herpes virus, adenovirus, poliovirus, rhinovirus and RNA tumor virus with mixed results[5]. An extensive series of thiosemicarbazones obtained from 2-acetylpyridine was tested by Klayman *et al* for antimalarial activity against

plasmodium berghi in mice. Recently, it has been shown that 2-formylpyridine thiosemicarbazones inhibited adenosine uptake in rodent erythrocytes and reticulocytes parasitized with plasmodium berghi. The thiosemicarbazone derived from 2-formylpyridine showed mild antileukemic activity against 1-1210 tumor in mice[6]. These observations have provided an impetus to the synthesis of large number of transition metal complexes of heterocyclic thiosemicarbazones.

Thiosemicarbazones possess a wide range of biological applications. Dogmak had reported the antitubercular activities of thiosemicarbazone in 1946[7]. The applications of thiosemicarbazones include antitumour, antiviral[8], antibacterial[9], antimalarial and antifungal activities[1]. A thiosemicarbazone possessing antitumour activity against leukemia in mice was first reported by Brockman et al[10]. Blanz and French studied formyl thiosemicarbazone of different heterocyclic systems and showed that thiosemicarbazone side chain adjacent to the heterocyclic nitrogen and a conjugated NNS tridentate ligand system is necessary for anticancer activity[11]. Metal complexes of thiosemicarbazones are found to possess antifungal activity, which is effected by a substituent group at N(1) and N(4) positions of thiosemicarbazone moiety[12]. Because of promising the biological activity. 2-formyl, 2-benzoylpyridine and 2-acetylpyridine N(4)-substitutedthiosemicarbazones have been extensively studied[13-16]. Heterocyclic thiosemicarbazones exercise therapeutic properties in cells by inhibiting ribonucleotide reductase, a key enzyme in the synthesis of DNA[11].

Thiosemicarbazones inactivate the non-heme subunit and this inhibitory action is due to the coordination of iron *via* their tridentate ligating system, either by a preformed iron complex binding to the enzyme[17]. Studies have shown that iron and-copper complexes are more active in cell destruction as well as in the inhibition DNA synthesis than the uncomplexed thiosemicarbazone[18]. 5-Hydroxy 2-formyl thiosemicarbazone has shown to cause lesions in DNA[19].

Therefore there may be a second site of action in addition to inhibition of ribonucleotide reductase. These observations provide an impetus to the synthesis of a large number of 2-heterocyclic thiosemicarbazones. Copper(II) complexes of heterocyclic thiosemicarbazones have shown more fungal growth inhibition property. For example, copper(II) complexes of 2-acetylpyridine N(4)-substitutedthiosemicarbazones are found to be more active in the growth inhibition of the fungus *Paecilomyces variolii* at higher concentrations than nickel(II)

complexes[20]. . But increased activity is reported in nickel(II) complexes against *Aspergillius ninger* with an increase in size of the substituent at the N(4) position[21]. Against *Aspergillius ninger,* nickel(II) complexes of 2-acetylpyridine N(4)-substitutedthiosemicarbazones, the bulkiest the ligands, show modest activity of the thio semi carbazone, while smaller complexes are inactive[22]. It is also observed that nickel(II) complex of 2-acetylpyridine N(4)-dimethylthiosemicarbazone where ligand is in the monoanionic form. showed an inhibitory zone of 27.7 mm at a concentration of 200 μg ml^{-1} and 20.2 mm at 20 μg ml^{-1} and was more active than nickel(II) complex of 2-acetylpyridine N(4)-dipropylthiosemicarbazone where ligand is in the monoanionic form. It is reported that the activity of nickel(II) complex of the larger pyrazine thiosemicarbazone is greater[22]. The considerably lower activity of the complex may be due to its lack of planarity based on magnetic moment. A non-planar complex may have greater difficulty in passing through the cell wall of the fungus or positioning itself once in the fungal cell. Sarayan *et al.*[23] reported the antitumour activities of α-N heterocyclic thiosemicarbazones. Brockman *et al* showed that 2-formylpyridine thiosemicarbazone is active against leukemic activity in mice[24]. It is also reported that 2-formyl 3-hydroxypyridine thiosemicarbazone[25], 2-formyl 5-hydroxypyridine thiosemicarbazone[26] are good anticancer agents. A thiosemicarbazone side chain and a conjugated NNS tridentate ligand system is essential for anticancer activity[11]. Further studies are done by modifying the sites such as aldehydic or ketonic carbon, thione group and the N(4) position along with the position of attachment to the pyridine/isoqunoline moiety in α-N heterocyclic thiosemicarbazones. The structure activity relations of antitumour compounds were studied in detail, and can be found in reviews by Satorelli[27] and Petering[28].

Hamre *et al*[29,30] in 1950 studied the antiviral properties of thiosemicarbazones such as p-aminobenzaldehyde 3-thiosemicarbazone. They reported that the compound is found to be very effective against vaccina virus in mice. Bauer and co-workers studied activity against virus and structure-activity relations of a series of compounds[31,32]. It was found that by substitution of thiosemicarbazone moiety with aromatic ring lowered the activity against virus. The most active against vaccina virus were found to be 2-acetylpyridine N(4)-methyl and N(4)-ethyl thiosemicarbazones. The compound, 2-acetylpyridine N(4)-methylthiosemicarbazone, known as 'methisazone' is used against smallpox[33-35]. Thiosemicarbazones have also been

tested against a series of other viral infections including herpes, virus, adenovirus, rhinovirus, and RNA tumor virus with mixed results[36]. Heterocyclic thiosemicarbazones inhibit the replication of the virus to a greater extent than they inhibit cellular DNA or protein synthesis[37]

Thiosemicarbazones are good antimalarial chemotherapeutic agents[38]. The features essential for antimalarial activity were found to be due to 2-pyridyl ethylidene moiety, thione sulfur, and bulky substituents at the N(4) nitrogen atom of thiosemicarbazones. For example, 2-acetylpyridine N(4)-dialkyl thiosemicarbazones was found to be most active against *Neisseria gonorrhoeae*[39]. It has been shown that 2-formylpyridine thiosemicarbazone inhibited adenosine uptake in rodent erythrocytes and reticulocytes parasitized with *Plasmodium Berghei*[40].

4.2 EXPERIMENTAL

4.2.1 Evaluation Techniques

The following conditions must be met for the screening of antimicrobial activity:

(A) There should be intimate contact between the test organisms and substance to be evaluated.

(B) Required conditions should be provided for the growth of micro organisms.

(C) Conditions should be same through the study.

(D) Aseptic / sterile environment should be maintained.

Various methods have been used from time to time by several workers to evaluate the antimicrobial activity. The evaluation can be done by the following methods:

(a) Turbidometric method

(b) Agar streak dilution method

(c) Serial dilution method

(d) Agar diffusion method

Following Techniques are used as agar diffusion method:

(a) Agar Cup method

(b) Agar Ditch method

(c) Paper Disc method

We have used the **"Broth Dilution Method"** to evaluate the antibacterial activity.

It is one of the non automated in vitro bacterial susceptibility tests. This classic method yields a quantitative result for the among of antimicrobial agents that is needed to inhibit growth of specific micro organisms. It is carried out in tubes.

1. Macro-dilution Method in Tubes.
2. Micro-dilution format using plastic trays.

4.2.2 Materials and Methods

Determination of minimal bactericidal concentrations by agar cup method

All the synthesized drugs were used for antibacterial and antifungal test producers

All necessary controls like:

- Drug control
- Vehicle control
- Agar control
- Organism control
- Known antibacterial drugs control

4.2.3 Antimicrobial evaluation

All the synthesized compounds were tested for their antibacterial and antifungal activity (MIC) *in vitro* by broth dilution method[41,42] with two Gram-positive bacteria *Staphylococcus aureus* MTCC-96, *Streptococcus epidermidis* MTCC 442, one Gram-negative bacteria *Escherichia coli* MTCC 443 and four fungal strains *Candida albicans* MTCC 227, *Aspergillus niger* MTCC 282, *S. cerevisiae* MTCC 170, *E. floccosum* MTCC 7880 taking gentamycin, ampicillin, chloramphenicol, ciprofloxacin, norfloxacin, nystatin, and greseofulvin as standard drugs. The standard strains were procured from the Microbial Type Culture Collection (MTCC) and microcare laboratory, surat, gujarat, India.

The minimal inhibitory concentration (MIC) values for all the newly synthesized compounds, defined as the lowest concentration of the compound preventing the visible growth, were determined by using microdilution broth method according to NCCLS standards[41]. Serial dilutions of the test compounds and

reference drugs were prepared in Muellere-Hinton agar. Drugs (10 mg) were dissolved in dimethylsulfoxide (DMSO, 1 mL). Further progressive dilutions with melted Muellere-Hinton agar were performed to obtain the required concentrations. In primary screening 1000 μg mL^{-1}, 500 μg mL^{-1} and 250 μg mL^{-1} concentrations of the synthesized drugs were taken. The active synthesized drugs found in this primary screening were further tested in a second set of dilution at 200 μg mL^{-1}, 100 μg mL^{-1}, 50 μg mL^{-1}, 25 μg mL^{-1}, 12.5 μg mL^{-1}, and 6.25 μg mL^{-1} concentration against all microorganisms. The tubes were inoculated with 108 cfu mL^{-1} (colony forming unit/mL) and incubated at 37 ºC for 24 h. The MIC was the lowest concentration of the tested compound that yields no visible growth (turbidity) on the plate. To ensure that the solvent had no effect on the bacterial growth, a control was performed with the test medium supplemented with DMSO at the same dilutions as used in the experiments and it was observed that DMSO had no effect on the microorganisms in the concentrations studied.

The results obtained from antimicrobial susceptibility testing are depicted in Table.

THE STANDARD DRUGS

MINIMUM INHIBITION CONCENTRATION

DRUG (MICROGRAMME/ML)	*E. COLI* MTCC 443	*S. EPIDERMIDIS* MTCC 442	*S. AUREUS* MTCC 96
Gentamycin	0.05	0.25	0.25
Ampicillin	100	200	250
Chloramphenicol	50	25	50
Ciprofloxacin	25	50	50
Norfloxacin	10	15	10

MINIMAL FUNGICIDAL CONCENTRATION

DRUG (MICROGRAMME/ML)	*C. ALBICANS* MTCC 227	*A. NIGER* MTCC 282	*S. CEREVISIAE* MTCC 170	*E. FLOCCOSUM* MTCC 7880
Nystatin	100	100	100	100
Greseofulvin	500	100	500	500

4.3 ACTIVITY TABLES

ANTIBACTERIAL ACTIVITY OF SYNTHESIZED LIGANDS

MINIMUM INHIBITION CONCENTRATION (μG/ML)				
Sr. No.	**CODE no.**	***E. COLI*** **MTCC 443**	***S. EPIDERMIDIS*** **MTCC 442**	***S. AUREUS*** **MTCC 96**
1	TRM - 1	200	100	62.5
2	TRM – 2	500	250	150
3	TRM – 3	250	250	200
4	TRM – 4	125	500	250
5	TRM – 5	100	100	62.5
6	TRM – 6	100	250	150
7	TRM – 7	62.5	100	100
8	TRM – 8	200	250	100
9	TRM – 9	500	250	500
10	TRM – 10	62.5	25	25
11	TRM – 11	250	500	250
12	TRM – 12	500	250	500
13	TRM – 13	250	250	250
14	TRM – 14	100	62.5	62.5
15	TRM – 15	100	100	150

ANTIFUNGAL ACTIVITY OF SYNTHESIZED LIGANDS

MINIMAL FUNGICIDAL CONCENTRATION (μG/ML)					
Sr. No.	**CODE NO.**	***C. ALBICANS*** **MTCC 227**	***A. NIGER*** **MTCC 282**	***S. CEREVISIAE*** **MTCC 170**	***E. FLOCCOSUM*** **MTCC 7880**
1	TRM - 1	500	200	500	>1000
2	TRM – 2	500	500	500	500
3	TRM – 3	250	500	250	500
4	TRM – 4	250	500	250	>1000
5	TRM – 5	500	200	500	>1000
6	TRM – 6	500	250	200	500
7	TRM – 7	150	200	200	500
8	TRM – 8	250	500	500	1000
9	TRM – 9	500	250	500	1000
10	TRM – 10	150	200	250	500
11	TRM – 11	500	500	500	>1000
12	TRM – 12	250	500	200	1000
13	TRM – 13	500	250	500	1000
14	TRM – 14	250	200	500	500
15	TRM – 15	500	250	500	>1000

ANTIBACTERIAL ACTIVITY OF SYNTHESIZED METAL COMPLEXES

MINIMUM INHIBITION CONCENTRATION (μg/ml)

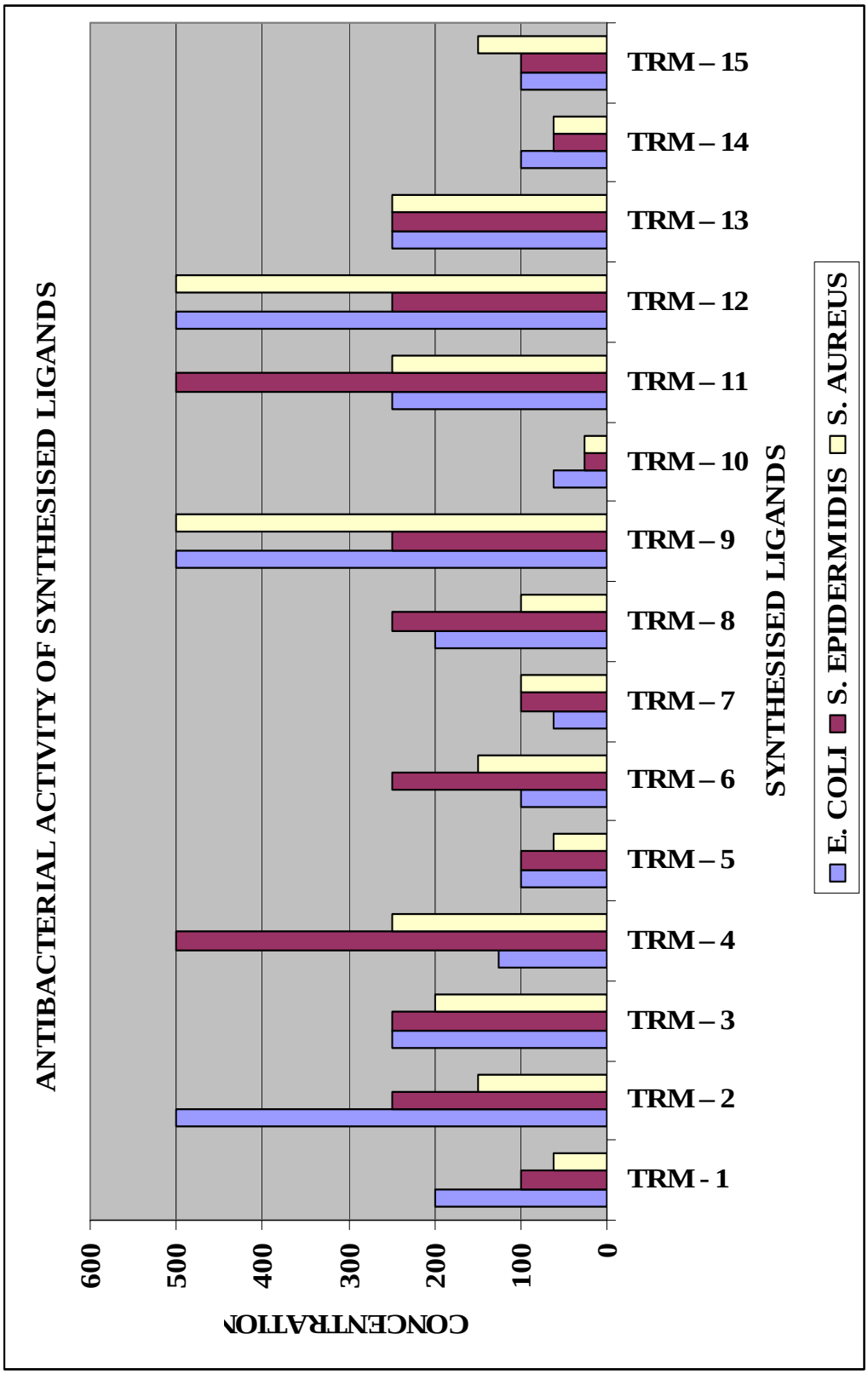
Sr. No.	CODE No.	*E. COLI* MTCC 443	*S. EPIDERMIDIS* MTCC 442	*S. AUREUS* MTCC 96
1	RMT - 1	500	500	200
2	RMT- 2	250	125	62.5
3	RMT – 3	>1000	250	500
4	RMT – 4	125	500	250
5	RMT – 5	250	200	500
6	RMT – 6	200	62.5	250
7	RMT – 7	500	200	200
8	RMT – 8	62.5	31.25	100
9	RMT – 9	1000	500	>1000
10	RMT – 10	500	500	250
11	RMT – 11	250	62.5	100
12	RMT – 12	500	200	250
13	RMT – 13	125	62.5	100
14	RMT – 14	62.5	31.25	125
15	RMT - 15	100	62.5	125
16	RMT – 16	1000	500	>1000
17	RMT – 17	500	250	250
18	RMT – 18	500	250	1000
19	RMT – 19	62.5	31.25	31.25
20	RMT – 20	100	62.5	62.5
21	RMT – 21	125	100	100
22	RMT – 22	500	250	250
23	RMT – 23	1000	250	500
24	RMT – 24	>1000	500	1000
25	RMT – 25	62.5	31.25	62.5
26	RMT – 26	500	250	1000
27	RMT – 27	62.5	31.25	125
28	RMT – 28	31.25	31.25	62.5
29	RMT – 29	31.25	31.25	31.25
30	RMT – 30	62.5	62.5	125
31	RMT - 31	500	500	1000
32	RMT – 32	>1000	500	500
33	RMT – 33	500	500	500
34	RMT – 34	1000	250	500
35	RMT – 35	500	250	1000
36	RMT – 36	1000	500	>1000
37	RMT – 37	250	125	200
38	RMT – 38	250	200	250
39	RMT – 39	500	250	500
40	RMT – 40	250	125	125
41	RMT – 41	125	62.5	62.5
42	RMT – 42	250	250	250
43	RMT – 43	200	62.5	125
44	RMT – 44	125	125	250
45	RMT - 45	500	200	200

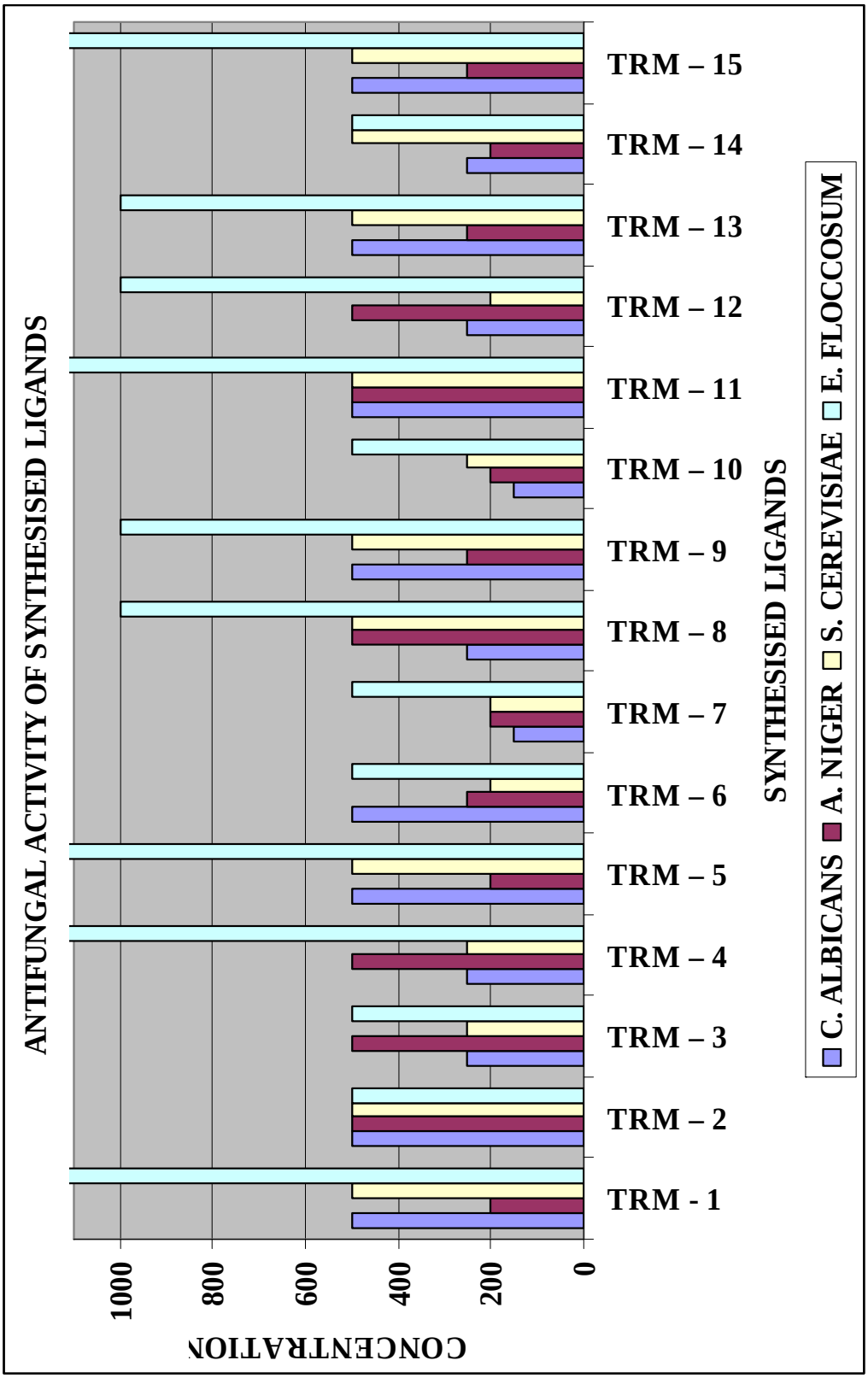
ANTIFUNGAL ACTIVITY OF SYNTHESIZED METAL COMPLEXES

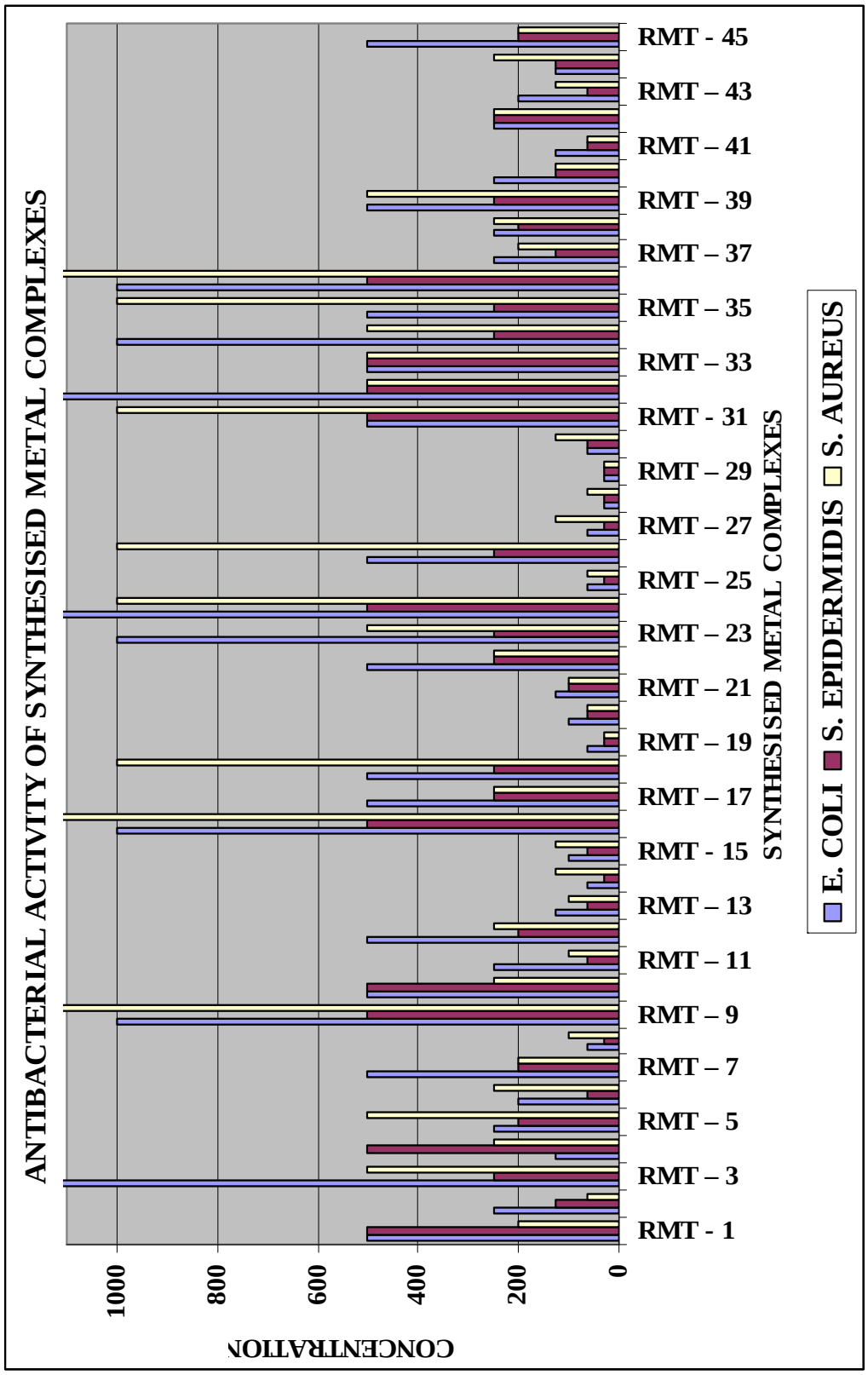
MINIMAL FUNGICIDAL CONCENTRATION (μG/ML)

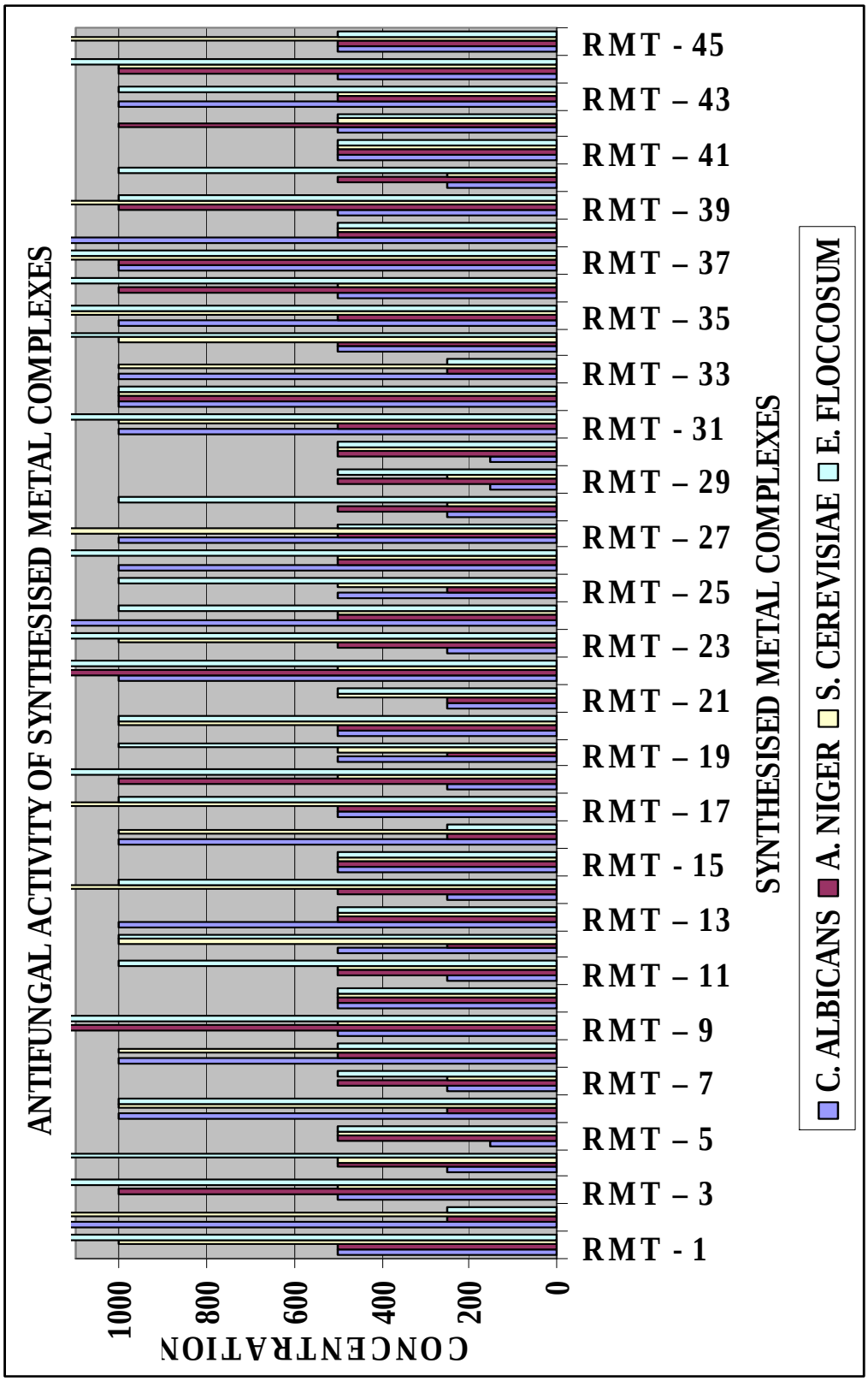
Sr. No.	CODE No.	*C. ALBICANS* MTCC 227	*A. NIGER* MTCC 282	*S. CEREVISIAE* MTCC 170	*E. FLOCCOSUM* MTCC 7880
1	RMT - 1	500	500	1000	>1000
2	RMT – 2	>1000	250	>1000	250
3	RMT – 3	500	1000	500	>1000
4	RMT – 4	250	500	500	>1000
5	RMT – 5	150	500	500	500
6	RMT – 6	1000	250	1000	1000
7	RMT – 7	250	500	250	500
8	RMT – 8	1000	500	1000	500
9	RMT – 9	500	>1000	500	>1000
10	RMT – 10	500	500	500	500
11	RMT – 11	250	500	500	1000
12	RMT – 12	500	250	1000	1000
13	RMT – 13	1000	500	500	500
14	RMT – 14	250	500	>1000	1000
15	RMT - 15	500	500	500	500
16	RMT – 16	1000	250	1000	250
17	RMT – 17	500	500	>1000	1000
18	RMT – 18	250	1000	500	>1000
19	RMT – 19	500	250	500	1000
20	RMT – 20	500	500	1000	1000
21	RMT – 21	250	250	500	500
22	RMT – 22	1000	>1000	500	>1000
23	RMT – 23	250	500	1000	>1000
24	RMT – 24	>1000	500	500	1000
25	RMT – 25	500	250	500	1000
26	RMT – 26	1000	500	500	>1000
27	RMT – 27	1000	500	>1000	500
28	RMT – 28	250	500	250	1000
29	RMT – 29	150	500	250	500
30	RMT – 30	150	500	500	500
31	RMT - 31	1000	500	1000	>1000
32	RMT – 32	1000	1000	1000	1000
33	RMT – 33	1000	250	1000	250
34	RMT – 34	500	500	1000	>1000
35	RMT – 35	1000	500	>1000	>1000
36	RMT – 36	500	1000	500	>1000
37	RMT – 37	1000	1000	>1000	>1000
38	RMT – 38	>1000	500	500	500
39	RMT – 39	500	1000	>1000	1000
40	RMT – 40	250	500	250	1000
41	RMT – 41	500	500	500	500
42	RMT – 42	500	1000	500	500
43	RMT – 43	1000	500	500	1000
44	RMT – 44	500	1000	1000	>1000
45	RMT - 45	500	500	>1000	500

4.4 ACTIVITY CHARTS




ANTIFUNGAL ACTIVITY OF SYNTHESISED LIGANDS
TRM – 15
TRM – 14
TRM – 13
TRM – 12
TRM – 11
TRM – 10
TRM – 9
TRM – 8
TRM – 7
TRM – 6
TRM – 5
TRM – 4
TRM – 3
TRM – 2
TRM - 1
1000
800
600
400
200
0
CONCENTRATION
SYNTHESISED LIGANDS
C. ALBICANS
A. NIGER
S. CEREVISIAE
E. FLOCCOSUM


ANTIBACTERIAL ACTIVITY OF SYNTHESISED METAL COMPLEXES
SYNTHESISED METAL COMPLEXES
CONCENTRATION
E. COLI
S. EPIDERMIDIS
S. AUREUS
RMT - 45
RMT – 43
RMT – 41
RMT – 39
RMT – 37
RMT – 35
RMT – 33
RMT - 31
RMT – 29
RMT – 27
RMT – 25
RMT – 23
RMT – 21
RMT – 19
RMT – 17
RMT - 15
RMT – 13
RMT – 11
RMT – 9
RMT – 7
RMT – 5
RMT – 3
RMT - 1
1000
800
600
400
200
0


ANTIFUNGAL ACTIVITY OF SYNTHESISED METAL COMPLEXES
SYNTHESISED METAL COMPLEXES
CONCENTRATION
1000
800
600
400
200
0
RMT - 45
RMT – 43
RMT – 41
RMT – 39
RMT – 37
RMT – 35
RMT – 33
RMT - 31
RMT – 29
RMT – 27
RMT – 25
RMT – 23
RMT – 21
RMT – 19
RMT – 17
RMT - 15
RMT – 13
RMT – 11
RMT – 9
RMT – 7
RMT – 5
RMT – 3
RMT - 1
C. ALBICANS
A. NIGER
S. CEREVISIAE
E. FLOCCOSUM

4.5 REFERENCES

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Summary

The work presented in the Thesis entitled **"Synthesis and Characterization of Some Transition Metal Complexes"** can be summarized as below.

Section A Summarizes the preparation and structure characterization of various thiosemicarbazones, 1-substituted aryl/pyrazolyl/quinolinyl thiosemicarbazide, 1-substituted arylidene-4-(pyridin-2-yl)thiosemicarbazide, 1-substituted arylidene-4-(4-bromophenyl)thiosemicarbazide.

Section B Summarizes synthesis and structure characterization of transition metals Cu(II), Ni(II) and Co(II) complexes of all synthesized thiosemicarbazone ligands.

Section C The practical proton-ligand and metal-ligand stability constants were determined by Calvin-Bjerrum titration technique using nitric acid and constant ionic strength was maintained with sodium nitrate. It was pointed out by Irving and Rossotti, that it is neither necessary to convert pH meter reading "B" to stoichiometric hydrogen ion concentration nor to know the stoichiometric concentration of the neutral salt added to maintain constant ionic strength. The method is valid both in water and water-dioxane medium. The nitrate ion has very slight complexing tendency and the competition between nitrate ion and the ligand under study is of minor importance.

The pH meter was calibrated with aqueous buffer and to keep metal chelate in homogeneous medium, the water:dioxane (40:60) was used as solvent and the true value of pH corresponding to aqueous solution was calculated from the pH meter reading by using Van Uitret and Hass relation method.

This may be studied by comparing the stabilities of complexes of series of metal ions with a given ligand. For a given ligand, irrespective of its nature, the order of stability constants of complexes of bivalent ions of the first transition series are usually in the natural orders (some times called the Irving-Williams order).

$$Cu(II) > Ni(II) > Co(II)$$

A theoretical justification of this stability order follow from consideration of reciprocal of ionic radi. and second ionization potentials of metal concerned violation of this order had been attributed to the formation of low spin complexes, stereo

chemical consideration and entropy factors. On examining the stability constant data given in section C. from the view point of stability order irrespective of nature of ligands, it was found as order

$$Cu(II) > Ni(II) > Co(II)$$

Section D The *in vitro* antimicrobial activities of thiosemicarbazone ligands and its Cu(II), Co(II) and Ni(II) metal complexes were carried out by the MIC of all the compounds were determined. Gentamycin, Norfloxacin, Ciprofloxacin, Chloramphenicol, Ampicillin, Nystatin, Greseofulvin were used as the standard drugs, where as DMSO poured disk was used as negative control and then minimum inhibitory concentration (MIC) was evaluated by the macro-dilution test using standard inoculums of 10^{-5} CFL ml^{-1}.

The distinct difference in the antibacterial and antifungal property of the thiosemicarbazone ligands and its Cu(II), Co(II) and Ni(II) metal complexes further justifies the purpose of this study. The importance of such work lies in the possibility that the new compound might be more effective against bacteria or fungus for which a thorough investigation regarding the SAR toxicity and the biological effects which would be helpful in designing more potent antibacterial or antifungal agent for therapeutic use is required.

Thus, 60 compounds are synthesized and characterized in entire thesis work. The synthesized compounds are screened for antimicrobial activity, results of which are incorporated in the thesis. Compounds were moderately active. It is therefore need to carry out systematic study of chemical structure for further manipulation.

Publications

- **List of published research papers**

1. Synthesis and characterization of some new thiosemicarbazide derivatives and their transition metal complexes.

   Rakesh Tada, Naimish Chavda, Manish K. Shah*; J. Chem. Pharm. Res., 2011, 3(2):290-297.

2. Synthesis and Characterization of Copper(II) complex with 1-(4,5-dimethoxy-2-nitrobenzylidene)thiosemicarbazide.

   R. M. Tada, T. S. Mehta, M. K. Shah*; Acta ciencia Indica Chemistry, (accept article).

- **List of research papers published in conference**

Oral Presentation

1. Synthesis and Characterization of Copper(II) complex with 1-(4,5-dimethoxy-2-nitrobenzylidene)thiosemi-carbazide.

   R. M. Tada, N. K. Chavda, M. K. Shah*; 46 annual convention of chemists 2009 international conference on recent research trends in chemical sciences, 2-6 December, 2009, VIT university Vellore, Tamil Nadu.

Poster Presentations

1. Synthesis and Characterization of Copper(II) complex with 1-(3-bromo-4-hydroxy-5-methoxybenzylidene) thiosemicarbazide.

   Rakesh M. Tada, Manish K. Shah*; Indian Council of chemist 28th annual conference,7-10 November, 2009, Department of Chemistry Hemchandracharya north Gujarat university Patan.

2. Preparation and spectral study of 1-(3-bromo-4-hydroxy-5-methoxybenzylidene)-4-(4-bromophenyl) thiosemi-carbazide and their transition metal complexes.

   Rakesh Tada, Naimish Chavda, Manish K.Shah*; Indian Council of chemist XXIX annual conference, 19-21 December, 2010, Department of chemistry, panjab university, Chandigarh.

Conferences/Workshops Attended

1. "11th CRSI National Symposium in Chemistry" at National Chemical Laboratory, Pune on 6-8 February-2009.
2. DST-FIST, UGC (SAP) supported and GUJCOST Sponsored "National Conference on Selected Topics in Spectroscopy and Stereochemistry" organized by the Department of Chemistry, Saurashtra University, Rajkot on 18-20th March, 2009.
3. "Two Days National Workshop on Patents & Intellectual Property Rights Related Updates" Sponsored by TIFAC & GUJCOST and Organized by DST-FIST, UGC-SAP & DST-DPRP Funded Department of Chemistry, Saurashtra University, Rajkot on 19-20th September, 2009.
4. National seminar on "Emerging Trends in Polymer Science and Technology POLY-2009" Sponsored by UGC-SAP & DST-FIST Funded Department of Chemistry, Saurashtra University, Rajkot on 8-10th October, 2009.
5. 28th Annual Conference of Indian Council of Chemists at Department of Chemistry, Hemchandacharya North Gujarat University, Patan on 7-10th November-2009.
6. "International Seminar on Recent Developments in Structure and Ligandbased Drug Design" jointly organized by Schrodinger LLC, USA; National Facility for Drug Discovery through New Chemicals Entities Development & Instrumentation support to Small Manufacturing Pharma Enterprises and DST-FIST, UGC-SAP & DST-DPRP Funded Department of Chemistry, Saurashtra University, Rajkot on 23rd December, 2009.
7. 46th Annual Convention of Chemists 2009 & International Conference on Recent Research Trends in Chemical Sciences at VIT University, Vellore on 2-6th December-2009.
8. 29th Annual Conference of Indian Council of Chemists at Department of Chemistry, Panjab University, Chandigarh on 19-21st December-2010.
9. ISCB Conference "International conference on Bridging gaps in discovery and development: Chemical & Biological science for affordable health, wellness & sustainbility" at Department of Chemistry, Saurashtra University, Rajkot on 4-7th February-2011

10. National seminar on “Recent Advances in Chemical Sciences & an Approach to Green Chemistry” at Department of Chemistry, Saurashtra University, Rajkot on 11-13th October, 2006.